Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

4,5,6-Tri-*O*-acetyl-2,3-di-*S*-ethyl-2,3-dithio-D-allose diethyl dithioacetal

Xiao-Dong Xi,[a] Da-Xin Shi,[a] Hui Li,[b] Yun-Zheng Li[a] and Qin-Pei Wu[a]*

[a]School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081, People's Republic of China, and [b]School of Science, Beijing Institute of Technology, Beijing 100081, People's Republic of China
Correspondence e-mail: qpwu@bit.edu.cn

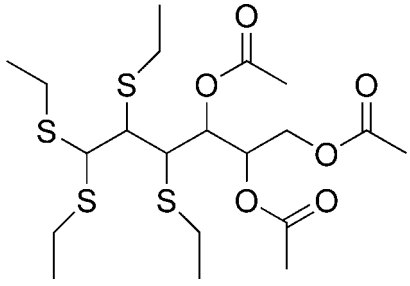
Received 14 April 2009; accepted 27 April 2009

Key indicators: single-crystal X-ray study; T = 113 K; mean σ(C–C) = 0.002 Å; disorder in main residue; R factor = 0.032; wR factor = 0.066; data-to-parameter ratio = 20.3.

The title compound, $C_{20}H_{36}O_6S_4$, was obtained by ethanethiolysis of 3,5,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose. One of the ethyl groups is disordered over two sites with refined occupancies of 0.869 (6) and 0.131 (6). Compared with the precursor, the absolute configuration of the stereocenters at positions C-3 and C-2 are inverted and maintained, respectively.

Related literature

For the bioactiviy of nucleosides, see: Zhang *et al.* (2007); Merino *et al.* (2008). For the structure of the precursor, 3,5,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose, see: Wu *et al.* (2009). For related structures, see: Bethel & Ferrier (1972); Berrang & Hortor (1970); Divjaković *et al.* (1992).



Experimental

Crystal data

$C_{20}H_{36}O_6S_4$
M_r = 500.73
Monoclinic, $P2_1$
a = 8.3395 (12) Å
b = 16.726 (2) Å
c = 9.2027 (14) Å
β = 95.772 (5)°
V = 1277.2 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.40 mm^{-1}
T = 113 K
0.26 × 0.20 × 0.18 mm

Data collection

Rigaku Saturn diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)
T_{min} = 0.902, T_{max} = 0.931
16052 measured reflections
6060 independent reflections
5802 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.066
S = 1.04
6060 reflections
298 parameters
23 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}
Absolute structure: Flack (1983), 2919 Friedel pairs
Flack parameter: −0.03 (4)

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

The authors thank the National Science Foundation of China (30340070) and the Ministry of Science and Technology of China (2006 A A100216) for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2804).

References

Berrang, B. & Hortor, D. (1970). *Chem. Commun.* pp. 1038–1039.
Bethel, G. S. & Ferrier, R. J. (1972). *J. Chem. Soc. Perkin Trans. 1*, pp. 1033–1037.
Divjaković, V., Miljković, D., Lajšić, S. & Klement, U. (1992). *Acta Cryst.* C**48**, 1685–1686.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Merino, P., Tejero, T. & Delso, I. (2008). *Curr. Med. Chem.* **15**, 954–967.
Rigaku/MSC (2005). *CrystalClear*. Rigaku/MSC Inc., The Woodlands, Texas, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Wu, Q.-P., Xi, X.-D., Li, H. & Zhang, Q.-Sh. (2009). *Chin. J. Chem.* In the press.
Zhang, J., Visser, F., King, K. M., Baldwin, S. A., Young, J. D. & Cass, C. E. (2007). *Cancer Metastasis Rev.* **26**, 85–110.

supporting information

Acta Cryst. (2009). E**65**, o1227 [doi:10.1107/S1600536809015694]

