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Crystal structure of ethyl 2-cyano-2-(1,3-dithian-2-ylidene)acetate

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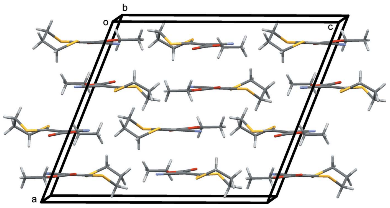
The title compound, $C_9H_{11}NO_2S_2$, contains a 1,3-dithiane ring which has a twist-boat conformation. The dihedral angle between the mean planes of the ethyl acetate group and the dithiane ring is 17.56 (13)°. In the crystal, molecules stack in layers up the *a*-axis direction, however, there are no significant intermolecular interactions present.



1. Chemical context

The derivatives of compounds such as α-oxo-ketene dithioacetals may undergo various transformations, in addition to the reactions involving the carbonyl group, C═C double bond, or the sulfur atoms. The emphasis in recent years has focused on the development of new and efficient intermediates. Some examples include (*a*) the preparation of highly regioselective compounds in a one-step reaction [the first example to be reported was the regiospecific synthesis of polysubstituted phenols from 1,5-dielectrophiles, *via* the five carbon atoms that are available in the structures of acenoyl ketene dithioacetals (Bi *et al.*, 2005)]; (*b*) the synthesis of complex molecules based on new efficient and cost-effective reactions because they allow more than one transformation into a single synthetic sequence (Dömling *et al.*, 2012; Tietze *et al.*, 2006); (*c*) the preparation of trifluoromethyl-containing organic compounds of particular interest in the pharmaceutical and agrochemical fields due to their lipophilicity, hydrophobic properties and stable metabolic character (Furuya *et al.*, 2011). Muzard and co-workers have been involved in the chemistry of trifluoromethylketene dithioacetals, especially perfluoroketene dithioacetals, and have reported in their work the preparation of trifluoromethylketene dithioacetals (Muzard & Portella, 1993).

The functionalization of ketene dithioacetals provides more powerful tools for the development of new intermediates (Wang *et al.*, 2011; Gao *et al.*, 2010; Hu *et al.*, 2012). Of such constructions on the skeleton of the ketene dithioacetals, especially those involving the formation of the C—C bonds using carboelectrophiles such as aldehydes, have provided an effective link between these compounds and a variety of organic compounds with other functional groups. Minami *et al.* (1996) reported in their work the synthesis of α-hydroxyphosphonoketene dithioacetals from aldehydes. In addition, Kouno *et al.* (1998) have shown that phosphorus enyne-containing groups and dithiolanes could be prepared by cross-

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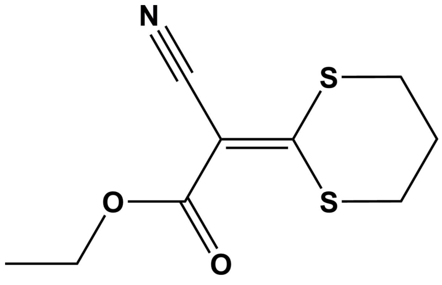
coupling of dithioacetal cyclic α-(iodopropane) with the corresponding alkyne phosphonoketene.

The direct formation of the C—C bond has been carried out by reacting α-cyano ketene dithioacetal and Morita–Baylis–Hillman (MBH) alcohols resulting from the reaction of acrylonitrile and aryl aldehydes. This reaction led to the corresponding 1,4-pentadiene derivatives (Zhao *et al.*, 2007).

New synthetic pathways of various intermediates characterized by several functional groups have been created by transforming the α-acetylcetaldithioacetal functional group into α-hydroxy, α-chloro and α-bromo (Liu *et al.*, 2003) and α-ethynyl ketene (Dong *et al.*, 2005). The creation of new pathways to access such multi-functionalized compounds has also been achieved by reactions involving cleavage of the C—S bond (Dong *et al.*, 2011). It should be noted here that the functionalization of the alkylthio group of these compounds has led to products useful in a wide range of applications (Mahata *et al.*, 2003)

Fiala *et al.* (2007) have studied the inhibitive action of some synthesized ketene dithioacetal derivatives towards the corrosion of copper in aerated nitric acid solutions. They concluded that these compounds are good inhibitors of copper corrosion in this medium. The inhibitory properties of the title compound with respect to the corrosion of a transition metal in an acid medium were investigated in a separate study.

Herein, we report on the synthesis and crystal structure of ethyl 2-cyano-2-(1,3-dithian-2-ylidene)acetate (I). We also examined the effect of the substitution of the methyl group of methyl 2-cyano-2-(1,3-dithian-2-ylidene)acetate (II) (Hamdouni *et al.*, 2017) by the ethyl group of the title compound.



