organic compounds

Acta Crystallographica Section E

Structure Reports Online

ISSN 1600-5368

2-*N*-Benzyl-2,6-dideoxy-2,6-imino-3,4-*O*-isopropylidene-D-allononitrile

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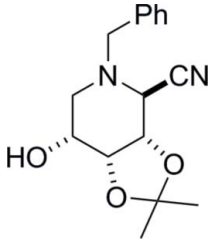
Received 28 October 2013; accepted 7 November 2013

Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.005 Å; R factor = 0.044; wR factor = 0.121; data-to-parameter ratio = 10.4.

X-ray crystallography firmly established the relative stereochemistry of the title compound, $C_{16}H_{20}N_2O_3$. The acetonide ring adopts an envelope conformation with one of the O atoms as the flap and the piperidine ring adopts a slightly twisted boat conformation. The absolute configuration was determined by use of D-ribose as the starting material. The compound exists as O—H···O hydrogen-bonded chains of molecules running parallel to the b axis.

Related literature

For the biological activity of polyhydroxylated piperidines, see: Nash *et al.* (2011); Watson *et al.* (2001). For a related α-iminonitrile, see: Ayers *et al.* (2012). For the hydrogen-atom treatment, see; Cooper *et al.* (2010). For details of the low temperature equipment used in the experiment, see: Cosier & Glazer (1986). For the weighting scheme, see: Prince (1982); Watkin (1994).



Experimental

Crystal data

$C_{16}H_{20}N_2O_3$ M_r = 288.35
Orthorhombic, $P2_12_12_1$
a = 8.3978 (3) Å
b = 11.2689 (4) Å
c = 15.9210 (6) Å
V = 1506.67 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 150 K
0.4 × 0.4 × 0.2 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.91, T_{max} = 0.98
11529 measured reflections
1970 independent reflections
1422 reflections with $I > 2.0\sigma(I)$
R_{int} = 0.079

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.121
S = 0.95
1970 reflections
190 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H11···O6^{i}	0.86	2.05	2.850 (5)	156 (1)

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

Data collection: *COLLECT* (Nonius, 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*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5665).

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Ayers, B. J., Jenkinson, S. F., Fleet, G. W. J. & Thompson, A. L. (2012). *Acta Cryst.* E**68**, o1474.
Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
Cooper, R. I., Thompson, A. L. & Watkin, D. J. (2010). *J. Appl. Cryst.* **43**, 1100–1107.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
Nash, R. J., Kato, A., Yu, C.-Y. & Fleet, G. W. J. (2011). *Future Med. Chem.* **3**, 1513–1521.
Nonius (2001). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Prince, E. (1982). In *Mathematical Techniques in Crystallography and Materials Science*. New York: Springer-Verlag.
Watkin, D. (1994). *Acta Cryst.* A**50**, 411–437.
Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.
Watson, A. A., Fleet, G. W. J., Asano, N., Molyneux, R. J. & Nash, R. J. (2001). *Phytochemistry*, **56**, 265–295.

supporting information

Acta Cryst. (2013). E**69**, o1772 [doi:10.1107/S1600536813030584]

2-*N*-Benzyl-2,6-dideoxy-2,6-imino-3,4-*O*-isopropylidene-D-allononitrile

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S1. Comment

Many polyhydroxylated piperidines have been found to display interesting biological properties (Nash *et al.*, 2011; Watson *et al.*, 2001). Piperidine α-iminonitrile **4** was prepared from 2,3-*O*-isopropylidene-5-*O*-toluenesulfonyl-*D*-ribose **3** by a tandem Strecker reaction and iminocyclization (Fig. 1). The title crystal structure establishes the relative configuration of **4**. The absolute configuration is determined by use of D-ribose **1** as the starting material. The acetonide ring adopts an envelope conformation with O4 out of the plane and the piperidine ring adopts a slightly twisted boat conformation with the nitrile group in the flagpole position (Fig. 2). The compound exists as O—H···O hydrogen bonded chains of molecules running parallel to the *b*-axis (Fig. 3). Only classical hydrogen bonding was considered.

