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(1*S*,1′*S*,2′*R*,4a′*S*,9a′*S*,9b′*R*)-1′-Acetyloxy-2,4′-dioxo-2′,4′,4a′,7′,8′,9′,9a′,9b′-octahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrano[4,3-*a*]pyrrolizin]-2′-ylmethyl acetate

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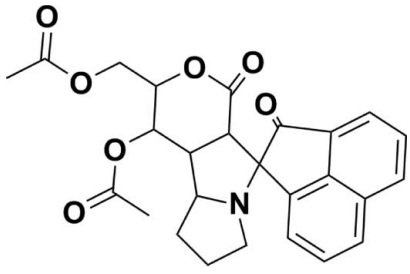
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.004 Å; disorder in main residue; R factor = 0.042; wR factor = 0.104; data-to-parameter ratio = 10.9.

In the title compound $C_{26}H_{25}NO_7$, the mean plane through the lactone-substituted ring of the pyrrolizidine moiety forms dihedral angles of 78.46 (6) and 58.28 (8)° with the acenaphthylene moiety and the sugar based-lactone ring, respectively. The sum of the angles at the the N atom of the pyrrolizidine ring (335.0°) is in accordance with sp^3 hybridization. Some atoms of the acetate group are disordered and were refined using a split model [occupancy ratio 0.673 (10):0.327 (10)].

Related literature

For the importance of pyrrolidine and pyrrolizidine compounds and background to this work, see: Boido *et al.* (1994); Cravotto *et al.* (2001); Gershbein (1975); Govind *et al.* (2003); Jellimann *et al.* (2000); Nishimura *et al.* (1985); Selvanayagam *et al.* (2004); Usha *et al.* (2005).



Experimental

Crystal data

$C_{26}H_{25}NO_7$
M_r = 463.47
Tetragonal, $P4_32_12$
a = 13.6792 (3) Å
c = 24.9625 (13) Å
V = 4671.0 (3) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 295 K
0.30 × 0.30 × 0.25 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.902, T_{max} = 0.976
21173 measured reflections
4010 independent reflections
2923 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.104
S = 1.06
4010 reflections
367 parameters
138 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2009).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NC2316).

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supplementary materials

Acta Cryst. (2013). E**69**, o1601 [doi:10.1107/S1600536813026111]

(1*S*,1′*S*,2′*R*,4a′*S*,9a′*S*,9b′*R*)-1′-Acetyloxy-2,4′-dioxo-2′,4′,4a′,7′,8′,9′,9a′,9b′-octahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrano[4,3-*a*]pyrrolizin]-2′-yl-methyl acetate

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1. Comment

Synthesis of polycyclic compounds incorporating pyrrolidine and pyrrolizidine rings has been the center of attraction for the past several decades since it constitutes significant class of substances with highly pronounced biological activities (Nishimura *et al.*,1985). Pyrrolizidine alkaloids represent a group of compounds present in a variety of plants throughout the world (Usha *et al.*, 2005). Acenaphthylene derivatives are found to have high *κ*-opioid receptor affinity and selectivity (Selvanayagam *et al.*, 2004). These derivatives are used as new conformationally restricted ligands for melatonin receptors (Jellimann *et al.*, 2000), liver regeneration (Gershbein *et al.*, 1975) and antitumoral agents (Boido *et al.*, 1994). Spiro compounds are often encountered in pharmacologically relevant alkaloids (Cravotto *et al.*, 2001). In view of the important biological activities, the structure determination of the title compound was undertaken (Fig.1).

The lactone substituted ring of the pyrrolizidine moiety [C12/N1/C16—C18] forms dihedral angles of 78.46 (6)°, 58.28 (8)° with the acenaphthylene moiety [C12/C1—C11] and sugar based-lactone ring [C18/C17/C21/C20/O2/C19] respectively. The sum of the angles at nitrogen atom of the pyrrolizidine ring [335.01 (0.6)°] is in accordance with sp^3 hybridization (Govind *et al.*,2003).

2. Experimental

To a solution of acenaphthoquinone (1 equiv) and proline (1.4 equiv) in dry toluene, *α*,*β*- unsaturated sugar lactone was added under nitrogen atmosphere. The solution was refluxed for 10 h until the reaction was complete which was monitored by TLC. The solvent was evaporated under reduced pressure and the residue was extracted with dichloro-methane and water. The organic layer was dried with anhydrous sodium sulfate and concentrated *in vacuo*. The crude product was purified by column chromatography using hexane/EtOAc (8:2) as an eluent. Crystals were obtained by slow evaporation of the solvent.

