

Andreas Glawar,^a Benjamin A. Mayes,^b David Watkin^{a*} and George W. J. Fleet^b^aChemical Crystallography, Chemical Research Laboratory, University of Oxford, Oxford OX1 3TA, England, and ^bDepartment of Organic Chemistry, Chemical Research Laboratory, Mansfield Road, Oxford OX1 3TA, EnglandCorrespondence e-mail:
david.watkin@chem.ox.ac.uk

Key indicators

Single-crystal X-ray study
T = 190 K
Mean $\sigma(C-C)$ = 0.002 Å
R factor = 0.032
wR factor = 0.069
Data-to-parameter ratio = 10.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**(2R,3S,4S,5R)-Methyl 5-cyano-2,3:4,5-di-O-isopropylidene-2,3,4,5-tetrahydropentanoate**The title nitrile, C₁₃H₁₉NO₆, a formal oxidation product, was unexpectedly isolated during hydrogenation of an azide precursor in the presence of palladium black.

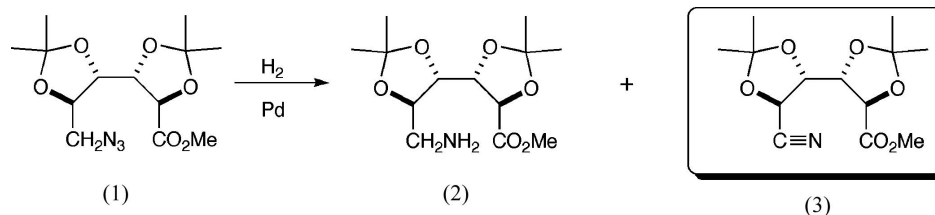
Received 15 July 2005

Accepted 25 July 2005

Online 27 July 2005

Comment

The azide group is synthetically important due to its ability to be reduced under a variety of conditions, thus permitting the controlled introduction of an amine functionality (Scriven & Turnbull, 1988). Further reagents for the reduction of azides to form amines and amides continue to be discovered (Fazio & Wong, 2003); ruthenium(III) has been shown to be an efficient promoter for the formation of amides from azides and thioacids (Shangguan *et al.*, 2003). Although catalytic hydrogenation is a particularly useful method of azide reduction, often providing excellent yields whilst leaving other sensitive functionalities intact, surprising complications are still discovered; thus catalytic reduction of a series of bicyclic azides (RN₃) resulted in the formation of a number of azoamines (RN=N–NH₂) arising from simple addition of hydrogen to the terminal nitrogen of the azide (Beacham *et al.*, 1998). When the azido ester (1) was hydrogenated in the presence of palladium black in 1,4-dioxan, the majority of the products were derived from the amino ester (2) (Mayes, Simon *et al.*, 2004; Mayes, Stetz, Watterson *et al.*, 2004; Mayes, Stetz, Ansell & Fleet, 2004). However, significant amounts of the nitrile (3) were also formed during the reduction; this is unexpected, since the formation of the nitrile appears to be a formal oxidation occurring under reducing conditions. Although previous examples of the catalytic decomposition of primary azides to nitriles have been reported (Hayashi *et al.*, 1976; Kappe, 1990; Kotsuki *et al.*, 1997), this is the first example of the formation of a nitrile being formed under hydrogenation conditions. The structure of the unexpected product (3), including the relative configuration at C-5 (atom C13) bearing the nitrile, was firmly established by X-ray crystallographic analysis (Fig. 1); the absolute configuration arises from the use of D-galactose as the original starting material.