4,5,6-Tri-*O*-acetyl-2,3-di-*S*-ethyl-2,3-dithio-D-allose diethyl dithioacetal

Xiao-Dong Xi, Da-Xin Shi, Hui Li, Yun-Zheng Li and Qin-Pei Wu

S1. Comment

Nucleosides are important compounds due to their extensive bioactivity in antitumor and antivirus (Zhang *et al.*, 2007, Merino *et al.*, 2008). In the course of our studies in the synthesis of nucleoside analogues, an ethanethio substituted thio-acetal product was obtained as ethanethiolysis of 3,5,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-*α*-*D*-glucofuranose (Wu *et al.*, 2009). The purpose of the structure determination was to establish the position of the substituents of the ethanethio groups and the molecular conformation of the title compound. In contrast to its precursor, the absolute configuration of C-3 and C-2 are inverted and maintained, respectively, which is similar to the documented results (Berrang & Hortor, 1970; Bethel & Ferrier, 1972), but disagrees with the molecular structure reported by Divjaković (Divjakovic *et al.*, 1992). Both the molecular conformation and structure are consistent with our desired intermediates for the synthesis of the corresponding 2′,3′-dideoxy-2′,3′-dimercaptoribonucleosides.

S2. Experimental

$ZnBr_2$ (0.54 g, 2.4 mmol) was added to a solution of 3,5,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-*α*-D-glucofuranose (0.67 g, 2.0 mmol) and ethanethiol (0.78 ml, 10 mmol) in dry CH_2Cl_2 (10 ml). After 5 h, saturated aqueous solution of $NaHCO_3$ (20 ml) was added and separated. The organic layer was washed with brine, dried with $MgSO_4$ and concentrated under reduced pressure. The residue was isolated through short column chromatography on silica gel, which was eluded with EtOAc-petroleum to give the target compound (0.78 g, 78%). M. p. 62°, ^{1}H-NMR($CDCl_3$, p.p.m.): 1.28 (m, 12 H), 2.06 (m, 9 H), 2.75 (m, 8 H), 3.07 (dd, 1 H), 3.48 (dd, 1 H), 4.20 (m, 1 H), 4.49 (dd, 1 H), 4.6 4 (d, 1 H), 5.54 (m, 1 H), 5.89 (dd, 1 H); ^{13}C-NMR($CDCl_3$, p.p.m.):14.60, 14.74, 14.85, 14.92, 15.02, 21.23, 21.27, 25.79, 26.39, 28.31, 30.24, 51.47, 57.30, 57.48, 62.56, 71.96, 72.78, 169.19, 169.61, 170.82; HRMS (EI) m/*z* calculated for $C_{20}H_{36}O_6S_4$ 500.13, found 500.14.

50 mg of the obtained product was dissolved in petroleum ether (5 ml) and the solution was kept at room temperature for 2 days to give colorless single crystals.

S3. Refinement

C—H were included in the riding model approximation with C—H distances 0.98–1.00 Å, and with U_{iso}=1.2U_{eq}(C) or 1.5U_{eq}(C_{methyl}).

One of the ethyl groups is disordered over two sites with refined occupancies of 0.869 (6) and 0.131 (6). The restained distance of C13—C14 refined to 1.513 (4)Å and C13′-C14′ refined to 1.502 (19) Å.

