

2-Methylsulfanyl-5,6-dihydro-2H-1,3-dithiolo[4,5-*b*][1,4]dioxin-2-ium tetra-fluoroborate

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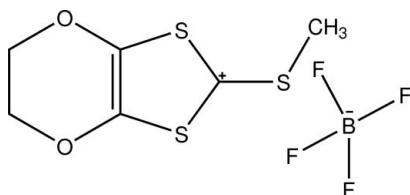
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Key indicators: single-crystal X-ray study; $T = 223$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; disorder in main residue; R factor = 0.063; wR factor = 0.174; data-to-parameter ratio = 13.9.

The title compound, $\text{C}_6\text{H}_7\text{O}_2\text{S}_3^+\cdot\text{BF}_4^-$, consists of a planar 2-thioxo-1,3-dithiol-4,5-yl unit [maximum deviation from the ring plane = 0.020 (3) Å], with an ethylenedioxy group fused at the 4,5-positions; the ethylenedioxy C atoms are disordered over two positions with site-occupancy factors of 0.5. The 1,4-dioxine ring has a twist-chair conformation. Weak cation–anion $\text{S}\cdots\text{F}$ interactions [3.022 (4)–3.095 (4) Å] and an $\text{S}\cdots\text{O}$ [3.247 (4) Å] interaction are present.

Related literature

For background on metal–organic coordination compounds, see: Chen *et al.* (2000); Xiong *et al.* (1999). For the preparation and crystal structure of a related compound, see: Han & Zhang (2010); Kanchanadevi *et al.* (2010).



Experimental

Crystal data

$\text{C}_6\text{H}_7\text{O}_2\text{S}_3^+\cdot\text{BF}_4^-$	$V = 1103.7$ (2) Å ³
$M_r = 294.14$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.7410$ (13) Å	$\mu = 0.71$ mm ⁻¹
$b = 10.1175$ (10) Å	$T = 223$ K
$c = 10.1874$ (11) Å	$0.40 \times 0.35 \times 0.35$ mm
$\beta = 94.488$ (4)°	

Data collection

Rigaku Saturn CCD diffractometer	6014 measured reflections
Absorption correction: multi-scan (<i>REQAB</i> ; Jacobson, 1998)	2046 independent reflections
$T_{\min} = 0.593$, $T_{\max} = 0.781$	1749 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.063$	6 restraints
$wR(F^2) = 0.174$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.69$ e Å ⁻³
2046 reflections	$\Delta\rho_{\text{min}} = -0.55$ e Å ⁻³
147 parameters	

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSK, 2005); 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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RK2328).

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supplementary materials

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2-Methylsulfanyl-5,6-dihydro-2*H*-1,3-dithiolo[4,5-*b*][1,4]dioxin-2-ium tetrafluoroborate

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Comment

The construction of metal-organic coordination compounds has attracted much attention owing to potential functions, such as permittivity, fluorescence, magnetism and optical properties (Chen *et al.*, 2000; Xiong *et al.*, 1999). We report here the molecular and crystal structures of the title compound, 5,6-dihydro-2-(methylthio)-[1,3]dithiolo[4,5-*b*][1,4]dioxine tetrafluoroborate, **I**. In **I**, (Fig. 1), the inductive effects of the oxygen atoms makes the between C4 and C5 bond length longer (1.493 Å). The C–S bond lengths range 1.681 (4) Å–1.723 (5) Å is small than that typical of C–S bond lengths, 1.82 Å, suggesting a degree of conjugation in the dithiol-2-thione system. Both conformers of the disordered dioxane ring adopt half-chair conformations. In **I**, there are weak S⋯F interaction (3.095 (4) Å–3.022 (4) Å) and S⋯O (3.247 (4) Å). These interaction (cation-anion) in the crystal structure, forming a one-dimensional network, see (Fig. 2).