The crystal structure of (3) is unexceptional, consisting of layers of molecules lying parallel to the *ab* plane (Fig. 2). One face of the layer is relatively flat and consists of nitrile and

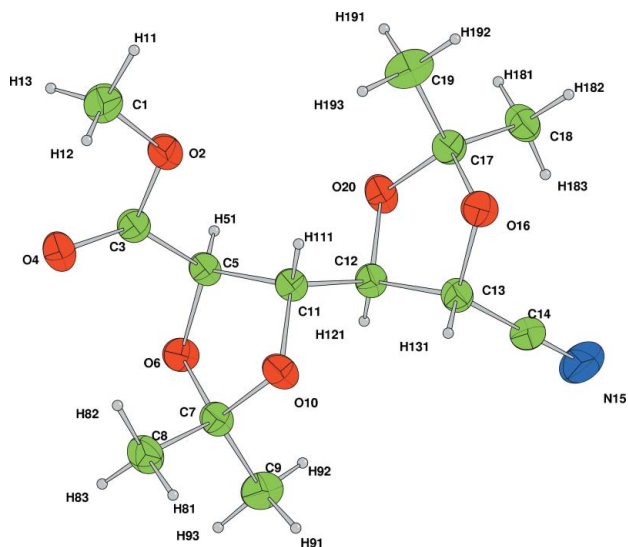


Figure 1

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

methyl groups facing an identical face of the next layer. The other face of the layer is pleated, with the methyl carboxylate groups of one layer interleaving with the corresponding groups on the adjacent face. There are no unexpectedly short *O*-methyl or *N*-methyl contacts.

Experimental

The azide ester (1) was hydrogenated in the presence of palladium black in 1,4-dioxan (Mayes, Simon *et al.*, 2004) and the title material crystallized from ethyl acetate/hexane.

Crystal data

$C_{13}H_{19}NO_6$	$D_x = 1.280 \text{ Mg m}^{-3}$
$M_r = 285.30$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 1417 reflections
$a = 10.4312 (3) \text{ \AA}$	$\theta = 3\text{--}27^\circ$
$b = 5.4469 (1) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$c = 13.0536 (5) \text{ \AA}$	$T = 190 \text{ K}$
$\beta = 93.4825 (10)^\circ$	Block, colourless
$V = 740.31 (4) \text{ \AA}^3$	$0.80 \times 0.50 \times 0.30 \text{ mm}$
$Z = 2$	

Data collection

Nonius KappaCCD diffractometer	1848 independent reflections
ω scans	1848 reflections with $I > -3\sigma(I)$
Absorption correction: multi-scan	$R_{\text{int}} = 0.020$
(<i>DENZO/SCALEPACK</i> ;	$\theta_{\text{max}} = 27.5^\circ$
Otwinowski & Minor, 1997)	$h = -13 \rightarrow 13$
$T_{\text{min}} = 0.87$, $T_{\text{max}} = 0.97$	$k = -6 \rightarrow 7$
4978 measured reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F^2) + (0.03P)^2 + 0.15P]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = [\max(F_o^2, 0) + 2F_c^2]/3$
$wR(F^2) = 0.069$	$(\Delta\rho)_{\text{max}} < 0.001$
$S = 0.99$	$\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
1848 reflections	$\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$
182 parameters	Extinction correction: Larson
H-atom parameters constrained	(1970), equation 22
	Extinction coefficient: $1.6 (3) \times 10^2$

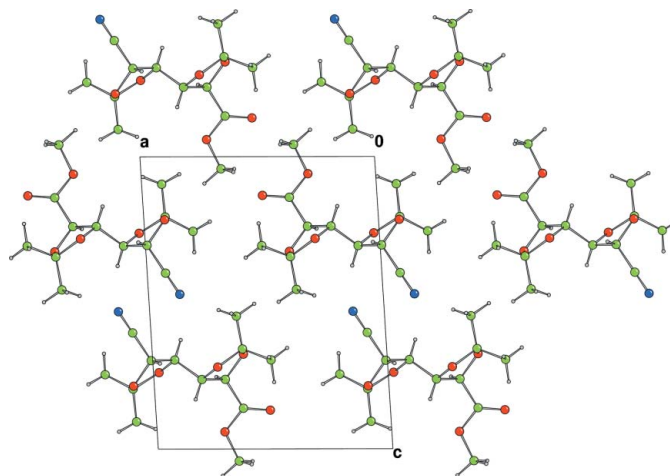


Figure 2

Packing diagram of (3), viewed along the *b* axis.

Table 1

Selected geometric parameters (\AA , $^\circ$).