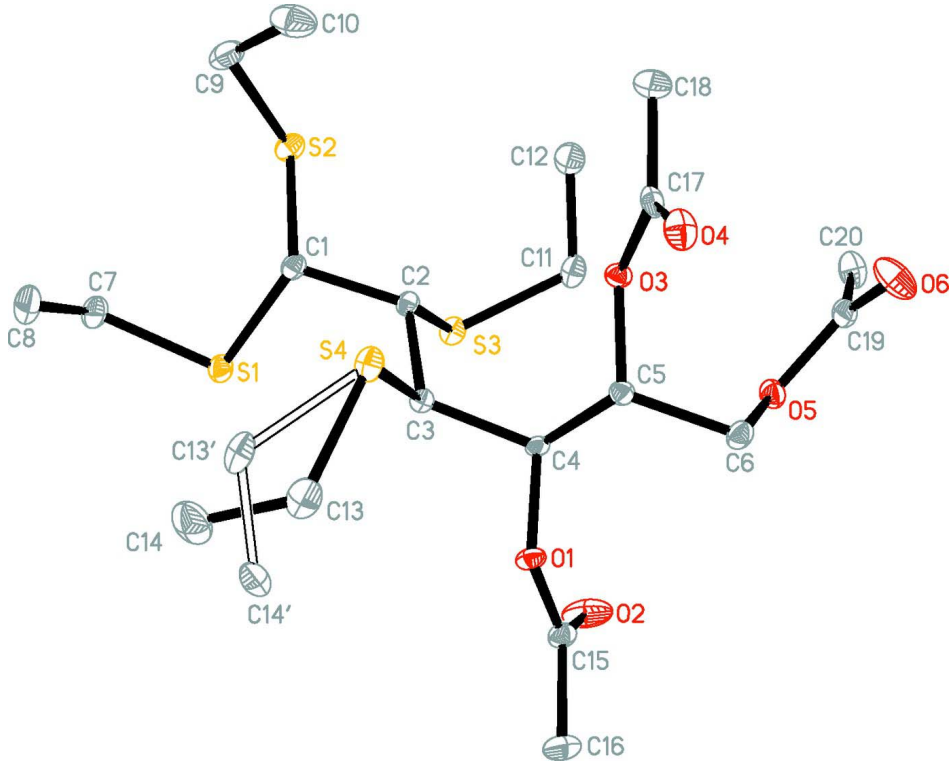


Figure 1

Molecular structure of the title compound with thermal displacement ellipsoids drawn at the 30% probability level. Open bonds show the disorder component.

4,5,6-Tri-*O*-acetyl-2,3-di-*S*-ethyl-2,3-dithio-D-allose diethyl dithioacetal

Crystal data

$C_{20}H_{36}O_6S_4$
$M_r = 500.73$
Monoclinic, $P2_1$
Hall symbol: P 2yb
$a = 8.3395\ (12)$ Å
$b = 16.726\ (2)$ Å
$c = 9.2027\ (14)$ Å
$\beta = 95.772\ (5)°$
$V = 1277.2\ (3)$ Å^3
$Z = 2$
$F(000) = 536$
$D_x = 1.302$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71070$ Å
Cell parameters from 4760 reflections
$\theta = 2.2–27.9°$
$\mu = 0.40$ mm^{-1}
$T = 113$ K
Block, colorless
0.26 × 0.20 × 0.18 mm

Data collection

Rigaku Saturn diffractometer
Radiation source: rotating anode
Confocal monochromator
Detector resolution: 14.63 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)
$T_{min} = 0.902$, $T_{max} = 0.931$
16052 measured reflections
6060 independent reflections
5802 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 27.9°$, $\theta_{min} = 2.2°$
$h = -10\rightarrow10$
$k = -21\rightarrow22$
$l = -12\rightarrow12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.066$
$S = 1.04$
6060 reflections
298 parameters
23 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
$w = 1/[\sigma^2(F_o^2) + (0.0326P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}
Absolute structure: Flack (1983), 2919 Friedel pairs
Absolute structure parameter: −0.03 (4)