2. Structural commentary

The molecular structure of the title compound (I), is illustrated in Fig. 1. The mean planes of the ethyl acetate group [C1/C2/O1/O2/C8/C9; maximum deviation of 0.051 (2) Å for atom O2] and the dithiazane ring (S1/S2/C1–C4) are inclined to one another by 17.56 (13)°. The dithiane ring (S1/S2/C4–C7) has a twist-boat conformation [puckering parameters: amplitude (Q) = 0.909 (2) Å, θ = 89.88 (19)°, and φ = 331.65 (16)°].

The C—S bond lengths differ as expected, with the Csp^2—S bonds [S1—C4 = 1.747 (2) and S2—C4 = 1.736 (2) Å] being shorter that the Csp^3—S bonds [S1—C5 = 1.805 (3) and S2—C7 = 1.817 (3) Å]. The C2═C4 bond length is 1.378 (3) Å. All the bond lengths and angles agree well with those reported for similar compounds, for example in methyl 2-cyano-2-(1,3-dithian-2-ylidene)acetate, compound (II) mentioned above.

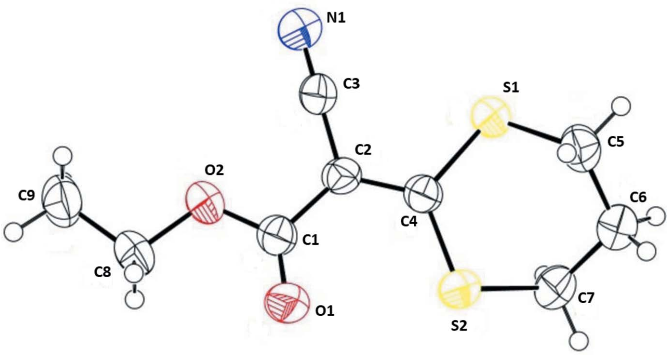


Figure 1
The molecular structure of the title compound (I), with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

3. Supramolecular features

In the crystal of (I), molecules stack in layers up the a-axis direction (Fig. 2); however, there are no significant intermolecular interactions present.

4. Database survey

A search of the Cambridge Structural Database (Version 5.38, update May 2017; Groom *et al.*, 2016) for the 2-(1,3-dithian-2-ylidene) skeleton yielded eight hits. They include a number of 1,2-bis(dithian-2-ylidenes), such as dimethyl 1,2-bis(dithian-2-ylidene)-ethane-1,2-dicarboxylate (ZIGVOA; Benati *et al.*, 1995). Since that update, the structure of the methyl analogue, (II), of the title compound has been reported by our group (Hamdouni *et al.*, 2017). The two structures differ essentially in the orientation of the twist-boat dithiazane ring, as shown by the structural overlap of the two molecules in Fig. 3. The puckering parameters for (I) are Q = 0.909 (2) Å, θ = 89.88 (19)° and φ = 331.65 (16)°, while those for (II) are Q = 0.632 (3) Å, θ = 106.5 (3)° and φ= 114.3 (3)°. The mean planes of the ethyl acetate group [C1/C2/O1/O2/C8/C9; maximum deviation of 0.051 (2) Å for atom O2] and the dithiazane ring

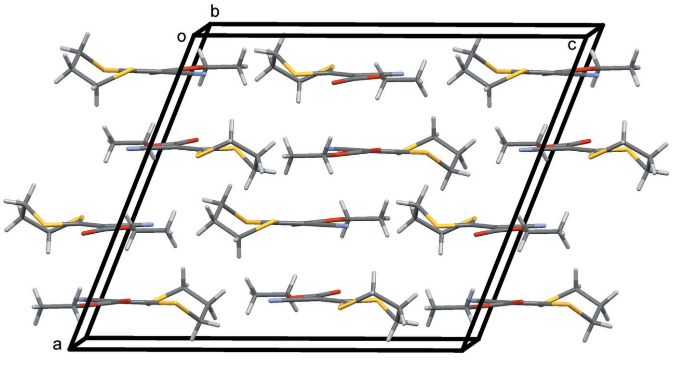


Figure 2
A view along the b axis of the crystal packing of the title compound (I).