C1—O2	1.456 (2)	C11—C12	1.530 (2)
O2—C3	1.3378 (18)	C12—C13	1.522 (2)
C3—O4	1.1996 (19)	C12—O20	1.4235 (19)
C3—C5	1.521 (2)	C13—C14	1.490 (2)
C5—O6	1.4178 (18)	C13—O16	1.420 (2)
C5—C11	1.523 (2)	C14—N15	1.136 (2)
O6—C7	1.438 (2)	O16—C17	1.443 (2)
C7—C8	1.516 (2)	C17—C18	1.513 (2)
C7—C9	1.510 (2)	C17—C19	1.510 (2)
C7—O10	1.4461 (19)	C17—O20	1.439 (2)
O10—C11	1.4222 (18)		
C1—O2—C3	115.80 (12)	O10—C11—C12	110.98 (12)
O2—C3—O4	123.87 (15)	C11—C12—C13	111.06 (12)
O2—C3—C5	110.05 (12)	C11—C12—O20	110.43 (12)
O4—C3—C5	126.05 (14)	C13—C12—O20	102.95 (11)
C3—C5—O6	112.57 (12)	C12—C13—C14	112.31 (15)
C3—C5—C11	113.63 (13)	C12—C13—O16	103.07 (13)
O6—C5—C11	103.27 (12)	C14—C13—O16	111.41 (13)
C5—O6—C7	109.03 (12)	C13—C14—N15	179.74 (19)
O6—C7—C8	110.98 (15)	C13—O16—C17	107.76 (13)
O6—C7—C9	108.91 (15)	O16—C17—C18	111.13 (16)
C8—C7—C9	112.88 (15)	O16—C17—C19	108.22 (16)
O6—C7—O10	105.41 (13)	C18—C17—C19	113.72 (16)
C8—C7—O10	108.12 (13)	O16—C17—O20	104.95 (13)
C9—C7—O10	110.29 (13)	C18—C17—O20	108.84 (14)
C7—O10—C11	109.36 (12)	C19—C17—O20	109.61 (14)
C5—C11—O10	103.10 (11)	C17—O20—C12	110.26 (12)
C5—C11—C12	111.47 (12)		

In the absence of significant anomalous scattering, Friedel pairs were merged, and the absolute configuration is arbitrarily assigned. The relatively large ratio of minimum to maximum corrections applied in the multiscan process (1:1.11) reflect changes in the illuminated volume of the crystal. The H atoms were all located in a difference map, but those attached to C atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry ($C-H = 0.93\text{--}0.98 \text{ \AA}$) and displacement parameters [$U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{parent atom})$], after which they were refined with riding constraints.

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*.

References

- Altomare, A., Casciaro, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Beacham, A. R., Smelt, K. H., Biggadike, K., Britten, C. J., Hackett, L., Winchester, B. G., Nash, R. J., Griffiths, R. C. & Fleet, G. W. J. (1998). *Tetrahedron Lett.* **39**, 151–154.
- Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
- Fazio, F. & Wong, C.-H. (2003). *Tetrahedron Lett.* **44**, 9083–9085.
- Hayashi, H., Ohno, A. & Oka, S. (1976). *Bull. Chem. Soc. Jpn*, **49**, 506–509.
- Kappe, C. O. (1990). *Liebigs Ann. Chem.* pp. 505–507.
- Kotsuki, H., Ohishi, T. & Araki, T. (1997). *Tetrahedron Lett.* **38**, 2129–2132.
- Mayes, B. A., Simon, L., Watkin, D. J., Ansell, C. W. G. & Fleet, G. W. J. (2004). *Tetrahedron Lett.* **45**, 157–162.
- Mayes, B. A., Stetz, R. J. E., Ansell, C. W. G. & Fleet, G. W. J. (2004). *Tetrahedron Lett.* **45**, 153–156.
- Mayes, B. A., Stetz, R. J. E., Watterson, M. P., Edwards, A. A., Ansell, C. W. G., Tranter, G. E. & Fleet, G. W. J. (2004). *Tetrahedron Asymmetry*, **15**, 627–638.
- 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.
- Scriven, E. F. V. & Turnbull, K. (1988). *Chem. Rev.* **88**, 297–368.
- Shangguan, N., Katukojvala, S., Greenberg, R. & Williams, L. J. (2003). *J. Am. Chem. Soc.* **125**, 7754–7755.
- Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.