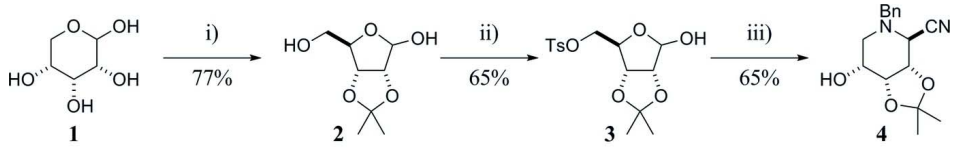
S2. Experimental

α-Iminonitrile **4** was recrystallized by diffusion from a mixture of ethyl acetate and cyclohexane: m.p. 342–344 K; $[\alpha]_D^{20}$ +20.3 (*c* 1.75, methanol).

S3. Refinement

In the absence of significant anomalous scattering, Friedel pairs were merged and the absolute configuration was assigned from the use of D-ribose as the starting material.

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 (Cooper *et al.*, 2010).



Reagents & conditions: i) acetone, $CuSO_4$, 45 °C, 17h; ii) TsCl, pyridine, -30 °C to RT, 4 h; iii) $BnNH_2$, AcOH, KCN, MeOH, RT 16 h.

Figure 1
Synthetic Scheme

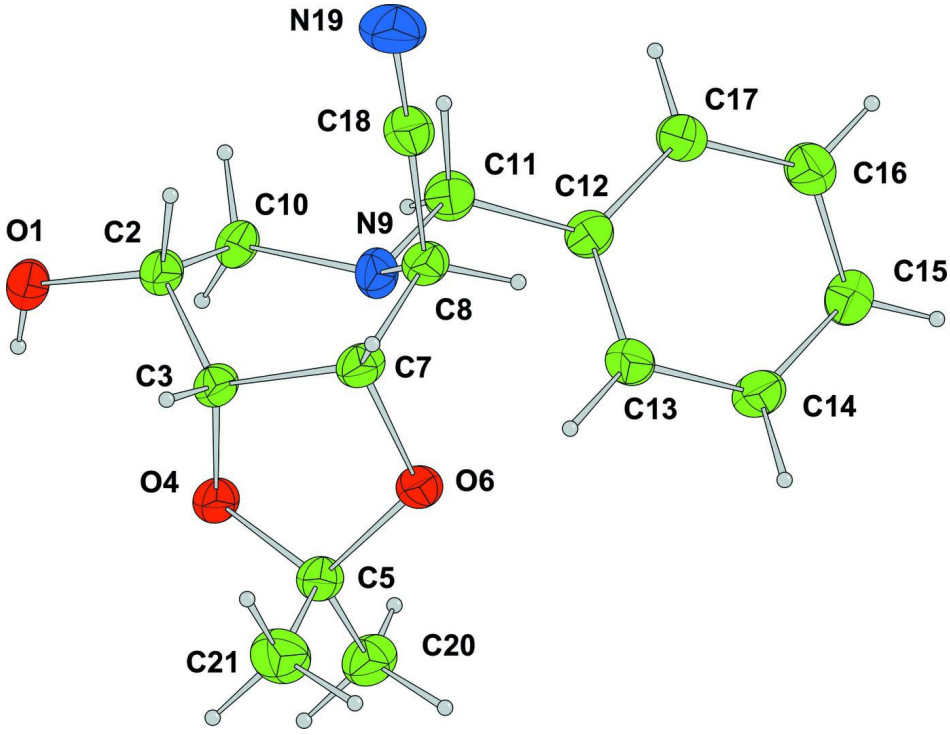


Figure 2

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

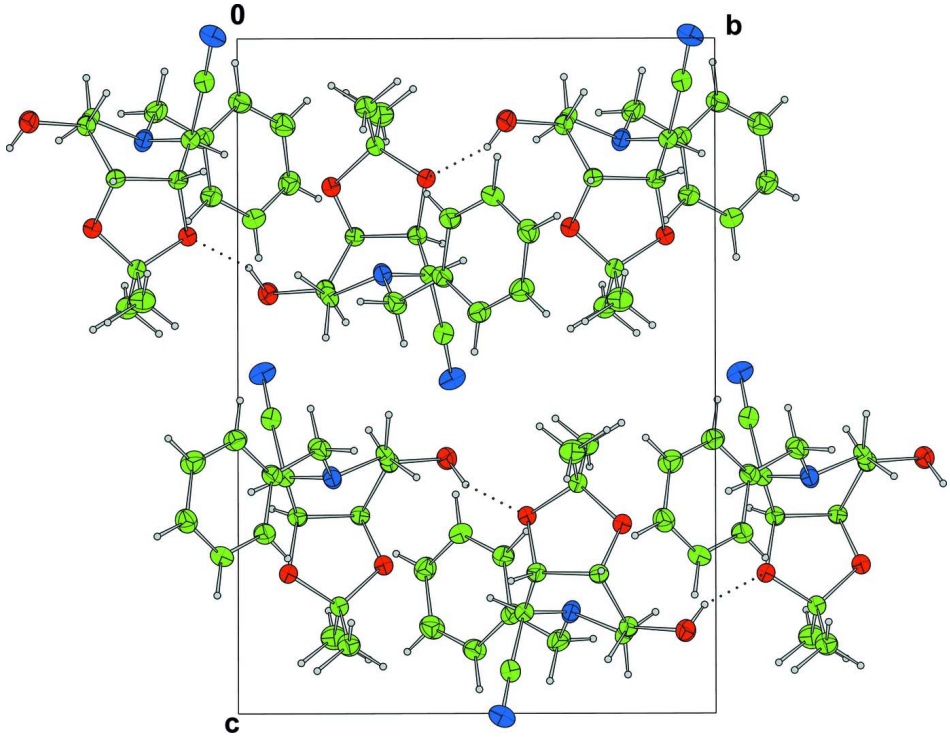


Figure 3

Packing diagram for the crystal projected along the *a*-axis. Hydrogen bonds are shown as dotted lines.

2-*N*-Benzyl-2,6-dideoxy-2,6-imino-3,4-*O*-isopropylidene-*D*-allononitrile

Crystal data

$C_{16}H_{20}N_2O_3$
M_r = 288.35
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
a = 8.3978 (3) Å
b = 11.2689 (4) Å
c = 15.9210 (6) Å
V = 1506.67 (9) Å^3
Z = 4
$F(000)$ = 616
D_x = 1.271 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1934 reflections
θ = 5–27°
