Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

7-Azido-*N*,*N*-diethyl-4,5-*O*-isopropylidene-4-*C*-methyl-3,6-anhydro-7-deoxy-D-*glycero*-D-*manno*-heptonamide

Sarah F. Jenkinson,[a]* Chen Wang,[a] Maria-Soledad Pino-González,[b] George W. J. Fleet[a] and David J. Watkin[c]

[a]Department of Organic Chemistry, Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Oxford OX1 3TA, England, [b]Departamento de Bioquímica, Biología Molecular y Química Orgánica, Facultad de Ciencias, Universidad de Málaga, 29071 Málaga, Spain, and [c]Department of Chemical Crystallography, Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Oxford OX1 3TA, England
Correspondence e-mail: sarah.jenkinson@chem.ox.ac.uk

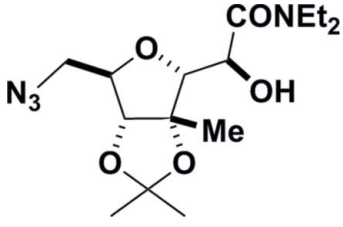
Received 19 December 2008; accepted 31 December 2008

Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.004 Å; R factor = 0.049; wR factor = 0.129; data-to-parameter ratio = 9.2.

The reaction of 5-azido-5-deoxy-2,3-*O*-isopropylidene-2-*C*-methyl-D-ribose with *N*,*N*-diethyl-2-(dimethylsulfuranylidene)acetamide gave the title compound, $C_{15}H_{26}N_4O_5$, as the major product arising from initial formation of an epoxide which was subsequently opened by intramolecular attack of the free 4-hydroxyl group. X-ray crystallography confirmed the relative stereochemistry of the title compound and the absolute configuration was determined by the use of D-ribose as the starting material. The crystal structure contains chains of molecules running parallel to the *a* axis, being linked by weak bifurcated O—H···(N,N) hydrogen bonds.

Related literature

For related literature see: Assiego *et al.* (2004); Pino-González *et al.* (2003, 2008); Valpuesta Fernández *et al.* (1990); Valpuesta *et al.* (1993); Görbitz (1999).



Experimental

Crystal data

$C_{15}H_{26}N_4O_5$
M_r = 342.40
Orthorhombic, $P2_12_12_1$
a = 8.64400 (10) Å
b = 13.4195 (2) Å
c = 15.9146 (3) Å
V = 1846.06 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 150 K
0.60 × 0.60 × 0.40 mm

Data collection

Area diffractometer
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.82, T_{max} = 0.96
23123 measured reflections
2354 independent reflections
2077 reflections with $I > 2\sigma(I)$
R_{int} = 0.077

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.129
S = 1.02
1992 reflections
217 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O17—H171···N10^{i}	0.88	2.30	3.112 (4)	152
O17—H171···N11^{i}	0.88	2.45	3.313 (4)	167

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

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*.

MSPG is grateful to Junta de Andalucia for a grant. The authors thank the Oxford University Crystallography Service for use of the instruments.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2750).

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Assiego, C., Pino-González, M.-S. & López-Herrera, F. J. (2004). *Tetrahedron Lett.* **45**, 2611–2613.
Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
Görbitz, C. H. (1999). *Acta Cryst.* B**55**, 1090–1098.
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.
Pino-González, M.-S., Assiego, C. & López-Herrera, F. J. (2003). *Tetrahedron Lett.* **44**, 8353–8356.
Pino-González, M.-S., Assiego, C. & Oña, N. (2008). *Tetrahedron Asymmetry*, **19**, 932–937.
Valpuesta, M., Durante, P. & López-Herrera, F. J. (1993). *Tetrahedron*, **42**, 9547–9560.
Valpuesta Fernández, M. V., Durante-Lanes, P. & López-Herrera, F. J. (1990). *Tetrahedron*, **46**, 7911–7922.
Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.

supporting information

Acta Cryst. (2009). E**65**, o263 [doi:10.1107/S1600536808044279]

7-Azido-*N*,*N*-diethyl-4,5-*O*-isopropylidene-4-*C*-methyl-3,6-anhydro-7-deoxy-D-*glycero*-D-*manno*-heptonamide

Sarah F. Jenkinson, Chen Wang, Maria-Soledad Pino-González, George W. J. Fleet and David J. Watkin

S1. Comment

The use of sulfur ylids in the stereoselective formation of epoxides and their subsequent regioselective opening has been utilized in the formation of iminosugars such as the seven-membered ring azepanes (Assiego *et al.*, 2004), pipecolic acid derivatives (Pino-González *et al.*,2008) and piperidines (Pino-González *et al.*, 2003). In order to extend this methodology the reaction of azido ribose derivative **1** with *N*,*N*-diethyl-2-(dimethylsulfuranylidene)acetamide was investigated.