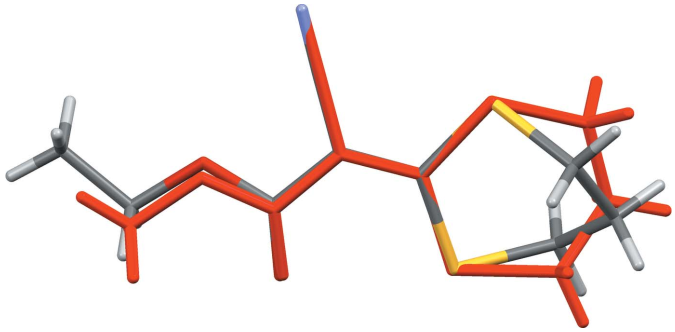


Figure 3
Structural overlap of compounds (I) and (II); the latter is shown in red.

(S1/S2/C1–C4) in compound (I) are inclined to one another by 17.56 (13)°. The corresponding dihedral angle in compound (II) is 11.60 (12)°. In the crystals, the molecules stack along [100] in (I) and [010] in (II), and there are no significant intermolecular interactions present in either.

5. Synthesis and crystallization

The title compound was prepared according to a method proposed by Thuillier & Vialle (1962). Potassium carbonate, K_2CO_3, (42 g, 0.3 mol) and the corresponding active methylene compound, ethyl 2-cyanoacetate, (0.1 mol) were taken in 50 ml of DMF. The reaction mixture was stirred magnetically, then carbon disulfide (9 ml, 0.15 mol) was added at all once at room temperature. The stirring was maintained for 10 min before the dropwise addition of 1,3-dibromopropane (0.12 mol) over a period of 20 min. After stirring at room temperature for 7 h, ice-cold water (500 ml) was added to the reaction mixture. The yellow precipitate that formed was filtered, dried and then purified by recrystallization from ethanol (yield 93%, m.p. 368 K). The title compound exhibited the following characteristics: molar mass is $M_w = 229$ g mol^{-1}. FT–IR (cm^{-1}): 1700 ($\mathrm{C{=}O}$), 1246–1004 [$\mathrm{C{-}O}$ (ester)], 2206 ($\mathrm{C{\equiv}N}$), 1437 ($\mathrm{C{=}C}$). ^{1}H NMR ($CDCl_3$, δ p.p.m., 250 MHz): 1.35 (*t*, 3H, $\mathrm{CH_3{-}CH_2}$), 2.30 (*m*, 2H, CH_2), 3.00 (*t*, 2H, CH_2S), 3.10 (*t*, 2H, CH_2S), 4.30 (*q*, 2H, CH_2O). ^{13}C NMR ($CDCl_3$, δ p.p.m., 250 MHz):14.22 (*s*, $\mathrm{CH_3{-}CH_2{-}O}$), 23.36 (*s*, $\mathrm{S{-}CH_2{-}CH_2{-}CH_2{-}S}$), 28.99 (*s*, $\mathrm{S{-}CH_2{-}CH_2{-}CH_2{-}S}$), 61.26 (*s*, $\mathrm{CH_3{-}CH_2}$), 120.55 (*s*, CN), 76.69 (s, $\mathrm{O{=}C{-}C{=}C}$), 165.56 (*s*, $\mathrm{O{-}{-}C{=}O}$). MS: *m*/*z* 229.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The H atoms were included in calculated positions and treated as riding atoms: $\mathrm{C{-}H} = 0.96$–0.97 Å with $U_{\rm iso}(\mathrm{H}) = 1.5U_{\rm eq}$(C-methyl) and $1.2U_{\rm eq}$(C) for other H-atoms.

Acknowledgements

We thank Mr F. Saidi, Engineer at the Laboratory of Crystallography, University Constantine 1, for assistance in collecting the X-ray data on the Xcalibur diffractometer.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_9H_{11}NO_2S_2$
M_r	229.31
Crystal system, space group	Monoclinic, *I*2/*a*
Temperature (K)	293
a, *b*, *c* (Å)	15.826 (3), 8.0772 (6), 18.431 (2)
β (°)	111.830 (16)
V (Å^3)	2187.1 (5)
Z	8
Radiation type	Mo *Kα*
μ (mm^{-1})	0.46
Crystal size (mm)	0.48 × 0.27 × 0.13
Data collection	
Diffractometer	Agilent Xcalibur Eos
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2013)
$T_{\rm min}$, $T_{\rm max}$	0.334, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4539, 2132, 1667
$R_{\rm int}$	0.035
$(\sin \theta/\lambda)_{\rm max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.049, 0.138, 1.08
No. of reflections	2132
No. of parameters	127
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\rm max}$, $\Delta\rho_{\rm min}$ (e Å^{-3})	0.46, −0.34

Computer programs: *CrysAlis PRO* (Agilent, 2013), *SIR92* (Altomare *et al.*, 1994), *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008), *SHELXL2016* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