supporting information

Acta Cryst. (2005). E61, o2727–o2729 [https://doi.org/10.1107/S1600536805023834]

(2*R*,3*S*,4*S*,5*R*)-Methyl 5-cyano-2,3:4,5-di-*O*-isopropylidene-2,3,4,5-tetrahydroxypentanoate

Andreas Glawar, Benjamin A. Mayes, David Watkin and George W. J. Fleet

(2*R*,3*S*,4*S*,5*R*)-Methyl 5-cyano-2,3:4,5-di-*O*-isopropylidene-2,3,4,5-tetrahydroxypentanoate

Crystal data

C₁₃H₁₉NO₆

M_r = 285.30

Monoclinic, *P*2₁

a = 10.4312 (3) Å

b = 5.4469 (1) Å

c = 13.0536 (5) Å

β = 93.4825 (10)°

V = 740.31 (4) Å³

Z = 2

F(000) = 304

D_x = 1.280 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 1417 reflections

θ = 3–27°

μ = 0.10 mm⁻¹

T = 190 K

Block, colourless

0.80 × 0.50 × 0.30 mm

Data collection

Nonius KappaCCD
diffractometer

Graphite monochromator

ω scans

Absorption correction: multi-scan

(DENZO/SCALEPACK; Otwinowski & Minor,
1997)

T_{min} = 0.87, *T_{max}* = 0.97

4978 measured reflections

1848 independent reflections

1848 reflections with *I* > -3σ(*I*)

R_{int} = 0.020

θ_{max} = 27.5°, θ_{min} = 4.7°

h = -13→13

k = -6→7

l = -16→16

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.032

wR(*F*²) = 0.069

S = 0.99

1848 reflections

182 parameters

1 restraint

Primary atom site location: structure-invariant
direct methods

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

w = 1/[σ²(*F*²) + (0.03*P*)² + 0.15*P*]

where *P* = [max(*F_o*², 0) + 2*F_c*²]/3

(Δ/σ)_{max} = 0.000365

Δρ_{max} = 0.18 e Å⁻³

Δρ_{min} = -0.15 e Å⁻³

Extinction correction: Larson 1970

Crystallographic Computing eq 22

Extinction coefficient: 160 (30)

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C1	0.65764 (17)	0.6699 (5)	1.04143 (13)	0.0426
O2	0.71146 (10)	0.6530 (3)	0.94132 (9)	0.0372