Reaction of azido ribose derivative **1** with the sulfur ylid gave the title compound, furan **3**, as the major product (Fig. 1). The product was confirmed, by both X-ray crystallography and the use of D-ribose as the starting material, to have the D-*glycero*-D-*manno* stereochemistry (Fig. 2) arising from initial attack of the ylid on the *Si* face of the aldehyde, as predicted from a Felkin-Ahn model (Valpuesta Fernández *et al.*, 1990; Valpuesta *et al.*, 1993), resulting in formation of epoxide **2**, followed by intramolecular opening of the epoxide to give the title compound **3**.

The compound was seen to adopt weakly (O—H···N) hydrogen bonded chains of molecules running parallel to the *a*-axis. The hydrogen bond is bifurcated (Fig. 3). Only classical hydrogen bonding has been considered.

S2. Experimental

The title compound was recrystallized by vapour diffusion from a mixture of ethyl acetate and cyclohexane: m.p. 371–373 K; $[\alpha]_D^{23}$ +16.4 (*c*, 1.0 in $CHCl_3$).

S3. Refinement

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

The relatively large ratio of minimum to maximum corrections applied in the multiscan process (1:1.16) reflects changes in the illuminated volume of the crystal. Changes in illuminated volume were kept to a minimum, and were taken into account (Görbitz, 1999) by the multi-scan inter-frame scaling (*DENZO*/*SCALEPACK*, Otwinowski & Minor, 1997).

The refinement was performed excluding the data for which I was less than 3σ(I).

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, 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.