μ = 0.09 mm^{-1}
T = 150 K
Plate, colourless
0.4 × 0.4 × 0.2 mm

Data collection

Nonius KappaCCD diffractometer
Graphite monochromator
ω scans
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.91, T_{max} = 0.98
11529 measured reflections
1970 independent reflections
1422 reflections with $I > 2.0\sigma(I)$
R_{int} = 0.079
θ_{max} = 27.5°, θ_{min} = 5.1°
h = −10→10
k = −14→14
l = −20→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.121
S = 0.95
1970 reflections
190 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: difference Fourier map
H-atom parameters constrained
Method, part 1, Chebychev polynomial, (Watkin, 1994, *P*rince, 1982) [*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 belo*w* 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: 9.51 13.9 7.19 2.01
$(\Delta/\sigma)_{max}$ = 0.0000939
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems open-flow nitrogen cryostat (Cosier & Glazer, 1986) with a nominal stability of 0.1 K.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.6465 (3)	0.06340 (19)	0.37776 (14)	0.0305
C2	0.5963 (4)	0.1832 (3)	0.37195 (18)	0.0259
C3	0.6544 (4)	0.2450 (3)	0.29350 (18)	0.0245
O4	0.5816 (3)	0.19584 (18)	0.21979 (12)	0.0272
C5	0.5779 (4)	0.2890 (3)	0.15876 (18)	0.0261
O6	0.5489 (3)	0.39518 (18)	0.20739 (13)	0.0271