3. Refinement

Both acetate groups are disordered over two positions with side occupancies of 0.673 (10) and 0.327 (10) respectively. The disorder was refined using restraints for the bond distances of 1.50 (1) A° for C—C, 1.32 (1) A° and 1.20 (1) A° for C—O and C=O respectively. Restraints were also used to refine the atomic displacement parameters. The hydrogen atoms were placed in calculated positions and were refined with U_{iso}(H) = 1.2U_{eq}(C) for non methyl group and U_{iso}(H) = 1.5U_{eq}(C) for methyl group using a riding model.The absolute structure was not determined since no strong anomalous scattering atoms are present.

Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2009).

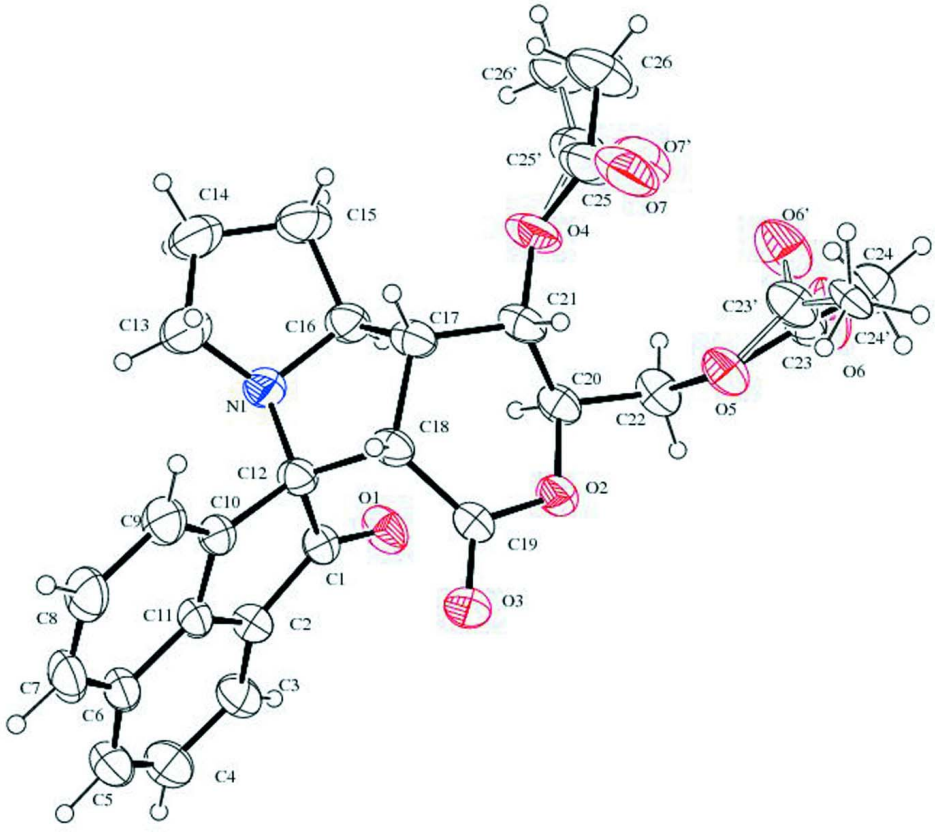

Figure 1

The molecular structure of the title compound with the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as small spheres of arbitrary radius and disordering is shown with full and open bonds.

(1*S*,1′*S*,2′*R*,4a′*S*,9a′*S*,9b′*R*)-1′-Acetyloxy-2,4′-dioxo-2′,4′,4a′,7′,8′,9′,9a′,9b′-octahydro-1′*H*,2*H*-spiro[acenaphthylene-1,5′-pyrano[4,3-*a*]pyrrolizin]-2′-ylmethyl acetate