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
S1	0.74081 (5)	−0.08494 (3)	0.79166 (5)	0.02103 (10)	
S2	0.70511 (5)	0.08746 (3)	0.88989 (5)	0.02203 (10)	
S3	0.41930 (5)	0.00547 (3)	0.66199 (5)	0.01940 (10)	
S4	0.85901 (5)	0.02564 (3)	0.42590 (5)	0.02148 (10)	
O1	0.56270 (15)	−0.06561 (7)	0.23706 (13)	0.0182 (3)	
O2	0.32000 (18)	−0.12020 (10)	0.25917 (18)	0.0405 (4)	
O3	0.54225 (14)	0.14186 (7)	0.33931 (12)	0.0169 (3)	
O4	0.68402 (15)	0.21225 (8)	0.18563 (14)	0.0269 (3)	
O5	0.25647 (13)	0.10093 (8)	0.19236 (13)	0.0209 (3)	
O6	0.26208 (18)	0.22570 (8)	0.10243 (18)	0.0378 (4)	
C1	0.74322 (19)	0.02080 (11)	0.74033 (17)	0.0171 (3)	
H1	0.8521	0.0336	0.7099	0.021*	
C2	0.61765 (18)	0.03465 (11)	0.60845 (18)	0.0156 (3)	
H2	0.6143	0.0933	0.5873	0.019*	
C3	0.66042 (18)	−0.00888 (10)	0.46908 (17)	0.0147 (3)	
H3	0.6708	−0.0670	0.4933	0.018*	
C4	0.53286 (19)	−0.00125 (11)	0.33657 (17)	0.0148 (3)	
H4	0.4224	−0.0068	0.3689	0.018*	
C5	0.5413 (2)	0.07353 (10)	0.24304 (18)	0.0164 (4)	
H5	0.6440	0.0727	0.1957	0.020*	
C6	0.3999 (2)	0.08169 (12)	0.12490 (18)	0.0202 (4)	
H6A	0.4227	0.1244	0.0554	0.024*	
H6B	0.3843	0.0309	0.0700	0.024*	

C7	0.8968 (2)	−0.08772 (14)	0.94224 (19)	0.0284 (4)	
H7A	0.8763	−0.0444	1.0112	0.034*	
H7B	0.8888	−0.1391	0.9944	0.034*	
C8	1.0684 (2)	−0.07889 (15)	0.9010 (3)	0.0398 (5)	
H8A	1.0926	−0.1230	0.8366	0.060*	
H8B	1.1441	−0.0801	0.9896	0.060*	
H8C	1.0788	−0.0279	0.8503	0.060*	
C9	0.8906 (2)	0.14400 (14)	0.9124 (2)	0.0311 (5)	
H9A	0.8924	0.1759	1.0031	0.037*	
H9B	0.9821	0.1061	0.9247	0.037*	
C10	0.9154 (3)	0.19954 (14)	0.7876 (3)	0.0395 (5)	
H10A	0.9222	0.1683	0.6984	0.059*	
H10B	1.0155	0.2297	0.8104	0.059*	
H10C	0.8245	0.2368	0.7729	0.059*	
C11	0.2932 (2)	0.08823 (13)	0.59307 (19)	0.0237 (4)	
H11A	0.3106	0.0975	0.4896	0.028*	
H11B	0.1789	0.0730	0.5962	0.028*	
C12	0.3242 (2)	0.16570 (13)	0.6765 (2)	0.0302 (5)	
H12A	0.2985	0.1585	0.7773	0.045*	
H12B	0.2561	0.2080	0.6296	0.045*	
H12C	0.4378	0.1806	0.6766	0.045*	
C13	0.9482 (3)	−0.06248 (16)	0.3541 (3)	0.0317 (8)	0.869 (6)
H13A	0.8677	−0.0883	0.2826	0.038*	0.869 (6)
H13B	1.0406	−0.0461	0.3013	0.038*	0.869 (6)
C14	1.0059 (4)	−0.1230 (2)	0.4699 (3)	0.0428 (9)	0.869 (6)
H14A	1.0905	−0.0991	0.5378	0.064*	0.869 (6)
H14B	1.0490	−0.1700	0.4233	0.064*	0.869 (6)
H14C	0.9154	−0.1392	0.5235	0.064*	0.869 (6)
C13′	0.9867 (15)	−0.0625 (8)	0.4615 (17)	0.024 (5)	0.131 (6)
H13C	1.0967	−0.0488	0.4379	0.029*	0.131 (6)
H13D	0.9937	−0.0741	0.5674	0.029*	0.131 (6)
C14′	0.935 (2)	−0.1377 (8)	0.381 (2)	0.036 (4)	0.131 (6)
H14D	0.8573	−0.1665	0.4339	0.054*	0.131 (6)
H14E	1.0297	−0.1717	0.3722	0.054*	0.131 (6)
H14F	0.8855	−0.1240	0.2827	0.054*	0.131 (6)
C15	0.4443 (2)	−0.12014 (11)	0.20382 (19)	0.0200 (4)	
C16	0.4899 (3)	−0.17588 (12)	0.0885 (2)	0.0277 (4)	
H16A	0.4155	−0.2214	0.0805	0.042*	
H16B	0.6000	−0.1952	0.1143	0.042*	
H16C	0.4843	−0.1477	−0.0053	0.042*	
C17	0.6157 (2)	0.20907 (11)	0.2941 (2)	0.0209 (4)	
C18	0.5959 (3)	0.27634 (12)	0.3979 (2)	0.0326 (5)	
H18A	0.6485	0.3244	0.3644	0.049*	
H18B	0.6454	0.2617	0.4954	0.049*	
H18C	0.4810	0.2871	0.4021	0.049*	
C19	0.2065 (2)	0.17773 (11)	0.1783 (2)	0.0221 (4)	
C20	0.0766 (2)	0.19526 (13)	0.2743 (2)	0.0301 (5)	
H20A	0.1246	0.2033	0.3748	0.045*	