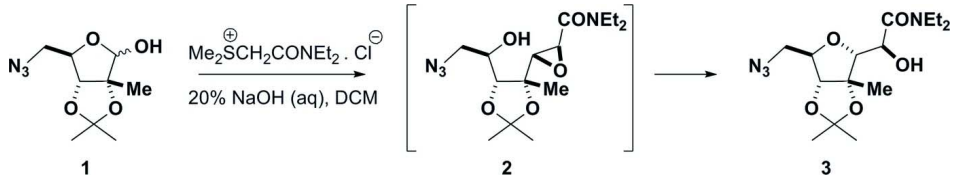


Figure 1

Synthetic Scheme

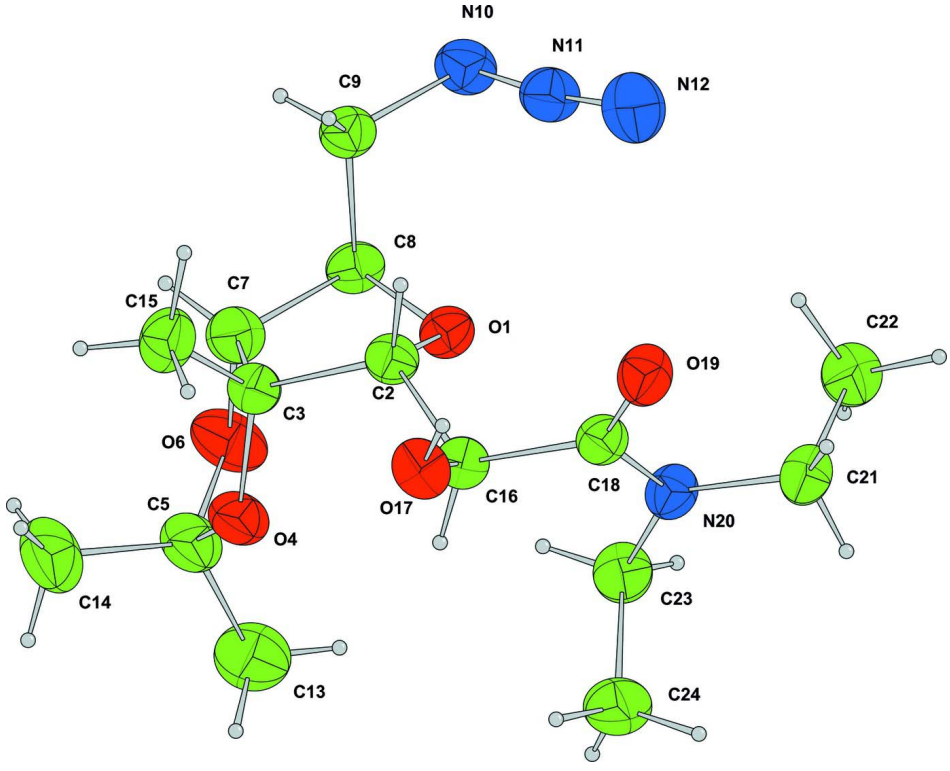


Figure 2

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

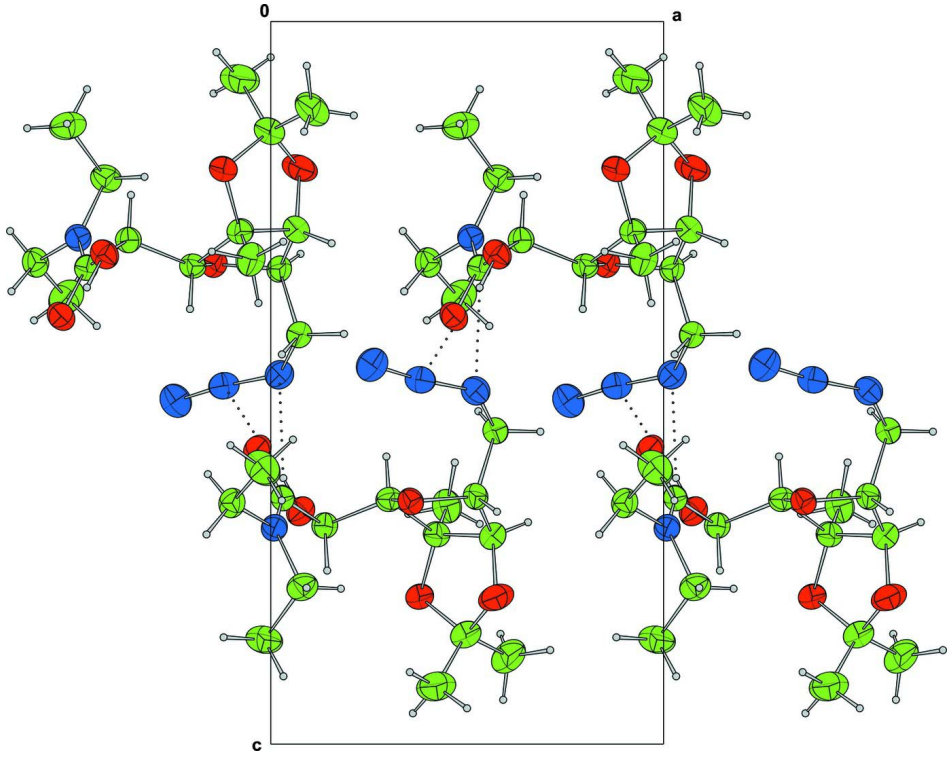


Figure 3

Packing diagram for the title compound projected along the *b*-axis. Hydrogen bonds are indicated by dotted lines.

7-Azido-*N*,*N*-diethyl-4,5-*O*-isopropylidene-4-*C*- methyl-3,6-anhydro-7-deoxy-D-*glycero*-*D*-*manno*-heptonamide

Crystal data

$C_{15}H_{26}N_4O_5$
$M_r = 342.40$
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
$a = 8.6440\ (1)$ Å
$b = 13.4195\ (2)$ Å
$c = 15.9146\ (3)$ Å
$V = 1846.06\ (5)$ Å^3
$Z = 4$
$F(000) = 736$
$D_x = 1.232$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2356 reflections
$\theta = 5$–$27°$
$\mu = 0.09$ mm^{-1}
$T = 150$ K
Plate, colourless
0.60 × 0.60 × 0.40 mm