Crystal data

$C_{26}H_{25}NO_7$
$M_r = 463.47$
Tetragonal, $P4_32_12$
Hall symbol: P4nw2abw
$a = 13.6792$ (3) Å
$c = 24.9625$ (13) Å
$V = 4671.0$ (3) Å^3
$Z = 8$
$F(000) = 1952$
$D_x = 1.318$ Mg m^{-3}
Melting point: 481.15 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5405 reflections
$\theta = 2.2$–22.2°
$\mu = 0.10$ mm^{-1}
$T = 295$ K
Block, yellow
0.30 × 0.30 × 0.25 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scan
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.902, T_{max} = 0.976
21173 measured reflections
4010 independent reflections
2923 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 25.1°, θ_{min} = 2.1°
h = −16→16
k = −11→16
l = −27→28

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.104
S = 1.06
4010 reflections
367 parameters
138 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 0.438P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0038 (5)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.49450 (18)	0.37963 (17)	0.34572 (10)	0.0529 (6)	
C2	0.52973 (19)	0.38194 (18)	0.40078 (10)	0.0567 (7)	
C3	0.5995 (2)	0.4377 (2)	0.42606 (12)	0.0727 (8)	
H3	0.6377	0.4823	0.4073	0.087*	
C4	0.6103 (2)	0.4243 (3)	0.48143 (14)	0.0894 (10)	
H4	0.6574	0.4609	0.4994	0.107*	
C5	0.5552 (3)	0.3604 (3)	0.51006 (13)	0.0843 (9)	
H5	0.5649	0.3551	0.5468	0.101*	
C6	0.4840 (2)	0.3023 (2)	0.48530 (10)	0.0650 (7)	
C7	0.4197 (2)	0.2338 (2)	0.50876 (12)	0.0785 (9)	
H7	0.4215	0.2233	0.5456	0.094*	
C8	0.3560 (2)	0.1837 (2)	0.47842 (11)	0.0763 (8)	
H8	0.3157	0.1380	0.4949	0.092*	
C9	0.3474 (2)	0.19735 (19)	0.42248 (11)	0.0660 (7)	
H9	0.3017	0.1621	0.4028	0.079*	

C10	0.40725 (18)	0.26315 (17)	0.39801 (9)	0.0522 (6)	
C11	0.47403 (18)	0.31481 (17)	0.42968 (9)	0.0538 (6)	
C12	0.41909 (17)	0.29582 (17)	0.34043 (9)	0.0508 (6)	
C13	0.4556 (3)	0.1226 (2)	0.31434 (13)	0.0898 (10)	
H13A	0.3875	0.1058	0.3201	0.108*	
H13B	0.4939	0.1007	0.3448	0.108*	
C14	0.4941 (3)	0.0793 (2)	0.26195 (13)	0.0945 (11)	
H14A	0.5650	0.0791	0.2612	0.113*	