C3	0.62621 (14)	0.6379 (3)	0.86076 (12)	0.0272
O4	0.51203 (10)	0.6423 (3)	0.86742 (9)	0.0389
C5	0.69562 (14)	0.6225 (3)	0.76183 (11)	0.0250
O6	0.61174 (11)	0.5653 (2)	0.67559 (9)	0.0284
C7	0.61457 (16)	0.3048 (3)	0.65796 (13)	0.0275
C8	0.49552 (15)	0.1822 (4)	0.69526 (14)	0.0354
C9	0.63211 (18)	0.2588 (4)	0.54558 (13)	0.0396
O10	0.72462 (10)	0.2156 (2)	0.71971 (9)	0.0296
C11	0.79554 (14)	0.4185 (3)	0.76192 (12)	0.0240
C12	0.90623 (14)	0.4853 (3)	0.69547 (12)	0.0249
C13	1.00643 (15)	0.2819 (3)	0.69727 (13)	0.0289
C14	1.07823 (16)	0.2771 (4)	0.60205 (14)	0.0384
N15	1.13337 (18)	0.2738 (4)	0.52965 (14)	0.0613
O16	1.08841 (12)	0.3413 (2)	0.78462 (9)	0.0320
C17	1.09141 (16)	0.6051 (3)	0.79421 (13)	0.0291
C18	1.20660 (15)	0.7121 (4)	0.74499 (14)	0.0371
C19	1.0856 (2)	0.6692 (5)	0.90635 (14)	0.0486
O20	0.97635 (10)	0.6886 (2)	0.73847 (9)	0.0317
H11	0.7301	0.6879	1.0916	0.0619*
H12	0.6097	0.5201	1.0535	0.0644*
H13	0.6005	0.8096	1.0434	0.0632*
H51	0.7344	0.7826	0.7521	0.0275*
H81	0.5034	0.0085	0.6846	0.0524*
H82	0.4877	0.2168	0.7692	0.0517*
H83	0.4225	0.2499	0.6549	0.0524*
H91	0.6504	0.0870	0.5351	0.0585*
H92	0.7051	0.3564	0.5250	0.0583*
H93	0.5536	0.3026	0.5039	0.0582*
H111	0.8278	0.3770	0.8310	0.0273*
H121	0.8747	0.5279	0.6267	0.0290*
H131	0.9680	0.1242	0.7065	0.0337*
H181	1.2034	0.8935	0.7523	0.0530*
H182	1.2828	0.6540	0.7793	0.0551*
H183	1.2058	0.6714	0.6734	0.0540*
H191	1.0804	0.8469	0.9130	0.0725*
H192	1.1623	0.6100	0.9426	0.0726*
H193	1.0081	0.5924	0.9306	0.0724*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0387 (9)	0.0557 (12)	0.0331 (8)	0.0046 (10)	0.0010 (7)	-0.0069 (10)
O2	0.0275 (5)	0.0516 (8)	0.0322 (6)	0.0015 (6)	-0.0013 (4)	-0.0073 (6)
C3	0.0267 (7)	0.0211 (8)	0.0336 (8)	0.0008 (7)	0.0005 (6)	-0.0007 (7)
O4	0.0250 (5)	0.0508 (8)	0.0408 (6)	0.0015 (6)	0.0026 (5)	-0.0050 (7)
C5	0.0230 (7)	0.0199 (8)	0.0318 (8)	-0.0001 (6)	-0.0009 (6)	0.0025 (7)
O6	0.0312 (6)	0.0210 (6)	0.0322 (6)	0.0029 (5)	-0.0045 (5)	0.0017 (5)
C7	0.0261 (8)	0.0215 (8)	0.0346 (8)	0.0015 (6)	-0.0016 (6)	0.0014 (7)

C8	0.0285 (7)	0.0304 (9)	0.0473 (10)	-0.0042 (8)	0.0022 (7)	-0.0009 (8)
C9	0.0445 (10)	0.0384 (10)	0.0357 (9)	-0.0002 (9)	0.0008 (7)	-0.0034 (8)
O10	0.0265 (5)	0.0184 (6)	0.0431 (6)	-0.0008 (5)	-0.0050 (5)	0.0031 (5)
C11	0.0243 (7)	0.0188 (7)	0.0288 (7)	-0.0002 (6)	0.0000 (6)	0.0030 (6)
C12	0.0251 (7)	0.0200 (8)	0.0296 (7)	0.0011 (6)	0.0018 (6)	0.0025 (6)
C13	0.0248 (7)	0.0244 (8)	0.0376 (8)	0.0005 (7)	0.0014 (6)	-0.0035 (7)
C14	0.0315 (8)	0.0381 (11)	0.0455 (10)	-0.0015 (8)	0.0024 (7)	-0.0165 (9)
N15	0.0566 (10)	0.0740 (15)	0.0553 (11)	-0.0094 (11)	0.0200 (9)	-0.0304 (11)
O16	0.0331 (6)	0.0235 (6)	0.0385 (7)	0.0049 (5)	-0.0052 (5)	0.0002 (5)
C17	0.0284 (8)	0.0234 (8)	0.0352 (8)	0.0021 (6)	-0.0006 (7)	-0.0018 (7)
C18	0.0252 (7)	0.0365 (10)	0.0491 (10)	-0.0020 (8)	-0.0008 (7)	-0.0053 (8)
C19	0.0621 (12)	0.0453 (12)	0.0385 (10)	-0.0004 (11)	0.0035 (9)	-0.0087 (10)
O20	0.0234 (5)	0.0189 (6)	0.0525 (7)	0.0002 (5)	0.0003 (5)	0.0012 (5)