Data collection

Area diffractometer
Graphite monochromator
ω scans
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min} = 0.82$, $T_{max} = 0.96$
23123 measured reflections
2354 independent reflections
2077 reflections with $I > 2\sigma(I)$
$R_{int} = 0.077$
$\theta_{max} = 27.5°$, $\theta_{min} = 5.1°$
$h = -11 \rightarrow 11$
$k = -17 \rightarrow 17$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.129$
$S = 1.02$
1992 reflections
217 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.1P)^2 + 0.29P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max} = 0.000268$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.35653 (19)	0.34433 (12)	0.66423 (11)	0.0350
C2	0.3014 (3)	0.24404 (17)	0.66153 (15)	0.0332
C3	0.4224 (3)	0.18015 (18)	0.70965 (16)	0.0371
O4	0.3791 (2)	0.17151 (16)	0.79595 (11)	0.0446
C5	0.4967 (3)	0.2129 (2)	0.84827 (18)	0.0489
O6	0.5741 (3)	0.28402 (17)	0.79711 (13)	0.0567
C7	0.5654 (3)	0.2496 (2)	0.71213 (16)	0.0414
C8	0.5218 (3)	0.33863 (19)	0.65738 (15)	0.0359
C9	0.5726 (3)	0.32292 (19)	0.56645 (15)	0.0369
N10	0.5219 (3)	0.40493 (18)	0.51111 (14)	0.0432
N11	0.3807 (3)	0.40751 (17)	0.49594 (14)	0.0432
N12	0.2579 (3)	0.4190 (2)	0.47516 (19)	0.0629
C13	0.4212 (5)	0.2678 (3)	0.9201 (2)	0.0714
C14	0.6054 (4)	0.1311 (3)	0.8787 (2)	0.0650
C15	0.4486 (3)	0.0783 (2)	0.6708 (2)	0.0472
C16	0.1375 (3)	0.23817 (17)	0.69753 (16)	0.0343
O17	0.0763 (2)	0.14313 (12)	0.67786 (11)	0.0401
C18	0.0305 (3)	0.31779 (18)	0.65939 (15)	0.0334
O19	−0.0340 (2)	0.29828 (14)	0.59206 (12)	0.0424
N20	0.0093 (2)	0.40342 (15)	0.70067 (14)	0.0364
C21	−0.0987 (3)	0.47788 (19)	0.66655 (18)	0.0407
C22	−0.0208 (4)	0.5595 (3)	0.6178 (2)	0.0626
C23	0.0809 (3)	0.4266 (2)	0.78247 (16)	0.0430
C24	−0.0166 (4)	0.3904 (3)	0.85556 (18)	0.0562
H21	0.2943	0.2241	0.6020	0.0397*
H71	0.6551	0.2162	0.6930	0.0485*
H81	0.5759	0.3970	0.6784	0.0443*
H91	0.5284	0.2612	0.5394	0.0490*
H92	0.6863	0.3164	0.5677	0.0495*
H131	0.4998	0.2997	0.9504	0.1074*
H132	0.3617	0.2267	0.9575	0.1071*
H133	0.3543	0.3189	0.9005	0.1069*
H141	0.7116	0.1505	0.8701	0.1022*
H142	0.5918	0.1211	0.9387	0.1023*