H14B	0.4704	0.0131	0.2567	0.113*	
C15	0.4528 (3)	0.1477 (2)	0.22047 (12)	0.0893 (10)	
H15A	0.3920	0.1224	0.2061	0.107*	
H15B	0.4987	0.1568	0.1913	0.107*	
C16	0.4355 (2)	0.24436 (19)	0.25035 (10)	0.0639 (7)	
H16	0.4763	0.2958	0.2346	0.077*	
C17	0.33003 (19)	0.28012 (19)	0.25462 (9)	0.0587 (7)	
H17	0.2867	0.2230	0.2540	0.070*	
C18	0.32353 (17)	0.32766 (17)	0.31052 (9)	0.0505 (6)	
H18	0.2686	0.2968	0.3292	0.061*	
C19	0.30811 (17)	0.43601 (18)	0.31357 (10)	0.0532 (6)	
C20	0.34631 (19)	0.44821 (18)	0.21942 (9)	0.0567 (6)	
H20	0.4167	0.4371	0.2235	0.068*	
C21	0.2963 (2)	0.3508 (2)	0.21183 (9)	0.0607 (7)	
H21	0.2252	0.3589	0.2135	0.073*	
C22	0.33054 (19)	0.5216 (2)	0.17621 (10)	0.0660 (7)	
H22A	0.3560	0.5847	0.1873	0.079*	
H22B	0.3646	0.5016	0.1439	0.079*	
N1	0.46742 (16)	0.22513 (15)	0.30539 (8)	0.0636 (6)	
O1	0.51791 (14)	0.43233 (14)	0.30886 (7)	0.0734 (6)	
O2	0.30863 (12)	0.49008 (12)	0.26880 (6)	0.0599 (4)	
O3	0.29131 (15)	0.47673 (14)	0.35530 (7)	0.0734 (5)	
O5	0.22688 (12)	0.52899 (14)	0.16582 (7)	0.0674 (5)	
O4	0.32451 (17)	0.31189 (15)	0.16054 (7)	0.0873 (7)	
O6	0.2533 (3)	0.5940 (6)	0.08779 (18)	0.108 (2)	0.673 (10)
C23	0.1979 (6)	0.5579 (7)	0.1189 (2)	0.066 (2)	0.673 (10)
C24	0.0924 (7)	0.5520 (13)	0.1066 (6)	0.082 (3)	0.673 (10)
H24A	0.0823	0.5635	0.0691	0.123*	0.673 (10)
H24B	0.0579	0.6005	0.1270	0.123*	0.673 (10)
H24C	0.0685	0.4882	0.1158	0.123*	0.673 (10)
O6′	0.2525 (6)	0.5122 (12)	0.0794 (3)	0.101 (4)	0.327 (10)
C23′	0.1997 (12)	0.5354 (18)	0.1156 (4)	0.073 (4)	0.327 (10)
C24′	0.0906 (13)	0.540 (3)	0.1196 (11)	0.072 (5)	0.327 (10)
H24D	0.0625	0.4829	0.1039	0.109*	0.327 (10)
H24E	0.0674	0.5973	0.1009	0.109*	0.327 (10)
H24F	0.0718	0.5444	0.1566	0.109*	0.327 (10)
O7	0.1627 (7)	0.3021 (9)	0.1393 (4)	0.114 (3)	0.673 (10)
C25	0.2479 (7)	0.2915 (16)	0.1279 (5)	0.105 (3)	0.673 (10)
C26	0.2787 (9)	0.2525 (11)	0.0740 (5)	0.143 (4)	0.673 (10)
H26A	0.3158	0.1936	0.0787	0.215*	0.673 (10)
H26B	0.3182	0.3003	0.0560	0.215*	0.673 (10)