H20B	0.0012	0.1502	0.2712	0.045*
H20C	0.0187	0.2437	0.2397	0.045*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0232 (2)	0.0209 (2)	0.0183 (2)	−0.00083 (19)	−0.00179 (18)	0.00364 (18)
S2	0.0236 (2)	0.0275 (2)	0.0155 (2)	−0.00207 (19)	0.00384 (17)	−0.00323 (19)
S3	0.0155 (2)	0.0251 (2)	0.0183 (2)	−0.00173 (18)	0.00489 (16)	0.00091 (18)
S4	0.01363 (19)	0.0294 (3)	0.0218 (2)	−0.00129 (18)	0.00362 (16)	0.00257 (19)
O1	0.0183 (6)	0.0201 (7)	0.0166 (6)	−0.0007 (5)	0.0034 (5)	−0.0072 (5)
O2	0.0312 (8)	0.0411 (9)	0.0523 (10)	−0.0176 (7)	0.0194 (7)	−0.0234 (8)
O3	0.0213 (6)	0.0138 (6)	0.0157 (6)	−0.0013 (5)	0.0026 (5)	0.0002 (5)
O4	0.0221 (7)	0.0292 (8)	0.0298 (7)	−0.0023 (6)	0.0050 (6)	0.0102 (6)
O5	0.0175 (6)	0.0194 (7)	0.0253 (7)	0.0012 (5)	−0.0005 (5)	0.0021 (5)
O6	0.0368 (8)	0.0244 (8)	0.0556 (10)	0.0038 (6)	0.0209 (8)	0.0118 (7)
C1	0.0174 (8)	0.0212 (9)	0.0128 (8)	−0.0003 (7)	0.0018 (6)	−0.0010 (7)
C2	0.0128 (8)	0.0171 (8)	0.0167 (8)	−0.0016 (7)	0.0006 (6)	−0.0001 (6)
C3	0.0146 (8)	0.0165 (9)	0.0133 (8)	0.0000 (7)	0.0028 (6)	0.0000 (7)
C4	0.0153 (8)	0.0159 (8)	0.0132 (8)	0.0026 (7)	0.0009 (6)	−0.0056 (7)
C5	0.0152 (8)	0.0166 (9)	0.0172 (9)	0.0016 (7)	0.0016 (6)	−0.0023 (7)
C6	0.0209 (9)	0.0257 (10)	0.0138 (8)	0.0023 (8)	0.0011 (7)	−0.0024 (7)
C7	0.0352 (10)	0.0305 (11)	0.0176 (9)	0.0017 (9)	−0.0064 (8)	0.0041 (9)
C8	0.0276 (11)	0.0400 (13)	0.0482 (14)	0.0029 (10)	−0.0139 (9)	0.0012 (11)
C9	0.0263 (10)	0.0344 (12)	0.0317 (11)	−0.0028 (9)	−0.0008 (8)	−0.0138 (9)
C10	0.0338 (11)	0.0283 (12)	0.0586 (15)	−0.0064 (10)	0.0160 (11)	−0.0079 (11)
C11	0.0174 (8)	0.0356 (11)	0.0182 (9)	0.0039 (8)	0.0029 (7)	0.0010 (9)
C12	0.0293 (11)	0.0346 (12)	0.0271 (11)	0.0066 (9)	0.0041 (8)	−0.0036 (9)
C13	0.0213 (12)	0.0515 (18)	0.0234 (15)	0.0072 (11)	0.0073 (10)	−0.0077 (11)
C14	0.0442 (17)	0.046 (2)	0.0393 (18)	0.0195 (14)	0.0118 (13)	−0.0025 (14)
C13′	0.007 (7)	0.045 (12)	0.022 (10)	−0.005 (6)	0.004 (6)	0.002 (7)
C14′	0.032 (7)	0.024 (7)	0.050 (8)	0.010 (6)	−0.009 (6)	−0.005 (6)
C15	0.0265 (10)	0.0197 (9)	0.0138 (9)	−0.0023 (8)	0.0025 (7)	−0.0008 (7)
C16	0.0377 (11)	0.0240 (10)	0.0222 (10)	−0.0048 (9)	0.0067 (8)	−0.0076 (8)
C17	0.0155 (8)	0.0178 (9)	0.0281 (10)	0.0003 (7)	−0.0037 (7)	0.0074 (8)
C18	0.0386 (12)	0.0200 (10)	0.0382 (13)	−0.0062 (9)	−0.0003 (10)	−0.0018 (8)
C19	0.0166 (8)	0.0230 (10)	0.0253 (10)	0.0003 (8)	−0.0043 (7)	0.0008 (8)
C20	0.0242 (10)	0.0332 (12)	0.0329 (12)	0.0057 (9)	0.0033 (8)	0.0084 (9)