Experimental

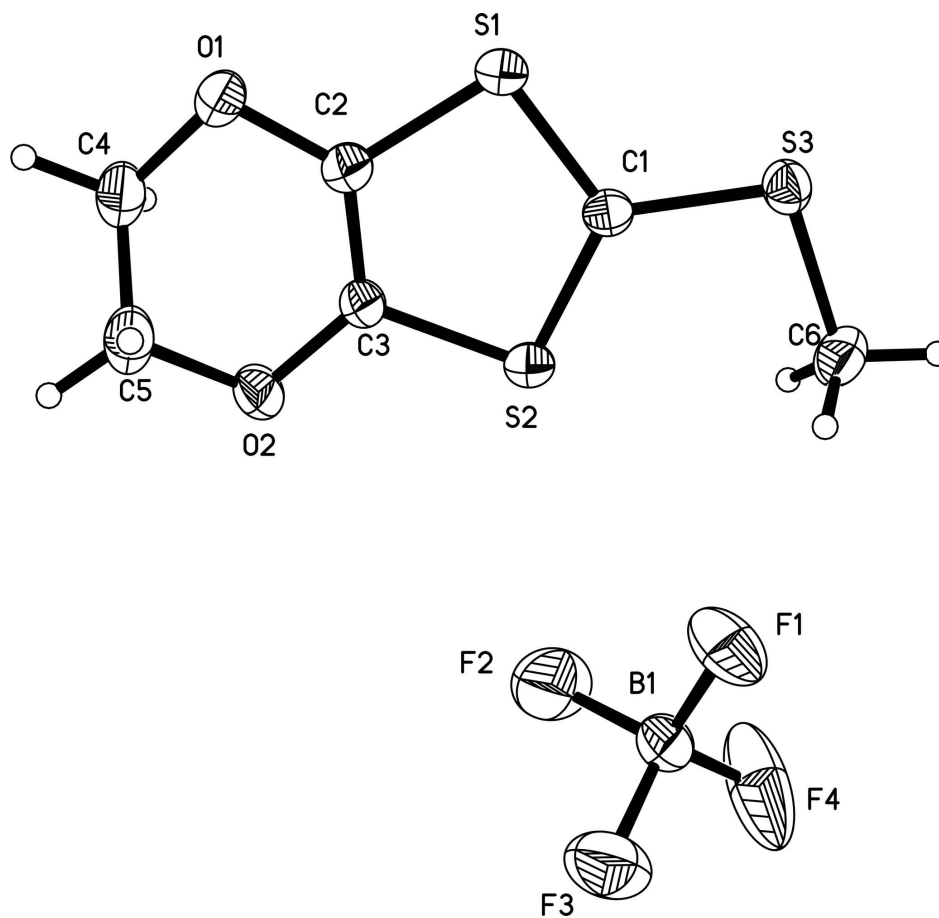
The 5,6-dihydro-[1,3]dithiolo[4,5-*b*][1,4]dioxine-2-thione dissolve in acetonitrile with $[(\text{CH}_3)_3\text{O}]^+\times[\text{BF}_4]^-$ and get the yellow compound. Slow evaporation of the compound in a solution of *THF* gave single crystals suitable for *X*-ray analysis.

Refinement

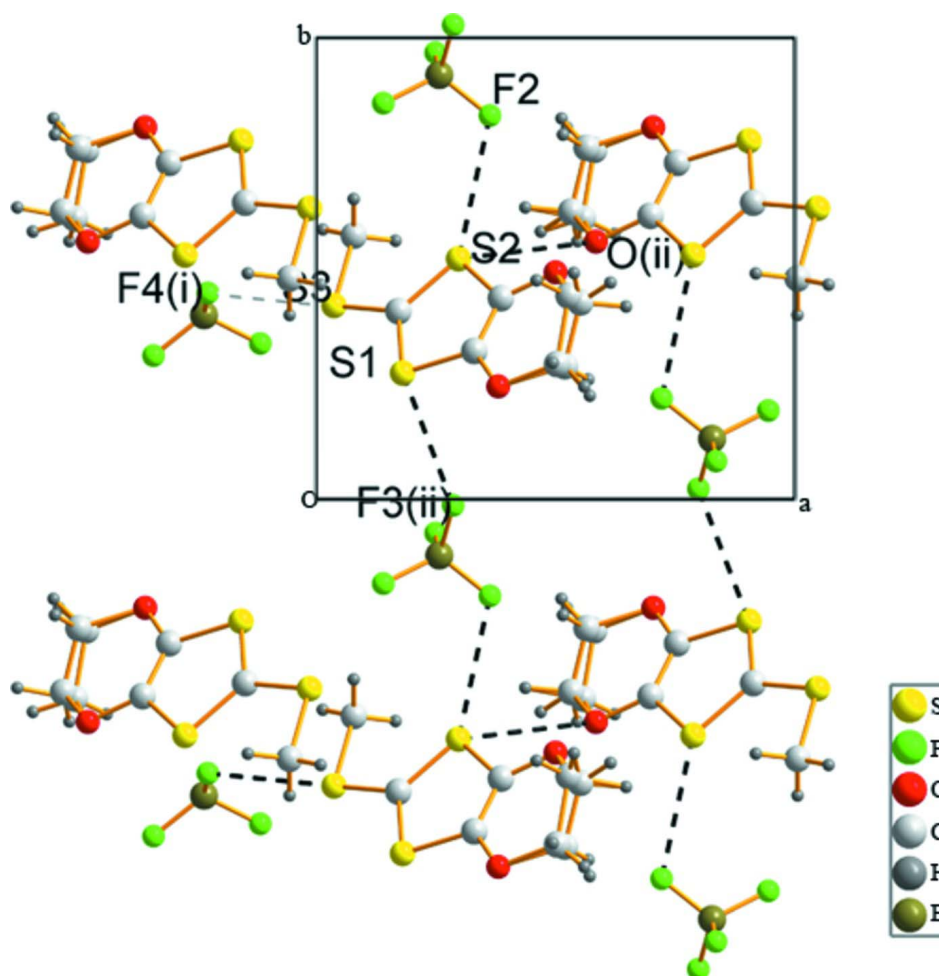
All the H atoms were placed in geometrically calculated positions, with C–H = 0.98 Å (methylene) and 0.97 Å (methyl) and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ (methylene) and $1.5 U_{\text{eq}}(\text{C})$ (methyl), and refined using a riding model.