H26C	0.2217	0.2388	0.0528	0.215*	0.673 (10)
O7′	0.1851 (18)	0.3144 (19)	0.1230 (9)	0.122 (5)	0.327 (10)
C25′	0.2665 (17)	0.282 (3)	0.1209 (12)	0.112 (4)	0.327 (10)
C26′	0.3264 (19)	0.2324 (18)	0.0783 (9)	0.119 (6)	0.327 (10)
H26D	0.2952	0.1724	0.0680	0.178*	0.327 (10)
H26E	0.3905	0.2186	0.0921	0.178*	0.327 (10)
H26F	0.3318	0.2745	0.0477	0.178*	0.327 (10)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0599 (16)	0.0540 (15)	0.0449 (16)	0.0000 (11)	0.0005 (12)	0.0049 (12)
C2	0.0620 (16)	0.0603 (16)	0.0476 (16)	0.0012 (12)	−0.0052 (13)	−0.0022 (12)
C3	0.0722 (19)	0.081 (2)	0.065 (2)	−0.0042 (15)	−0.0190 (15)	−0.0035 (15)
C4	0.093 (2)	0.097 (3)	0.078 (3)	−0.0003 (19)	−0.0338 (19)	−0.0095 (19)
C5	0.104 (3)	0.095 (2)	0.0541 (19)	0.026 (2)	−0.0200 (18)	−0.0050 (17)
C6	0.083 (2)	0.0668 (17)	0.0449 (17)	0.0219 (14)	−0.0037 (15)	0.0061 (14)
C7	0.105 (2)	0.084 (2)	0.0463 (18)	0.0269 (18)	0.0066 (18)	0.0209 (16)
C8	0.100 (2)	0.0702 (19)	0.059 (2)	0.0063 (16)	0.0176 (17)	0.0228 (16)
C9	0.0806 (19)	0.0600 (17)	0.0573 (18)	−0.0029 (13)	0.0101 (14)	0.0101 (13)
C10	0.0684 (16)	0.0467 (14)	0.0416 (15)	0.0005 (11)	0.0042 (12)	0.0068 (11)
C11	0.0700 (16)	0.0531 (14)	0.0382 (15)	0.0124 (12)	0.0000 (12)	0.0057 (11)
C12	0.0618 (15)	0.0496 (14)	0.0410 (15)	−0.0057 (11)	0.0025 (11)	0.0001 (11)
C13	0.120 (3)	0.066 (2)	0.084 (2)	0.0018 (17)	0.0054 (19)	−0.0087 (17)
C14	0.128 (3)	0.0651 (19)	0.091 (2)	0.0087 (19)	0.010 (2)	−0.0184 (18)
C15	0.113 (3)	0.082 (2)	0.072 (2)	0.0072 (19)	0.0118 (18)	−0.0235 (17)
C16	0.083 (2)	0.0637 (17)	0.0446 (17)	−0.0005 (13)	0.0097 (13)	−0.0034 (12)
C17	0.0706 (17)	0.0619 (16)	0.0438 (16)	−0.0159 (12)	0.0010 (12)	−0.0035 (12)
C18	0.0568 (15)	0.0555 (15)	0.0392 (15)	−0.0135 (10)	0.0036 (11)	0.0000 (11)
C19	0.0559 (15)	0.0629 (17)	0.0409 (16)	−0.0026 (11)	−0.0021 (12)	0.0011 (13)
C20	0.0592 (15)	0.0716 (17)	0.0392 (15)	−0.0074 (12)	0.0031 (11)	0.0029 (12)
C21	0.0710 (17)	0.0756 (18)	0.0357 (15)	−0.0145 (14)	−0.0006 (12)	−0.0027 (13)
C22	0.0589 (17)	0.0831 (19)	0.0559 (17)	−0.0138 (13)	−0.0011 (13)	0.0119 (14)
N1	0.0864 (16)	0.0562 (14)	0.0481 (14)	0.0016 (11)	0.0048 (11)	−0.0009 (10)
O1	0.0849 (13)	0.0802 (13)	0.0552 (12)	−0.0292 (10)	−0.0069 (10)	0.0176 (10)
O2	0.0759 (12)	0.0608 (11)	0.0430 (10)	−0.0020 (8)	−0.0031 (8)	0.0035 (8)
O3	0.1011 (14)	0.0731 (12)	0.0459 (11)	0.0151 (10)	0.0021 (9)	−0.0077 (10)
O5	0.0635 (12)	0.0933 (13)	0.0453 (11)	−0.0059 (9)	−0.0001 (9)	0.0081 (9)
O4	0.1211 (18)	0.1029 (16)	0.0377 (12)	−0.0152 (13)	−0.0072 (11)	−0.0139 (11)
O6	0.092 (3)	0.157 (5)	0.075 (3)	0.024 (3)	0.018 (2)	0.060 (3)
C23	0.075 (3)	0.080 (5)	0.042 (3)	0.012 (3)	0.002 (3)	0.001 (2)
C24	0.082 (4)	0.087 (5)	0.076 (7)	0.001 (3)	−0.015 (4)	0.002 (6)
O6′	0.096 (5)	0.158 (9)	0.050 (4)	0.004 (5)	0.015 (4)	0.012 (5)
C23′	0.069 (6)	0.101 (8)	0.049 (6)	−0.010 (5)	0.000 (5)	0.001 (5)
C24′	0.083 (7)	0.089 (10)	0.046 (8)	0.010 (7)	−0.036 (6)	−0.015 (8)
O7	0.144 (5)	0.126 (4)	0.072 (5)	−0.050 (3)	−0.041 (4)	0.001 (4)
C25	0.165 (7)	0.095 (6)	0.054 (5)	−0.022 (6)	−0.024 (6)	−0.010 (4)
C26	0.214 (10)	0.159 (8)	0.056 (5)	0.001 (8)	−0.032 (6)	−0.027 (5)
O7′	0.186 (12)	0.110 (8)	0.071 (10)	−0.011 (9)	−0.041 (8)	−0.007 (7)