Geometric parameters (Å, º)

S1—C7	1.8035 (18)	C9—C10	1.507 (3)
S1—C1	1.8313 (19)	C9—H9A	0.9900
S2—C9	1.807 (2)	C9—H9B	0.9900
S2—C1	1.8238 (17)	C10—H10A	0.9800
S3—C11	1.814 (2)	C10—H10B	0.9800
S3—C2	1.8387 (16)	C10—H10C	0.9800
S4—C13	1.806 (2)	C11—C12	1.515 (3)

S4—C13′	1.829 (13)	C11—H11A	0.9900
S4—C3	1.8348 (16)	C11—H11B	0.9900
O1—C15	1.357 (2)	C12—H12A	0.9800
O1—C4	1.4510 (19)	C12—H12B	0.9800
O2—C15	1.200 (2)	C12—H12C	0.9800
O3—C17	1.365 (2)	C13—C14	1.513 (4)
O3—C5	1.446 (2)	C13—H13A	0.9900
O4—C17	1.199 (2)	C13—H13B	0.9900
O5—C19	1.352 (2)	C14—H14A	0.9800
O5—C6	1.439 (2)	C14—H14B	0.9800
O6—C19	1.188 (2)	C14—H14C	0.9800
C1—C2	1.539 (2)	C13′—C14′	1.502 (19)
C1—H1	1.0000	C13′—H13C	0.9900
C2—C3	1.547 (2)	C13′—H13D	0.9900
C2—H2	1.0000	C14′—H14D	0.9800
C3—C4	1.541 (2)	C14′—H14E	0.9800
C3—H3	1.0000	C14′—H14F	0.9800
C4—C5	1.524 (2)	C15—C16	1.491 (2)
C4—H4	1.0000	C16—H16A	0.9800
C5—C6	1.527 (2)	C16—H16B	0.9800
C5—H5	1.0000	C16—H16C	0.9800
C6—H6A	0.9900	C17—C18	1.496 (3)
C6—H6B	0.9900	C18—H18A	0.9800
C7—C8	1.524 (3)	C18—H18B	0.9800
C7—H7A	0.9900	C18—H18C	0.9800
C7—H7B	0.9900	C19—C20	1.495 (3)
C8—H8A	0.9800	C20—H20A	0.9800
C8—H8B	0.9800	C20—H20B	0.9800
C8—H8C	0.9800	C20—H20C	0.9800