Computing details

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear* (Rigaku, 2005); data reduction: *CrystalStructure* (Rigaku/MSO, 2005); 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* (Sheldrick, 2008).

**Figure 1**

The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are presented as a small spheres of arbitrary radius. Only initial disordered C atoms are presented.


Figure 2

The crystal packing diagram view along c axis. Dashed lines indicate the weak interaction. Symmetry codes: (i) $-x, -1/2+y, 1/2-z$; (ii) $x, -1+y, z$; (iii) $1-x, 1-y, 1-z$.

2-Methylsulfanyl-5,6-dihydro-2H-1,3-dithiolo[4,5-*b*][1,4]dioxin- 2-ium tetrafluoroborate

Crystal data

$C_6H_7O_2S_3^+ \cdot BF_4^-$

$M_r = 294.14$

Monoclinic, $P2_1/c$

Hall symbol: $-P 2ybc$

$a = 10.7410$ (13) Å

$b = 10.1175$ (10) Å

$c = 10.1874$ (11) Å

$\beta = 94.488$ (4)°

$V = 1103.7$ (2) Å³

$Z = 4$

$F(000) = 592$

$D_x = 1.770$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å

Cell parameters from 2895 reflections

$\theta = 3.3$ – 27.5 °

$\mu = 0.71$ mm⁻¹

$T = 223$ K

Block, yellow

$0.40 \times 0.35 \times 0.35$ mm

Data collection

Rigaku Saturn CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 14.63 pixels mm⁻¹

ω -scan

Absorption correction: multi-scan

(*REQAB*; Jacobson, 1998)

$T_{\min} = 0.593$, $T_{\max} = 0.781$

6014 measured reflections

2046 independent reflections

1749 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 25.5^\circ$, $\theta_{\min} = 3.3^\circ$

$h = -12 \rightarrow 13$

$k = -10 \rightarrow 12$

$l = -11 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.063$

$wR(F^2) = 0.174$

$S = 1.07$

2046 reflections

147 parameters

6 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

$w = 1/[\sigma^2(F_o^2) + (0.0986P)^2 + 1.5661P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.69 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.55 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
S1	0.15907 (11)	0.25827 (11)	0.56191 (12)	0.0482 (4)	
S2	0.26927 (10)	0.49599 (10)	0.46964 (11)	0.0428 (3)	
S3	0.02403 (10)	0.39889 (11)	0.34288 (10)	0.0439 (3)	
F1	0.1210 (3)	0.8199 (4)	0.4652 (3)	0.0815 (11)	
F2	0.3311 (4)	0.7944 (4)	0.4588 (5)	0.1015 (14)	
F3	0.2587 (4)	0.9828 (4)	0.5236 (5)	0.0953 (13)	
F4	0.2242 (5)	0.9251 (8)	0.3140 (4)	0.161 (3)	
O1	0.3475 (3)	0.2304 (3)	0.7435 (3)	0.0566 (9)	
O2	0.4604 (3)	0.4681 (3)	0.6479 (3)	0.0528 (8)	
C1	0.1508 (4)	0.3871 (4)	0.4559 (4)	0.0368 (9)	
C2	0.3004 (4)	0.3043 (4)	0.6403 (4)	0.0427 (10)	
C3	0.3528 (4)	0.4142 (4)	0.5960 (4)	0.0388 (9)	
C4	0.4786 (15)	0.2727 (17)	0.7661 (15)	0.083 (3)	0.50
H4A	0.5251	0.2454	0.6916	0.099*	0.50
H4B	0.5169	0.2303	0.8457	0.099*	0.50
C4'	0.4634 (16)	0.2771 (19)	0.8065 (15)	0.083 (3)	0.50
H4'1	0.5278	0.2114	0.7917	0.099*	0.50
H4'2	0.4548	0.2801	0.9015	0.099*	0.50
C5	0.486 (2)	0.4194 (17)	0.7811 (18)	0.083 (3)	0.50
H5A	0.4229	0.4514	0.8384	0.099*	0.50