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supporting information

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Crystal structure of ethyl 2-cyano-2-(1,3-dithian-2-ylidene)acetate

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Computing details

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO* (Agilent, 2013); data reduction: *CrysAlis PRO* (Agilent, 2013); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2016* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

Ethyl 2-cyano-2-(1,3-dithian-2-ylidene)acetate

Crystal data

$C_9H_{11}NO_2S_2$
$M_r = 229.31$
Monoclinic, $I2/a$
$a = 15.826\ (3)$ Å
$b = 8.0772\ (6)$ Å
$c = 18.431\ (2)$ Å
$\beta = 111.830\ (16)°$
$V = 2187.1\ (5)$ Å^3
$Z = 8$

$F(000) = 960$
$D_x = 1.393$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1541 reflections
$\theta = 3.7–28.9°$
$\mu = 0.46$ mm^{-1}
$T = 293$ K
Needle, pale yellow
0.48 × 0.27 × 0.13 mm

Data collection

Agilent Xcalibur Eos diffractometer
Graphite monochromator
Detector resolution: 8.02 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2013)
$T_{\min} = 0.334$, $T_{\max} = 1.000$

4539 measured reflections
2132 independent reflections
1667 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.035$
$\theta_{\max} = 26.0°$, $\theta_{\min} = 3.4°$
$h = -17 \rightarrow 19$
$k = -9 \rightarrow 9$
$l = -22 \rightarrow 20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.138$
$S = 1.08$
2132 reflections
127 parameters
0 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

$w = 1/[\sigma^2(F_o^2) + (0.0673P)^2 + 0.4223P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
S2	0.12671 (5)	0.08363 (8)	0.29431 (4)	0.0555 (3)
S1	0.11241 (5)	0.40461 (8)	0.37170 (4)	0.0589 (3)
O1	0.14349 (14)	−0.1692 (2)	0.40827 (11)	0.0641 (5)
O2	0.12483 (13)	−0.1107 (2)	0.52062 (11)	0.0592 (5)
N1	0.1307 (2)	0.2907 (3)	0.55919 (14)	0.0741 (7)
C1	0.13376 (16)	−0.0706 (3)	0.45311 (14)	0.0477 (6)
C2	0.13016 (16)	0.1100 (3)	0.44342 (13)	0.0447 (6)
C3	0.13080 (18)	0.2096 (3)	0.50818 (15)	0.0512 (6)
C4	0.12494 (15)	0.1895 (3)	0.37572 (14)	0.0449 (6)
C5	0.1624 (2)	0.4577 (4)	0.30133 (16)	0.0620 (7)
H5A	0.166410	0.577323	0.299200	0.074*
H5B	0.224000	0.414405	0.319553	0.074*
C6	0.1113 (2)	0.3938 (3)	0.21943 (16)	0.0639 (7)
H6A	0.153558	0.381976	0.192819	0.077*
H6B	0.065809	0.474754	0.190915	0.077*
C7	0.06477 (19)	0.2289 (3)	0.21774 (15)	0.0615 (7)
H7A	0.053615	0.176859	0.167585	0.074*
H7B	0.006049	0.249883	0.221227	0.074*
C8	0.1298 (2)	−0.2859 (3)	0.54028 (17)	0.0617 (7)
H8A	0.185483	−0.334042	0.539292	0.074*
H8B	0.078396	−0.344992	0.503306	0.074*
C9	0.1279 (2)	−0.2958 (4)	0.62053 (19)	0.0731 (9)
H9A	0.131070	−0.409675	0.636284	0.110*
H9B	0.179046	−0.236653	0.656364	0.110*
H9C	0.072531	−0.247544	0.620570	0.110*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S2	0.0705 (5)	0.0497 (4)	0.0437 (4)	0.0033 (3)	0.0182 (3)	−0.0037 (3)
S1	0.0862 (5)	0.0418 (4)	0.0494 (4)	0.0049 (3)	0.0259 (4)	0.0024 (3)
O1	0.0886 (14)	0.0476 (10)	0.0518 (11)	0.0075 (9)	0.0211 (10)	−0.0022 (9)
O2	0.0821 (13)	0.0399 (9)	0.0561 (11)	0.0057 (8)	0.0262 (10)	0.0067 (8)
N1	0.115 (2)	0.0547 (14)	0.0513 (14)	0.0002 (13)	0.0293 (15)	−0.0027 (12)
C1	0.0463 (13)	0.0469 (13)	0.0407 (13)	0.0027 (10)	0.0057 (10)	0.0025 (11)
C2	0.0471 (12)	0.0443 (13)	0.0349 (11)	0.0026 (10)	0.0064 (10)	−0.0013 (10)