C7—S1—C1	101.38 (9)	C9—C10—H10A	109.5
C9—S2—C1	101.20 (9)	C9—C10—H10B	109.5
C11—S3—C2	102.08 (8)	H10A—C10—H10B	109.5
C13—S4—C13′	32.2 (5)	C9—C10—H10C	109.5
C13—S4—C3	103.66 (10)	H10A—C10—H10C	109.5
C13′—S4—C3	103.3 (4)	H10B—C10—H10C	109.5
C15—O1—C4	118.30 (13)	C12—C11—S3	114.35 (13)
C17—O3—C5	116.06 (13)	C12—C11—H11A	108.7
C19—O5—C6	115.63 (14)	S3—C11—H11A	108.7
C2—C1—S2	110.29 (11)	C12—C11—H11B	108.7
C2—C1—S1	108.94 (11)	S3—C11—H11B	108.7
S2—C1—S1	112.86 (9)	H11A—C11—H11B	107.6
C2—C1—H1	108.2	C11—C12—H12A	109.5
S2—C1—H1	108.2	C11—C12—H12B	109.5
S1—C1—H1	108.2	H12A—C12—H12B	109.5
C1—C2—C3	112.81 (13)	C11—C12—H12C	109.5
C1—C2—S3	107.93 (11)	H12A—C12—H12C	109.5
C3—C2—S3	112.69 (11)	H12B—C12—H12C	109.5

C1—C2—H2	107.7	C14—C13—S4	113.70 (19)
C3—C2—H2	107.7	C14—C13—H13A	108.8
S3—C2—H2	107.7	S4—C13—H13A	108.8
C4—C3—C2	114.75 (13)	C14—C13—H13B	108.8
C4—C3—S4	111.65 (11)	S4—C13—H13B	108.8
C2—C3—S4	108.65 (11)	H13A—C13—H13B	107.7
C4—C3—H3	107.1	C14′—C13′—S4	117.0 (11)
C2—C3—H3	107.1	C14′—C13′—H13C	108.0
S4—C3—H3	107.1	S4—C13′—H13C	108.0
O1—C4—C5	103.41 (12)	C14′—C13′—H13D	108.0
O1—C4—C3	106.83 (13)	S4—C13′—H13D	108.0
C5—C4—C3	116.60 (14)	H13C—C13′—H13D	107.3
O1—C4—H4	109.9	C13′—C14′—H14D	109.5
C5—C4—H4	109.9	C13′—C14′—H14E	109.5
C3—C4—H4	109.9	H14D—C14′—H14E	109.5
O3—C5—C4	107.49 (13)	C13′—C14′—H14F	109.5
O3—C5—C6	108.79 (13)	H14D—C14′—H14F	109.5
C4—C5—C6	113.55 (14)	H14E—C14′—H14F	109.5
O3—C5—H5	109.0	O2—C15—O1	123.03 (17)
C4—C5—H5	109.0	O2—C15—C16	126.52 (18)
C6—C5—H5	109.0	O1—C15—C16	110.42 (15)
O5—C6—C5	109.18 (13)	C15—C16—H16A	109.5
O5—C6—H6A	109.8	C15—C16—H16B	109.5
C5—C6—H6A	109.8	H16A—C16—H16B	109.5
O5—C6—H6B	109.8	C15—C16—H16C	109.5
C5—C6—H6B	109.8	H16A—C16—H16C	109.5
H6A—C6—H6B	108.3	H16B—C16—H16C	109.5
C8—C7—S1	115.40 (14)	O4—C17—O3	123.77 (18)
C8—C7—H7A	108.4	O4—C17—C18	126.18 (18)
S1—C7—H7A	108.4	O3—C17—C18	110.05 (15)
C8—C7—H7B	108.4	C17—C18—H18A	109.5
S1—C7—H7B	108.4	C17—C18—H18B	109.5
H7A—C7—H7B	107.5	H18A—C18—H18B	109.5
C7—C8—H8A	109.5	C17—C18—H18C	109.5
C7—C8—H8B	109.5	H18A—C18—H18C	109.5
H8A—C8—H8B	109.5	H18B—C18—H18C	109.5
C7—C8—H8C	109.5	O6—C19—O5	124.29 (17)
H8A—C8—H8C	109.5	O6—C19—C20	124.31 (18)
H8B—C8—H8C	109.5	O5—C19—C20	111.37 (16)
C10—C9—S2	114.64 (15)	C19—C20—H20A	109.5
C10—C9—H9A	108.6	C19—C20—H20B	109.5
S2—C9—H9A	108.6	H20A—C20—H20B	109.5
C10—C9—H9B	108.6	C19—C20—H20C	109.5
S2—C9—H9B	108.6	H20A—C20—H20C	109.5
H9A—C9—H9B	107.6	H20B—C20—H20C	109.5
C9—S2—C1—C2	−119.35 (13)	S4—C3—C4—C5	−39.69 (17)
C9—S2—C1—S1	118.55 (11)	C17—O3—C5—C4	153.04 (14)