C25′	0.179 (8)	0.098 (7)	0.058 (7)	−0.028 (7)	−0.022 (7)	0.003 (6)
C26′	0.210 (16)	0.106 (9)	0.040 (7)	0.004 (11)	−0.027 (10)	−0.021 (6)

Geometric parameters (Å, º)

C1—O1	1.212 (3)	C17—H17	0.9800
C1—C2	1.457 (3)	C18—C19	1.499 (3)
C1—C12	1.548 (3)	C18—H18	0.9800
C2—C3	1.375 (4)	C19—O3	1.203 (3)
C2—C11	1.394 (3)	C19—O2	1.340 (3)
C3—C4	1.402 (4)	C20—O2	1.454 (3)
C3—H3	0.9300	C20—C22	1.490 (3)
C4—C5	1.357 (5)	C20—C21	1.509 (4)
C4—H4	0.9300	C20—H20	0.9800
C5—C6	1.401 (4)	C21—O4	1.439 (3)
C5—H5	0.9300	C21—H21	0.9800
C6—C11	1.405 (3)	C22—O5	1.445 (3)
C6—C7	1.412 (4)	C22—H22A	0.9700
C7—C8	1.343 (4)	C22—H22B	0.9700
C7—H7	0.9300	O5—C23	1.299 (6)
C8—C9	1.414 (4)	O5—C23′	1.310 (9)
C8—H8	0.9300	O4—C25′	1.333 (10)
C9—C10	1.362 (3)	O4—C25	1.356 (7)
C9—H9	0.9300	O6—C23	1.192 (7)
C10—C11	1.400 (3)	C23—C24	1.477 (7)
C10—C12	1.514 (3)	C24—H24A	0.9600
C12—N1	1.462 (3)	C24—H24B	0.9600
C12—C18	1.567 (3)	C24—H24C	0.9600
C13—N1	1.429 (4)	O6′—C23′	1.199 (9)
C13—C14	1.529 (4)	C23′—C24′	1.498 (10)
C13—H13A	0.9700	C24′—H24D	0.9600
C13—H13B	0.9700	C24′—H24E	0.9600
C14—C15	1.505 (4)	C24′—H24F	0.9600
C14—H14A	0.9700	O7—C25	1.210 (8)
C14—H14B	0.9700	C25—C26	1.508 (8)
C15—C16	1.537 (4)	C26—H26A	0.9600
C15—H15A	0.9700	C26—H26B	0.9600
C15—H15B	0.9700	C26—H26C	0.9600
C16—N1	1.465 (3)	O7′—C25′	1.199 (10)
C16—C17	1.527 (4)	C25′—C26′	1.504 (10)
C16—H16	0.9800	C26′—H26D	0.9600
C17—C21	1.513 (3)	C26′—H26E	0.9600
C17—C18	1.542 (3)	C26′—H26F	0.9600
O1—C1—C2	128.0 (2)	C16—C17—C18	104.6 (2)
O1—C1—C12	123.5 (2)	C21—C17—H17	108.3
C2—C1—C12	108.5 (2)	C16—C17—H17	108.3
C3—C2—C11	120.5 (2)	C18—C17—H17	108.3
C3—C2—C1	132.4 (3)	C19—C18—C17	118.1 (2)
C11—C2—C1	107.0 (2)	C19—C18—C12	111.59 (18)