C3	0.0616 (15)	0.0447 (13)	0.0413 (13)	0.0019 (11)	0.0122 (12)	0.0057 (11)
C4	0.0417 (12)	0.0435 (13)	0.0422 (13)	0.0018 (9)	0.0073 (10)	0.0005 (10)
C5	0.0682 (17)	0.0556 (15)	0.0593 (17)	−0.0084 (13)	0.0203 (14)	0.0065 (13)
C6	0.080 (2)	0.0629 (17)	0.0485 (15)	−0.0046 (14)	0.0235 (14)	0.0030 (14)
C7	0.0710 (17)	0.0669 (17)	0.0389 (13)	−0.0043 (14)	0.0116 (13)	0.0008 (13)
C8	0.0763 (19)	0.0408 (13)	0.0678 (19)	0.0036 (12)	0.0266 (15)	0.0098 (12)
C9	0.098 (2)	0.0544 (17)	0.078 (2)	0.0146 (15)	0.0454 (19)	0.0181 (15)

Geometric parameters (Å, º)

S2—C4	1.736 (2)	C5—H5B	0.9700
S2—C7	1.817 (3)	C6—C7	1.517 (4)
S1—C4	1.747 (2)	C6—H6A	0.9700
S1—C5	1.805 (3)	C6—H6B	0.9700
O1—C1	1.198 (3)	C7—H7A	0.9700
O2—C1	1.343 (3)	C7—H7B	0.9700
O2—C8	1.456 (3)	C8—C9	1.492 (4)
N1—C3	1.146 (3)	C8—H8A	0.9700
C1—C2	1.469 (3)	C8—H8B	0.9700
C2—C4	1.378 (3)	C9—H9A	0.9600
C2—C3	1.436 (3)	C9—H9B	0.9600
C5—C6	1.514 (4)	C9—H9C	0.9600
C5—H5A	0.9700		
C4—S2—C7	100.12 (13)	C5—C6—H6B	108.9
C4—S1—C5	101.16 (13)	C7—C6—H6B	108.9
C1—O2—C8	116.8 (2)	H6A—C6—H6B	107.7
O1—C1—O2	124.3 (2)	C6—C7—S2	115.69 (19)
O1—C1—C2	125.9 (2)	C6—C7—H7A	108.4
O2—C1—C2	109.8 (2)	S2—C7—H7A	108.4
C4—C2—C3	118.1 (2)	C6—C7—H7B	108.4
C4—C2—C1	124.0 (2)	S2—C7—H7B	108.4
C3—C2—C1	117.9 (2)	H7A—C7—H7B	107.4
N1—C3—C2	179.1 (3)	O2—C8—C9	106.2 (2)
C2—C4—S2	122.55 (18)	O2—C8—H8A	110.5
C2—C4—S1	117.99 (18)	C9—C8—H8A	110.5
S2—C4—S1	119.43 (14)	O2—C8—H8B	110.5
C6—C5—S1	114.9 (2)	C9—C8—H8B	110.5
C6—C5—H5A	108.5	H8A—C8—H8B	108.7
S1—C5—H5A	108.5	C8—C9—H9A	109.5
C6—C5—H5B	108.5	C8—C9—H9B	109.5
S1—C5—H5B	108.5	H9A—C9—H9B	109.5
H5A—C5—H5B	107.5	C8—C9—H9C	109.5
C5—C6—C7	113.3 (2)	H9A—C9—H9C	109.5
C5—C6—H6A	108.9	H9B—C9—H9C	109.5
C7—C6—H6A	108.9		
C8—O2—C1—O1	1.6 (4)	C7—S2—C4—C2	153.6 (2)

C8—O2—C1—C2	−178.2 (2)	C7—S2—C4—S1	−24.31 (17)
O1—C1—C2—C4	9.4 (4)	C5—S1—C4—C2	153.59 (19)
O2—C1—C2—C4	−170.8 (2)	C5—S1—C4—S2	−28.43 (18)
O1—C1—C2—C3	−171.5 (2)	C4—S1—C5—C6	65.6 (2)
O2—C1—C2—C3	8.2 (3)	S1—C5—C6—C7	−32.9 (3)
C3—C2—C4—S2	178.22 (18)	C5—C6—C7—S2	−37.1 (3)
C1—C2—C4—S2	−2.7 (3)	C4—S2—C7—C6	65.9 (2)
C3—C2—C4—S1	−3.9 (3)	C1—O2—C8—C9	174.2 (2)
C1—C2—C4—S1	175.18 (18)		