H143	0.5851	0.0695	0.8476	0.1021*
H151	0.5319	0.0397	0.6952	0.0807*
H152	0.3501	0.0445	0.6815	0.0799*
H153	0.4686	0.0848	0.6104	0.0790*
H161	0.1438	0.2430	0.7599	0.0419*
H211	−0.1602	0.4457	0.6266	0.0494*
H212	−0.1637	0.5025	0.7098	0.0491*
H222	−0.1025	0.5966	0.5865	0.1080*
H221	0.0567	0.5295	0.5787	0.1079*
H223	0.0279	0.6004	0.6627	0.1076*
H232	0.1785	0.3960	0.7850	0.0507*
H231	0.0915	0.4974	0.7838	0.0496*
H243	0.0323	0.4135	0.9063	0.0898*
H242	−0.0188	0.3185	0.8585	0.0891*
H241	−0.1201	0.4187	0.8522	0.0890*
H171	0.0318	0.1201	0.6319	0.0671*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0338 (8)	0.0344 (8)	0.0368 (8)	−0.0019 (7)	0.0028 (7)	−0.0011 (7)
C2	0.0358 (12)	0.0336 (11)	0.0303 (10)	−0.0013 (9)	−0.0010 (9)	−0.0023 (9)
C3	0.0367 (12)	0.0413 (12)	0.0333 (11)	0.0024 (10)	0.0011 (10)	0.0029 (10)
O4	0.0404 (9)	0.0598 (11)	0.0336 (9)	0.0000 (9)	−0.0027 (8)	0.0075 (8)
C5	0.0477 (15)	0.0614 (17)	0.0376 (12)	0.0017 (13)	−0.0068 (12)	0.0052 (12)
O6	0.0642 (13)	0.0683 (13)	0.0375 (9)	−0.0153 (11)	−0.0124 (10)	0.0036 (9)
C7	0.0361 (12)	0.0505 (14)	0.0375 (12)	−0.0017 (12)	−0.0042 (10)	−0.0010 (11)
C8	0.0316 (11)	0.0403 (12)	0.0358 (11)	−0.0059 (10)	0.0019 (10)	−0.0031 (11)
C9	0.0333 (11)	0.0418 (12)	0.0357 (11)	−0.0024 (10)	0.0015 (10)	0.0000 (10)
N10	0.0422 (12)	0.0454 (12)	0.0421 (11)	−0.0054 (10)	0.0024 (10)	0.0055 (9)
N11	0.0482 (14)	0.0450 (12)	0.0365 (10)	0.0012 (10)	0.0022 (10)	0.0005 (9)
N12	0.0513 (16)	0.080 (2)	0.0577 (15)	0.0105 (15)	−0.0074 (13)	0.0077 (15)
C13	0.079 (2)	0.092 (3)	0.0433 (15)	0.010 (2)	−0.0073 (17)	−0.0083 (16)
C14	0.0592 (19)	0.077 (2)	0.0588 (18)	0.0085 (17)	−0.0179 (17)	0.0139 (17)
C15	0.0442 (14)	0.0386 (12)	0.0586 (16)	0.0043 (12)	0.0040 (13)	0.0010 (12)
C16	0.0347 (12)	0.0340 (11)	0.0342 (10)	−0.0023 (10)	−0.0002 (10)	−0.0002 (10)
O17	0.0411 (9)	0.0356 (8)	0.0437 (9)	−0.0075 (8)	−0.0057 (8)	0.0017 (7)
C18	0.0286 (10)	0.0371 (11)	0.0345 (11)	−0.0013 (9)	0.0011 (9)	0.0013 (9)
O19	0.0397 (10)	0.0462 (9)	0.0413 (9)	0.0055 (8)	−0.0070 (8)	−0.0070 (8)
N20	0.0348 (10)	0.0377 (10)	0.0366 (9)	0.0027 (8)	−0.0017 (8)	−0.0055 (8)
C21	0.0356 (12)	0.0413 (12)	0.0451 (13)	0.0055 (10)	−0.0023 (11)	−0.0043 (11)
C22	0.063 (2)	0.0606 (19)	0.0639 (19)	0.0157 (16)	0.0146 (17)	0.0167 (16)
C23	0.0496 (15)	0.0401 (12)	0.0393 (13)	0.0020 (12)	−0.0046 (12)	−0.0080 (11)
C24	0.070 (2)	0.0591 (17)	0.0393 (13)	0.0089 (16)	0.0069 (14)	−0.0047 (13)

Geometric parameters (Å, º)

O1—C2	1.429 (3)	C14—H142	0.972
O1—C8	1.435 (3)	C14—H143	0.979
C2—C3	1.554 (3)	C15—H151	0.968
C2—C16	1.530 (3)	C15—H152	0.979
C2—H21	0.986	C15—H153	0.982
C3—O4	1.428 (3)	C16—O17	1.415 (3)
C3—C7	1.548 (4)	C16—C18	1.538 (3)
C3—C15	1.517 (4)	C16—H161	0.997
O4—C5	1.427 (4)	O17—H171	0.882
C5—O6	1.422 (4)	C18—O19	1.236 (3)
C5—C13	1.509 (5)	C18—N20	1.336 (3)
C5—C14	1.524 (4)	N20—C21	1.471 (3)
O6—C7	1.431 (3)	N20—C23	1.475 (3)
C7—C8	1.526 (4)	C21—C22	1.501 (4)
C7—H71	0.946	C21—H211	0.934
C8—C9	1.527 (3)	C21—H212	0.947
C8—H81	0.972	C22—H222	0.998
C9—N10	1.476 (3)	C22—H221	0.999
C9—H91	1.009	C22—H223	0.994
C9—H92	0.987	C23—C24	1.516 (4)
N10—N11	1.245 (4)	C23—H232	0.940
N11—N12	1.122 (4)	C23—H231	0.955
C13—H131	0.936	C24—H243	0.962
C13—H132	0.960	C24—H242	0.967
C13—H133	0.950	C24—H241	0.973
C14—H141	0.964		