C2—C3—C4	116.9 (3)	C17—C18—C12	105.41 (19)
C2—C3—H3	121.5	C19—C18—H18	107.1
C4—C3—H3	121.5	C17—C18—H18	107.1
C5—C4—C3	123.0 (3)	C12—C18—H18	107.1
C5—C4—H4	118.5	O3—C19—O2	117.9 (2)
C3—C4—H4	118.5	O3—C19—C18	121.9 (2)
C4—C5—C6	121.3 (3)	O2—C19—C18	120.2 (2)
C4—C5—H5	119.4	O2—C20—C22	107.3 (2)
C6—C5—H5	119.4	O2—C20—C21	107.08 (18)
C5—C6—C11	115.7 (3)	C22—C20—C21	116.0 (2)
C5—C6—C7	128.8 (3)	O2—C20—H20	108.8
C11—C6—C7	115.5 (3)	C22—C20—H20	108.8
C8—C7—C6	120.6 (3)	C21—C20—H20	108.8
C8—C7—H7	119.7	O4—C21—C20	108.5 (2)
C6—C7—H7	119.7	O4—C21—C17	108.0 (2)
C7—C8—C9	122.9 (3)	C20—C21—C17	109.7 (2)
C7—C8—H8	118.5	O4—C21—H21	110.2
C9—C8—H8	118.5	C20—C21—H21	110.2
C10—C9—C8	118.7 (3)	C17—C21—H21	110.2
C10—C9—H9	120.6	O5—C22—C20	108.6 (2)
C8—C9—H9	120.6	O5—C22—H22A	110.0
C9—C10—C11	118.2 (2)	C20—C22—H22A	110.0
C9—C10—C12	133.3 (2)	O5—C22—H22B	110.0
C11—C10—C12	108.51 (19)	C20—C22—H22B	110.0
C2—C11—C10	113.4 (2)	H22A—C22—H22B	108.3
C2—C11—C6	122.6 (2)	C13—N1—C12	120.3 (2)
C10—C11—C6	124.0 (2)	C13—N1—C16	106.8 (2)
N1—C12—C10	114.91 (19)	C12—N1—C16	107.92 (19)
N1—C12—C1	103.87 (19)	C19—O2—C20	119.44 (19)
C10—C12—C1	102.06 (19)	C23—O5—C23′	14.1 (14)
N1—C12—C18	106.01 (17)	C23—O5—C22	118.9 (4)
C10—C12—C18	116.43 (19)	C23′—O5—C22	117.1 (7)
C1—C12—C18	113.00 (19)	C25′—O4—C25	14.2 (14)
N1—C13—C14	102.0 (2)	C25′—O4—C21	127.9 (12)
N1—C13—H13A	111.4	C25—O4—C21	113.8 (5)
C14—C13—H13A	111.4	O6—C23—O5	121.3 (7)
N1—C13—H13B	111.4	O6—C23—C24	120.6 (7)
C14—C13—H13B	111.4	O5—C23—C24	117.9 (7)
H13A—C13—H13B	109.2	O6′—C23′—O5	122.1 (12)
C15—C14—C13	102.6 (3)	O6′—C23′—C24′	131.5 (16)
C15—C14—H14A	111.2	O5—C23′—C24′	102.8 (13)
C13—C14—H14A	111.2	C23′—C24′—H24D	109.5
C15—C14—H14B	111.2	C23′—C24′—H24E	109.5
C13—C14—H14B	111.2	H24D—C24′—H24E	109.5
H14A—C14—H14B	109.2	C23′—C24′—H24F	109.5
C14—C15—C16	105.0 (2)	H24D—C24′—H24F	109.5
C14—C15—H15A	110.7	H24E—C24′—H24F	109.5
C16—C15—H15A	110.7	O7—C25—O4	125.4 (8)
C14—C15—H15B	110.7	O7—C25—C26	121.5 (8)

C16—C15—H15B	110.7	O4—C25—C26	113.2 (8)
H15A—C15—H15B	108.8	O7′—C25′—O4	114 (2)
N1—C16—C17	105.9 (2)	O7′—C25′—C26′	134.7 (18)
N1—C16—C15	104.8 (2)	O4—C25′—C26′	109.8 (16)
C17—C16—C15	117.1 (2)	C25′—C26′—H26D	109.5
N1—C16—H16	109.6	C25′—C26′—H26E	109.5
C17—C16—H16	109.6	H26D—C26′—H26E	109.5
C15—C16—H16	109.6	C25′—C26′—H26F	109.5
C21—C17—C16	116.3 (2)	H26D—C26′—H26F	109.5
C21—C17—C18	110.6 (2)	H26E—C26′—H26F	109.5