C7	0.6006 (4)	0.3759 (3)	0.29150 (18)	0.0256
C8	0.4595 (4)	0.4018 (3)	0.35050 (19)	0.0263
N9	0.3478 (3)	0.3035 (2)	0.34958 (16)	0.0261
C10	0.4160 (4)	0.1919 (3)	0.38247 (19)	0.0270
C11	0.1968 (4)	0.3292 (3)	0.3920 (2)	0.0318
C12	0.1021 (4)	0.4285 (3)	0.35313 (19)	0.0274
C13	0.0911 (5)	0.4450 (3)	0.26682 (19)	0.0315
C14	−0.0032 (5)	0.5344 (3)	0.23328 (19)	0.0323
C15	−0.0876 (4)	0.6088 (3)	0.2858 (2)	0.0308
C16	−0.0756 (5)	0.5947 (3)	0.3724 (2)	0.0343
C17	0.0182 (4)	0.5058 (3)	0.4056 (2)	0.0292
C18	0.5178 (5)	0.4307 (3)	0.4370 (2)	0.0328
N19	0.5612 (5)	0.4487 (3)	0.50421 (18)	0.0470
C20	0.4377 (4)	0.2689 (3)	0.1017 (2)	0.0328
C21	0.7352 (5)	0.3002 (4)	0.1127 (2)	0.0385
H21	0.6469	0.2260	0.4201	0.0308*
H31	0.7717	0.2399	0.2892	0.0303*
H71	0.6919	0.4291	0.3037	0.0311*
H81	0.4052	0.4724	0.3289	0.0310*
H101	0.3912	0.1842	0.4427	0.0319*
H102	0.3691	0.1265	0.3501	0.0317*
H111	0.2187	0.3478	0.4519	0.0382*
H112	0.1318	0.2571	0.3895	0.0380*
H131	0.1502	0.3963	0.2302	0.0381*
H141	−0.0094	0.5442	0.1754	0.0379*
H151	−0.1536	0.6691	0.2632	0.0372*
H161	−0.1325	0.6461	0.4082	0.0410*
H171	0.0255	0.4957	0.4642	0.0353*
H201	0.4276	0.3351	0.0634	0.0489*
H202	0.3408	0.2637	0.1346	0.0490*
H203	0.4527	0.1972	0.0698	0.0487*
H212	0.7322	0.3683	0.0748	0.0564*
H213	0.8215	0.3108	0.1527	0.0572*
H211	0.7541	0.2275	0.0804	0.0572*
H11	0.5995	0.0236	0.3393	0.0472*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0390 (13)	0.0236 (11)	0.0289 (11)	0.0062 (10)	−0.0064 (10)	0.0008 (9)
C2	0.0334 (17)	0.0206 (14)	0.0237 (14)	0.0016 (14)	−0.0040 (13)	0.0000 (12)
C3	0.0305 (15)	0.0222 (13)	0.0208 (13)	0.0006 (14)	−0.0048 (14)	0.0002 (12)
O4	0.0383 (13)	0.0206 (9)	0.0227 (10)	−0.0004 (11)	−0.0020 (10)	0.0007 (9)
C5	0.0354 (17)	0.0203 (13)	0.0225 (14)	−0.0022 (14)	0.0008 (14)	0.0010 (12)
O6	0.0408 (13)	0.0194 (9)	0.0210 (10)	−0.0008 (10)	−0.0012 (10)	−0.0008 (8)
C7	0.0325 (16)	0.0229 (14)	0.0214 (14)	−0.0036 (13)	−0.0041 (14)	0.0010 (12)
C8	0.0354 (18)	0.0217 (14)	0.0218 (13)	−0.0011 (14)	−0.0012 (13)	0.0010 (12)
N9	0.0293 (13)	0.0201 (12)	0.0289 (12)	0.0013 (11)	0.0032 (12)	0.0036 (11)

C10	0.0359 (17)	0.0205 (14)	0.0247 (14)	0.0011 (14)	0.0014 (14)	0.0061 (12)
C11	0.0353 (19)	0.0314 (17)	0.0285 (16)	0.0043 (15)	0.0085 (15)	0.0053 (14)
C12	0.0306 (17)	0.0264 (15)	0.0253 (14)	−0.0003 (14)	0.0030 (13)	0.0033 (13)
C13	0.0408 (19)	0.0280 (15)	0.0257 (14)	0.0045 (16)	0.0066 (15)	0.0009 (13)
C14	0.042 (2)	0.0315 (16)	0.0236 (15)	−0.0002 (16)	−0.0002 (15)	0.0040 (13)
C15	0.0306 (17)	0.0283 (15)	0.0336 (16)	0.0003 (15)	−0.0043 (15)	0.0030 (14)
C16	0.0340 (19)	0.0366 (18)	0.0323 (16)	0.0076 (16)	−0.0012 (15)	−0.0040 (14)
C17	0.0304 (18)	0.0315 (17)	0.0258 (15)	0.0027 (14)	0.0001 (14)	−0.0024 (13)
C18	0.046 (2)	0.0235 (15)	0.0292 (16)	0.0004 (16)	0.0010 (15)	−0.0013 (13)
N19	0.072 (3)	0.0403 (17)	0.0285 (15)	−0.0022 (19)	−0.0039 (16)	−0.0078 (13)
C20	0.0394 (19)	0.0299 (17)	0.0289 (16)	−0.0040 (15)	−0.0061 (16)	0.0013 (13)
C21	0.040 (2)	0.0405 (19)	0.0349 (19)	0.0005 (18)	0.0091 (16)	0.0004 (18)

Geometric parameters (Å, º)