C2—O1—C8	106.25 (18)	C5—C14—H142	109.8
O1—C2—C3	106.27 (19)	H141—C14—H142	107.0
O1—C2—C16	110.26 (19)	C5—C14—H143	109.7
C3—C2—C16	114.23 (19)	H141—C14—H143	109.0
O1—C2—H21	107.7	H142—C14—H143	111.0
C3—C2—H21	111.4	C3—C15—H151	115.5
C16—C2—H21	106.8	C3—C15—H152	102.5
C2—C3—O4	110.0 (2)	H151—C15—H152	109.3
C2—C3—C7	102.59 (19)	C3—C15—H153	110.2
O4—C3—C7	103.5 (2)	H151—C15—H153	108.0
C2—C3—C15	113.4 (2)	H152—C15—H153	111.4
O4—C3—C15	110.9 (2)	C2—C16—O17	108.00 (19)
C7—C3—C15	115.7 (2)	C2—C16—C18	111.91 (19)
C3—O4—C5	110.1 (2)	O17—C16—C18	108.32 (19)
O4—C5—O6	105.2 (2)	C2—C16—H161	108.6
O4—C5—C13	108.9 (3)	O17—C16—H161	107.5
O6—C5—C13	108.1 (3)	C18—C16—H161	112.4
O4—C5—C14	110.1 (3)	C16—O17—H171	131.5
O6—C5—C14	112.1 (3)	C16—C18—O19	117.8 (2)

C13—C5—C14	112.2 (3)	C16—C18—N20	119.1 (2)
C5—O6—C7	107.4 (2)	O19—C18—N20	123.1 (2)
C3—C7—O6	105.1 (2)	C18—N20—C21	119.3 (2)
C3—C7—C8	105.0 (2)	C18—N20—C23	123.9 (2)
O6—C7—C8	107.4 (2)	C21—N20—C23	116.7 (2)
C3—C7—H71	111.2	N20—C21—C22	113.7 (2)
O6—C7—H71	114.5	N20—C21—H211	107.4
C8—C7—H71	112.9	C22—C21—H211	104.0
C7—C8—O1	104.13 (19)	N20—C21—H212	110.2
C7—C8—C9	111.2 (2)	C22—C21—H212	112.8
O1—C8—C9	111.5 (2)	H211—C21—H212	108.5
C7—C8—H81	108.4	C21—C22—H222	107.7
O1—C8—H81	114.2	C21—C22—H221	109.2
C9—C8—H81	107.4	H222—C22—H221	111.3
C8—C9—N10	112.2 (2)	C21—C22—H223	102.8
C8—C9—H91	114.2	H222—C22—H223	112.6
N10—C9—H91	104.2	H221—C22—H223	112.7
C8—C9—H92	106.3	N20—C23—C24	112.1 (2)
N10—C9—H92	112.0	N20—C23—H232	108.8
H91—C9—H92	108.2	C24—C23—H232	109.1
C9—N10—N11	115.3 (2)	N20—C23—H231	105.7
N10—N11—N12	171.3 (3)	C24—C23—H231	110.8
C5—C13—H131	107.4	H232—C23—H231	110.3
C5—C13—H132	114.9	C23—C24—H243	107.2
H131—C13—H132	109.5	C23—C24—H242	111.6
C5—C13—H133	111.5	H243—C24—H242	106.8
H131—C13—H133	106.3	C23—C24—H241	110.1
H132—C13—H133	107.0	H243—C24—H241	109.0
C5—C14—H141	110.3	H242—C24—H241	112.0

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H91···O19^{i}	1.01	2.30	3.140 (4)	140
C9—H92···O19^{ii}	0.99	2.46	3.441 (4)	172
C23—H232···O1	0.94	2.56	3.231 (4)	129
C23—H231···O17^{iii}	0.95	2.51	3.269 (4)	136
O17—H171···N10^{iv}	0.88	2.30	3.112 (4)	152
O17—H171···N11^{iv}	0.88	2.45	3.313 (4)	167

Symmetry codes: (i) $x+1/2, -y+1/2, -z+1$; (ii) $x+1, y, z$; (iii) $-x, y+1/2, -z+3/2$; (iv) $x-1/2, -y+1/2, -z+1$.