O1—C1—C2—C3	−3.5 (5)	N1—C12—C18—C17	−6.9 (2)
C12—C1—C2—C3	176.4 (3)	C10—C12—C18—C17	−136.1 (2)
O1—C1—C2—C11	173.5 (3)	C1—C12—C18—C17	106.2 (2)
C12—C1—C2—C11	−6.6 (3)	C17—C18—C19—O3	171.5 (2)
C11—C2—C3—C4	−0.7 (4)	C12—C18—C19—O3	−66.2 (3)
C1—C2—C3—C4	176.0 (3)	C17—C18—C19—O2	−5.7 (3)
C2—C3—C4—C5	−0.5 (5)	C12—C18—C19—O2	116.7 (2)
C3—C4—C5—C6	0.8 (5)	O2—C20—C21—O4	174.2 (2)
C4—C5—C6—C11	0.1 (4)	C22—C20—C21—O4	54.5 (3)
C4—C5—C6—C7	−179.0 (3)	O2—C20—C21—C17	−67.9 (3)
C5—C6—C7—C8	−179.5 (3)	C22—C20—C21—C17	172.3 (2)
C11—C6—C7—C8	1.5 (4)	C16—C17—C21—O4	48.0 (3)
C6—C7—C8—C9	−1.5 (5)	C18—C17—C21—O4	167.1 (2)
C7—C8—C9—C10	1.0 (4)	C16—C17—C21—C20	−70.2 (3)
C8—C9—C10—C11	−0.5 (4)	C18—C17—C21—C20	49.0 (3)
C8—C9—C10—C12	179.6 (3)	O2—C20—C22—O5	−69.4 (3)
C3—C2—C11—C10	−179.3 (2)	C21—C20—C22—O5	50.2 (3)
C1—C2—C11—C10	3.3 (3)	C14—C13—N1—C12	165.8 (2)
C3—C2—C11—C6	1.6 (4)	C14—C13—N1—C16	42.5 (3)
C1—C2—C11—C6	−175.8 (2)	C10—C12—N1—C13	32.2 (3)
C9—C10—C11—C2	−178.4 (2)	C1—C12—N1—C13	142.8 (3)
C12—C10—C11—C2	1.5 (3)	C18—C12—N1—C13	−97.9 (3)
C9—C10—C11—C6	0.7 (4)	C10—C12—N1—C16	154.9 (2)
C12—C10—C11—C6	−179.4 (2)	C1—C12—N1—C16	−94.5 (2)
C5—C6—C11—C2	−1.3 (4)	C18—C12—N1—C16	24.9 (2)
C7—C6—C11—C2	177.9 (2)	C17—C16—N1—C13	97.3 (2)
C5—C6—C11—C10	179.7 (3)	C15—C16—N1—C13	−27.0 (3)
C7—C6—C11—C10	−1.1 (4)	C17—C16—N1—C12	−33.3 (2)
C9—C10—C12—N1	−73.7 (4)	C15—C16—N1—C12	−157.7 (2)
C11—C10—C12—N1	106.4 (2)	O3—C19—O2—C20	168.5 (2)
C9—C10—C12—C1	174.6 (3)	C18—C19—O2—C20	−14.3 (3)
C11—C10—C12—C1	−5.3 (3)	C22—C20—O2—C19	175.71 (19)
C9—C10—C12—C18	51.1 (4)	C21—C20—O2—C19	50.5 (3)
C11—C10—C12—C18	−128.8 (2)	C20—C22—O5—C23	−154.5 (5)
O1—C1—C12—N1	67.3 (3)	C20—C22—O5—C23′	−138.6 (12)
C2—C1—C12—N1	−112.6 (2)	C20—C21—O4—C25′	−126 (3)
O1—C1—C12—C10	−173.0 (2)	C17—C21—O4—C25′	115 (3)
C2—C1—C12—C10	7.2 (3)	C20—C21—O4—C25	−123.5 (11)

O1—C1—C12—C18	−47.1 (3)	C17—C21—O4—C25	117.6 (11)
C2—C1—C12—C18	133.0 (2)	C23′—O5—C23—O6	−99 (4)
N1—C13—C14—C15	−41.0 (3)	C22—O5—C23—O6	−13.0 (10)
C13—C14—C15—C16	24.4 (3)	C23′—O5—C23—C24	85 (5)
C14—C15—C16—N1	0.1 (3)	C22—O5—C23—C24	171.8 (9)
C14—C15—C16—C17	−116.8 (3)	C23—O5—C23′—O6′	119 (6)
N1—C16—C17—C21	149.9 (2)	C22—O5—C23′—O6′	18 (3)
C15—C16—C17—C21	−93.8 (3)	C23—O5—C23′—C24′	−80 (4)
N1—C16—C17—C18	27.6 (2)	C22—O5—C23′—C24′	179.3 (14)
C15—C16—C17—C18	143.9 (2)	C25′—O4—C25—O7	171 (15)
C21—C17—C18—C19	−12.9 (3)	C21—O4—C25—O7	−1 (3)
C16—C17—C18—C19	113.0 (2)	C25′—O4—C25—C26	−9 (12)
C21—C17—C18—C12	−138.4 (2)	C21—O4—C25—C26	178.9 (10)
C16—C17—C18—C12	−12.4 (2)	C25—O4—C25′—O7′	12 (9)
N1—C12—C18—C19	−136.3 (2)	C21—O4—C25′—O7′	20 (6)
C10—C12—C18—C19	94.5 (2)	C25—O4—C25′—C26′	−180 (16)
C1—C12—C18—C19	−23.2 (3)	C21—O4—C25′—C26′	−171.1 (14)