H5B	0.5686	0.4469	0.8179	0.099*	0.50
C5'	0.509 (2)	0.4054 (18)	0.7666 (19)	0.083 (3)	0.50
H5'1	0.4964	0.4670	0.8387	0.099*	0.50
H5'2	0.5991	0.3969	0.7616	0.099*	0.50
C6	0.0632 (5)	0.5445 (5)	0.2538 (5)	0.0603 (13)	
H6A	0.0631	0.6207	0.3117	0.091*	
H6B	0.0021	0.5575	0.1797	0.091*	
H6C	0.1454	0.5340	0.2221	0.091*	
B1	0.2316 (5)	0.8787 (6)	0.4366 (6)	0.0508 (13)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0445 (7)	0.0429 (6)	0.0560 (7)	-0.0110 (4)	-0.0040 (5)	0.0114 (5)
S2	0.0417 (6)	0.0382 (6)	0.0480 (6)	-0.0064 (4)	0.0010 (5)	0.0072 (4)
S3	0.0439 (6)	0.0461 (6)	0.0408 (6)	0.0008 (5)	-0.0032 (5)	-0.0037 (4)
F1	0.059 (2)	0.108 (3)	0.078 (2)	-0.0333 (19)	0.0133 (17)	-0.009 (2)
F2	0.073 (3)	0.079 (2)	0.152 (4)	0.0122 (19)	0.008 (3)	-0.008 (2)
F3	0.090 (3)	0.071 (2)	0.125 (3)	-0.0072 (19)	0.005 (2)	-0.028 (2)
F4	0.094 (3)	0.311 (8)	0.073 (3)	-0.079 (4)	-0.022 (2)	0.071 (4)
O1	0.051 (2)	0.058 (2)	0.059 (2)	-0.0042 (15)	-0.0088 (16)	0.0206 (16)
O2	0.0385 (17)	0.061 (2)	0.0575 (19)	-0.0113 (15)	-0.0048 (15)	0.0072 (15)
C1	0.039 (2)	0.033 (2)	0.038 (2)	0.0008 (16)	0.0050 (17)	-0.0016 (15)
C2	0.042 (2)	0.042 (2)	0.044 (2)	-0.0021 (18)	0.0020 (18)	0.0048 (18)
C3	0.033 (2)	0.041 (2)	0.042 (2)	-0.0013 (16)	-0.0003 (17)	0.0028 (17)
C4	0.074 (5)	0.097 (4)	0.071 (5)	-0.025 (3)	-0.029 (4)	0.035 (3)
C4'	0.074 (5)	0.097 (4)	0.071 (5)	-0.025 (3)	-0.029 (4)	0.035 (3)
C5	0.074 (5)	0.097 (4)	0.071 (5)	-0.025 (3)	-0.029 (4)	0.035 (3)
C5'	0.074 (5)	0.097 (4)	0.071 (5)	-0.025 (3)	-0.029 (4)	0.035 (3)
C6	0.069 (3)	0.057 (3)	0.054 (3)	0.007 (3)	-0.007 (2)	0.013 (2)
B1	0.044 (3)	0.054 (3)	0.055 (3)	-0.005 (2)	0.003 (2)	-0.002 (2)

Geometric parameters (\AA , $^\circ$)