O1—C2	1.418 (4)	C11—C12	1.506 (5)
O1—H11	0.855	C11—H111	0.993
C2—C3	1.511 (4)	C11—H112	0.980
C2—C10	1.527 (5)	C12—C13	1.390 (4)
C2—H21	1.000	C12—C17	1.397 (4)
C3—O4	1.434 (4)	C13—C14	1.388 (5)
C3—C7	1.543 (4)	C13—H131	0.942
C3—H31	0.990	C14—C15	1.381 (5)
O4—C5	1.431 (3)	C14—H141	0.929
C5—O6	1.446 (4)	C15—C16	1.392 (5)
C5—C20	1.504 (5)	C15—H151	0.948
C5—C21	1.516 (5)	C16—C17	1.379 (5)
O6—C7	1.424 (3)	C16—H161	0.943
C7—C8	1.540 (5)	C17—H171	0.943
C7—H71	0.992	C18—N19	1.148 (4)
C8—N9	1.452 (4)	C20—H201	0.968
C8—C18	1.498 (4)	C20—H202	0.970
C8—H81	0.980	C20—H203	0.963
N9—C10	1.477 (4)	C21—H212	0.976
N9—C11	1.466 (4)	C21—H213	0.972
C10—H101	0.986	C21—H211	0.981
C10—H102	0.982		
C2—O1—H11	108.4	N9—C10—H102	107.3
O1—C2—C3	113.4 (3)	H101—C10—H102	111.1
O1—C2—C10	110.4 (3)	N9—C11—C12	114.5 (3)
C3—C2—C10	112.4 (3)	N9—C11—H111	108.9
O1—C2—H21	106.4	C12—C11—H111	109.6
C3—C2—H21	105.9	N9—C11—H112	107.4
C10—C2—H21	107.8	C12—C11—H112	107.8
C2—C3—O4	111.2 (2)	H111—C11—H112	108.5
C2—C3—C7	111.3 (3)	C11—C12—C13	122.8 (3)
O4—C3—C7	103.1 (2)	C11—C12—C17	118.9 (3)

C2—C3—H31	110.6	C13—C12—C17	118.3 (3)
O4—C3—H31	110.2	C12—C13—C14	121.0 (3)
C7—C3—H31	110.2	C12—C13—H131	119.9
C3—O4—C5	106.4 (2)	C14—C13—H131	119.1
O4—C5—O6	104.3 (2)	C13—C14—C15	120.0 (3)
O4—C5—C20	108.4 (3)	C13—C14—H141	120.0
O6—C5—C20	108.4 (3)	C15—C14—H141	120.0
O4—C5—C21	111.8 (3)	C14—C15—C16	119.6 (3)
O6—C5—C21	109.7 (3)	C14—C15—H151	120.3
C20—C5—C21	113.8 (3)	C16—C15—H151	120.1
C5—O6—C7	109.0 (2)	C15—C16—C17	120.3 (3)
C3—C7—O6	104.8 (2)	C15—C16—H161	119.4
C3—C7—C8	113.2 (3)	C17—C16—H161	120.3
O6—C7—C8	108.1 (3)	C12—C17—C16	120.8 (3)
C3—C7—H71	110.3	C12—C17—H171	118.9
O6—C7—H71	109.1	C16—C17—H171	120.3
C8—C7—H71	111.1	C8—C18—N19	177.4 (4)
C7—C8—N9	110.3 (2)	C5—C20—H201	109.5
C7—C8—C18	110.5 (3)	C5—C20—H202	109.9
N9—C8—C18	112.8 (3)	H201—C20—H202	108.3
C7—C8—H81	107.4	C5—C20—H203	110.1
N9—C8—H81	108.4	H201—C20—H203	109.0
C18—C8—H81	107.3	H202—C20—H203	110.1
C8—N9—C10	113.3 (3)	C5—C21—H212	110.0
C8—N9—C11	113.8 (3)	C5—C21—H213	110.1
C10—N9—C11	109.9 (2)	H212—C21—H213	109.1
C2—C10—N9	113.6 (3)	C5—C21—H211	109.0
C2—C10—H101	108.1	H212—C21—H211	109.6
N9—C10—H101	109.8	H213—C21—H211	109.0
C2—C10—H102	107.0		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H11···O6^{i}	0.86	2.05	2.850 (5)	156 (1)

Symmetry code: (i) −*x*+1, *y*−1/2, −*z*+1/2.