C7—S1—C1—C2	178.77 (11)	C17—O3—C5—C6	−83.62 (17)
C7—S1—C1—S2	−58.37 (11)	O1—C4—C5—O3	−169.73 (12)
S2—C1—C2—C3	169.79 (11)	C3—C4—C5—O3	−52.85 (18)
S1—C1—C2—C3	−65.83 (15)	O1—C4—C5—C6	69.89 (16)
S2—C1—C2—S3	−65.04 (13)	C3—C4—C5—C6	−173.23 (13)
S1—C1—C2—S3	59.34 (13)	C19—O5—C6—C5	104.90 (17)
C11—S3—C2—C1	134.39 (12)	O3—C5—C6—O5	−48.42 (19)
C11—S3—C2—C3	−100.37 (12)	C4—C5—C6—O5	71.22 (18)
C1—C2—C3—C4	176.29 (14)	C1—S1—C7—C8	−71.74 (18)
S3—C2—C3—C4	53.74 (17)	C1—S2—C9—C10	68.51 (17)
C1—C2—C3—S4	−57.96 (16)	C2—S3—C11—C12	−71.05 (15)
S3—C2—C3—S4	179.49 (9)	C13′—S4—C13—C14	18.1 (8)
C13—S4—C3—C4	−87.95 (15)	C3—S4—C13—C14	−75.1 (2)
C13′—S4—C3—C4	−121.1 (5)	C13—S4—C13′—C14′	−38.2 (11)
C13—S4—C3—C2	144.51 (13)	C3—S4—C13′—C14′	56.4 (13)
C13′—S4—C3—C2	111.4 (5)	C4—O1—C15—O2	−4.4 (3)
C15—O1—C4—C5	−116.96 (15)	C4—O1—C15—C16	173.80 (15)
C15—O1—C4—C3	119.46 (15)	C5—O3—C17—O4	−3.9 (2)
C2—C3—C4—O1	−160.52 (13)	C5—O3—C17—C18	175.50 (14)
S4—C3—C4—O1	75.30 (15)	C6—O5—C19—O6	8.6 (3)
C2—C3—C4—C5	84.49 (17)	C6—O5—C19—C20	−169.42 (14)