S1—C1	1.691 (4)	O2—C5	1.450 (15)
S1—C2	1.723 (5)	C2—C3	1.341 (6)
S2—C1	1.681 (4)	C4—C5	1.493 (18)
S2—C3	1.723 (4)	C4—H4A	0.9800
S3—C1	1.717 (4)	C4—H4B	0.9800
S3—C6	1.797 (5)	C4'—C5'	1.456 (16)
F1—B1	1.379 (6)	C4'—H4'1	0.9800
F2—B1	1.373 (7)	C4'—H4'2	0.9800
F3—B1	1.392 (7)	C5—H5A	0.9800
F4—B1	1.332 (7)	C5—H5B	0.9800
O1—C2	1.356 (5)	C5'—H5'1	0.9800
O1—C4'	1.435 (13)	C5'—H5'2	0.9800
O1—C4	1.473 (14)	C6—H6A	0.9700
O2—C3	1.347 (5)	C6—H6B	0.9700
O2—C5'	1.427 (15)	C6—H6C	0.9700

C1—S1—C2	95.1 (2)	O1—C4'—H4'2	107.9
C1—S2—C3	95.4 (2)	C5'—C4'—H4'2	107.9
C1—S3—C6	101.0 (2)	H4'1—C4'—H4'2	107.2
C2—O1—C4'	115.0 (6)	O2—C5—C4	103.7 (14)
C2—O1—C4	104.8 (6)	O2—C5—H5A	111.0
C4'—O1—C4	18.0 (12)	C4—C5—H5A	111.0
C3—O2—C5'	113.3 (9)	O2—C5—H5B	111.0
C3—O2—C5	108.7 (9)	C4—C5—H5B	111.0
C5'—O2—C5	13 (2)	H5A—C5—H5B	109.0
S2—C1—S1	116.8 (3)	O2—C5'—C4'	121.7 (15)
S2—C1—S3	124.5 (2)	O2—C5'—H5'1	106.9
S1—C1—S3	118.8 (2)	C4'—C5'—H5'1	106.9
C3—C2—O1	125.3 (4)	O2—C5'—H5'2	106.9
C3—C2—S1	116.5 (3)	C4'—C5'—H5'2	106.9
O1—C2—S1	118.2 (3)	H5'1—C5'—H5'2	106.7
C2—C3—O2	125.0 (4)	S3—C6—H6A	109.5
C2—C3—S2	116.2 (3)	S3—C6—H6B	109.5
O2—C3—S2	118.6 (3)	H6A—C6—H6B	109.5
O1—C4—C5	110.2 (18)	S3—C6—H6C	109.5
O1—C4—H4A	109.6	H6A—C6—H6C	109.5
C5—C4—H4A	109.6	H6B—C6—H6C	109.5
O1—C4—H4B	109.6	F4—B1—F2	111.2 (5)
C5—C4—H4B	109.6	F4—B1—F1	111.2 (5)
H4A—C4—H4B	108.1	F2—B1—F1	111.7 (5)
O1—C4'—C5'	117.8 (13)	F4—B1—F3	108.9 (5)
O1—C4'—H4'1	107.9	F2—B1—F3	104.1 (5)
C5'—C4'—H4'1	107.9	F1—B1—F3	109.4 (4)
C3—S2—C1—S1	1.2 (3)	C5'—O2—C3—C2	-6.9 (13)
C3—S2—C1—S3	-178.9 (3)	C5—O2—C3—C2	-20.1 (11)
C2—S1—C1—S2	-0.6 (3)	C5'—O2—C3—S2	168.9 (12)
C2—S1—C1—S3	179.5 (3)	C5—O2—C3—S2	155.7 (10)
C6—S3—C1—S2	2.2 (3)	C1—S2—C3—C2	-1.7 (4)
C6—S3—C1—S1	-177.9 (3)	C1—S2—C3—O2	-177.8 (3)
C4'—O1—C2—C3	-0.6 (12)	C2—O1—C4—C5	53.2 (14)
C4—O1—C2—C3	-16.3 (10)	C4'—O1—C4—C5	-74 (5)
C4'—O1—C2—S1	-178.1 (11)	C2—O1—C4'—C5'	8 (3)
C4—O1—C2—S1	166.1 (8)	C4—O1—C4'—C5'	67 (4)
C1—S1—C2—C3	-0.6 (4)	C3—O2—C5—C4	53.0 (19)
C1—S1—C2—O1	177.2 (4)	C5'—O2—C5—C4	-60 (6)
O1—C2—C3—O2	-0.1 (7)	O1—C4—C5—O2	-75 (2)
S1—C2—C3—O2	177.4 (3)	C3—O2—C5'—C4'	15 (3)
O1—C2—C3—S2	-176.0 (4)	C5—O2—C5'—C4'	87 (7)
S1—C2—C3—S2	1.5 (5)	O1—C4'—C5'—O2	-16 (4)