Geometric parameters (Å, °)

C1—O2	1.456 (2)	O10—C11	1.4222 (18)
C1—H11	0.975	C11—C12	1.530 (2)
C1—H12	0.975	C11—H111	0.970
C1—H13	0.968	C12—C13	1.522 (2)
O2—C3	1.3378 (18)	C12—O20	1.4235 (19)
C3—O4	1.1996 (19)	C12—H121	0.965
C3—C5	1.521 (2)	C13—C14	1.490 (2)
C5—O6	1.4178 (18)	C13—O16	1.420 (2)
C5—C11	1.523 (2)	C13—H131	0.958
C5—H51	0.973	C14—N15	1.136 (2)
O6—C7	1.438 (2)	O16—C17	1.443 (2)
C7—C8	1.516 (2)	C17—C18	1.513 (2)
C7—C9	1.510 (2)	C17—C19	1.510 (2)
C7—O10	1.4461 (19)	C17—O20	1.439 (2)
C8—H81	0.961	C18—H181	0.993
C8—H82	0.992	C18—H182	0.943
C8—H83	0.972	C18—H183	0.960
C9—H91	0.966	C19—H191	0.974
C9—H92	0.980	C19—H192	0.960
C9—H93	0.985	C19—H193	0.980
O2—C1—H11	106.5	O10—C11—C12	110.98 (12)
O2—C1—H12	108.7	C5—C11—H111	111.7
H11—C1—H12	111.2	O10—C11—H111	108.8
O2—C1—H13	110.2	C12—C11—H111	110.6
H11—C1—H13	110.9	C11—C12—C13	111.06 (12)
H12—C1—H13	109.3	C11—C12—O20	110.43 (12)
C1—O2—C3	115.80 (12)	C13—C12—O20	102.95 (11)
O2—C3—O4	123.87 (15)	C11—C12—H121	111.0
O2—C3—C5	110.05 (12)	C13—C12—H121	112.6
O4—C3—C5	126.05 (14)	O20—C12—H121	108.5
C3—C5—O6	112.57 (12)	C12—C13—C14	112.31 (15)

C3—C5—C11	113.63 (13)	C12—C13—O16	103.07 (13)
O6—C5—C11	103.27 (12)	C14—C13—O16	111.41 (13)
C3—C5—H51	106.5	C12—C13—H131	111.2
O6—C5—H51	109.5	C14—C13—H131	108.9
C11—C5—H51	111.3	O16—C13—H131	109.8
C5—O6—C7	109.03 (12)	C13—C14—N15	179.74 (19)
O6—C7—C8	110.98 (15)	C13—O16—C17	107.76 (13)
O6—C7—C9	108.91 (15)	O16—C17—C18	111.13 (16)
C8—C7—C9	112.88 (15)	O16—C17—C19	108.22 (16)
O6—C7—O10	105.41 (13)	C18—C17—C19	113.72 (16)
C8—C7—O10	108.12 (13)	O16—C17—O20	104.95 (13)
C9—C7—O10	110.29 (13)	C18—C17—O20	108.84 (14)
C7—C8—H81	107.9	C19—C17—O20	109.61 (14)
C7—C8—H82	110.2	C17—C18—H181	108.1
H81—C8—H82	110.0	C17—C18—H182	109.7
C7—C8—H83	106.8	H181—C18—H182	108.7
H81—C8—H83	111.5	C17—C18—H183	111.3
H82—C8—H83	110.3	H181—C18—H183	109.0
C7—C9—H91	109.5	H182—C18—H183	110.0
C7—C9—H92	108.5	C17—C19—H191	108.8
H91—C9—H92	108.9	C17—C19—H192	108.5
C7—C9—H93	110.5	H191—C19—H192	109.9
H91—C9—H93	108.8	C17—C19—H193	107.3
H92—C9—H93	110.6	H191—C19—H193	110.1
C7—O10—C11	109.36 (12)	H192—C19—H193	112.1
C5—C11—O10	103.10 (11)	C17—O20—C12	110.26 (12)
C5—C11—C12	111.47 (12)		
