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Crystal structure of 2-methoxy-2-[(4-methylphenyl)sulfanyl]-1-phenylethan-1-one

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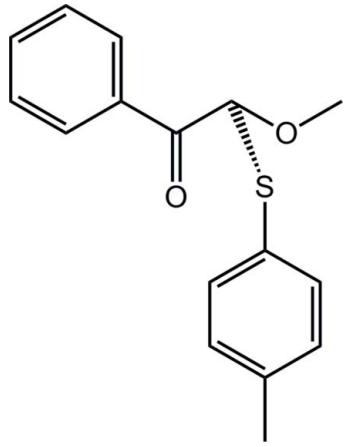
In the title β-thiocarbonyl compound, $C_{16}H_{16}O_2S$, the carbonyl and methoxy O atoms are approximately coplanar [O—C—C—O torsion angle = −18.2 (5)°] and *syn* to each other, and the tolyl ring is orientated to lie over them. The dihedral angle between the planes of the two rings is 44.03 (16)°. In the crystal, supramolecular chains are formed along the *c* axis mediated by C—H···O interactions involving methine and methyl H atoms as donors, with the carbonyl O atom accepting both bonds; these pack with no specific intermolecular interactions between them.

Keywords: crystal structure; β-thiocarbonyl; C—H···O interactions.

CCDC reference: 1035425

1. Related literature

For general background to β-thiocarbonyl and β-bis(thiocarbonyl) compounds, see: Vinhato *et al.* (2013); Zukerman-Schpector *et al.* (2008). For related structures, see: Olivato *et al.* (2013); Distefano *et al.* (1996). For further synthetic details, see: Ali & McDermott (2002); Zoretic & Soja (1976).



2. Experimental

2.1. Crystal data

$C_{16}H_{16}O_2S$
M_r = 272.35
Orthorhombic, $Pca2_1$
a = 17.8579 (9) Å
b = 8.1257 (4) Å
c = 9.8317 (5) Å
V = 1426.66 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.22 mm^{-1}
T = 293 K
0.41 × 0.14 × 0.08 mm

2.2. Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.690, T_{max} = 0.745
5399 measured reflections
2337 independent reflections
1648 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.090
S = 1.02
2337 reflections
174 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}
Absolute structure: Flack x determined using 552 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.02 (6)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1B···O2^{i}	0.96	2.49	3.366 (6)	152
C8—H8···O2^{ii}	0.98	2.46	3.323 (6)	146

Symmetry codes: (i) $-x+1, -y+2, z+\frac{1}{2}$; (ii) $-x+1, -y+2, z-\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SIR* (Burla *et al.*, 2014; program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *MarvinSketch* (ChemAxon, 2010) and *publCIF* (Westrip, 2010).

Acknowledgements

We thank Professor Regina H. A. Santos from IQSC–USP for the X-ray data collection. The Brazilian agencies CNPq (305626/2013-2 to JZS; 301180/2013-0 to PRO) and FAPESP are acknowledged for financial support.

Supporting information for this paper is available from the IUCr electronic archives (Reference: HG5421).

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supporting information

Acta Cryst. (2015). E**71**, o3–o4 [doi:10.1107/S205698901402550X]

Crystal structure of 2-methoxy-2-[(4-methylphenyl)sulfanyl]-1-phenylethan-1-one

Julio Zukerman-Schpector, Paulo R. Olivato, Henrique J. Traesel, Jéssica Valença, Daniel N. S. Rodrigues and Edward R. T. Tiekink

S1. Introduction

As part of our on-going research on the conformational and electronic interactions of some *β*-thio-carbonyl and *β*-bis-thio-carbonyl compounds, e.g. N,N-diethyl-2-[(4-substituted) phenylthio]acetamides, 1-methyl-3-phenylsulfonyl-2-piperidone, 3,3-bis[(4-substituted)phenylsulfanyl]-1-methyl-2-piperidones, 2-alkylthio-2-alkylsulfinyl-acetophenones, 2-alkylthio-2-phenylsulfonyl-acetophenones and 2-alkylsulfinyl-2-alkylsulfonyl-acetophenones, utilizing spectroscopic , theoretical and X-ray diffraction methods (Vinhato *et al.*, 2013; Zukerman-Schpector *et al.*, 2008; Olivato *et al.*, 2013; Distefano *et al.*, 1996) the title compound was synthesized and its crystal structure determined.

S2. Experimental

S2.1. Synthesis and crystallization

4-Methylthiopenol (5.0 g, 40 mmol) was reacted with bromine (1.1 ml, 20 mmol) in dichloromethane (250 mL) on hydrated silica gel support (25 g of SiO_2 and 12 mL of water) to give 4-methylphenyl disulfide (4.1 g, yield = 83%). A white solid was obtained after filtration and evaporation without further purification (Ali & McDermott, 2002). A solution of 2-methoxy acetophenone (0.4 mL, 2.76 mmol, Sigma-Aldrich) in THF (10 ml) was added drop wise to a cooled (195 K) solution of diisopropylamine (0.42 ml, 3.04 mmol) and butyllithium (2.0 ml, 2.76 mmol) in THF (10 ml). After 30 minutes, a solution of 4-methylphenyl disulfide (0.748 g, 3.04 mmol) with hexamethylphosphoramide (HMPA) (0.5 ml, 2.76 mmol) dissolved in THF (10 ml) was added drop wise to the enolate solution (Zoretic & Soja, 1976). After stirring for 3 h, water (50 ml) was added at room temperature and extraction with diethyl ether was performed. The organic layer was then treated with a saturated solution of ammonium chloride until neutral pH and dried over anhydrous magnesium sulfate. A brown oil was obtained after evaporation of the solvent. Purification through flash chromatography with n-hexane was used to remove the non-polar reactant (disulfide) then acetone to give a mixture of both aceto-phenones (product and reactant). Crystallization was performed by vapour diffusion of n-hexane into a chloroform solution held at 283 K to give pure product (0.3 g, yield = 40%). Suitable crystals for X-ray diffraction were obtained by same pathway; m.p. 359.3–359.8 K.

^{1}H NMR ($CDCl_3$, 500 MHz, ppm): *δ* 2.33 (s, 3*H*), 3.67 (s, 3*H*), 5.81 (s, 1*H*), 7.08–7.10 (m ,2*H*), 7.23-7.25 (m, 2*H*), 7.43–7.46(m, 2*H*),7.56–7.59 (m, 1*H*), 7.95–7.96 (m, 2*H*). HRMS: calcd. for $C_{16}H_{16}O_2S$ $[M + H]^+$ 272.0871; found: 272.0864.

S2.2. Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H = 0.93 to 0.98 Å) and were included in the refinement in the riding model approximation, with U_{iso}(H) = 1.2–1.5U_{eq}(C).

S3. Results and discussion

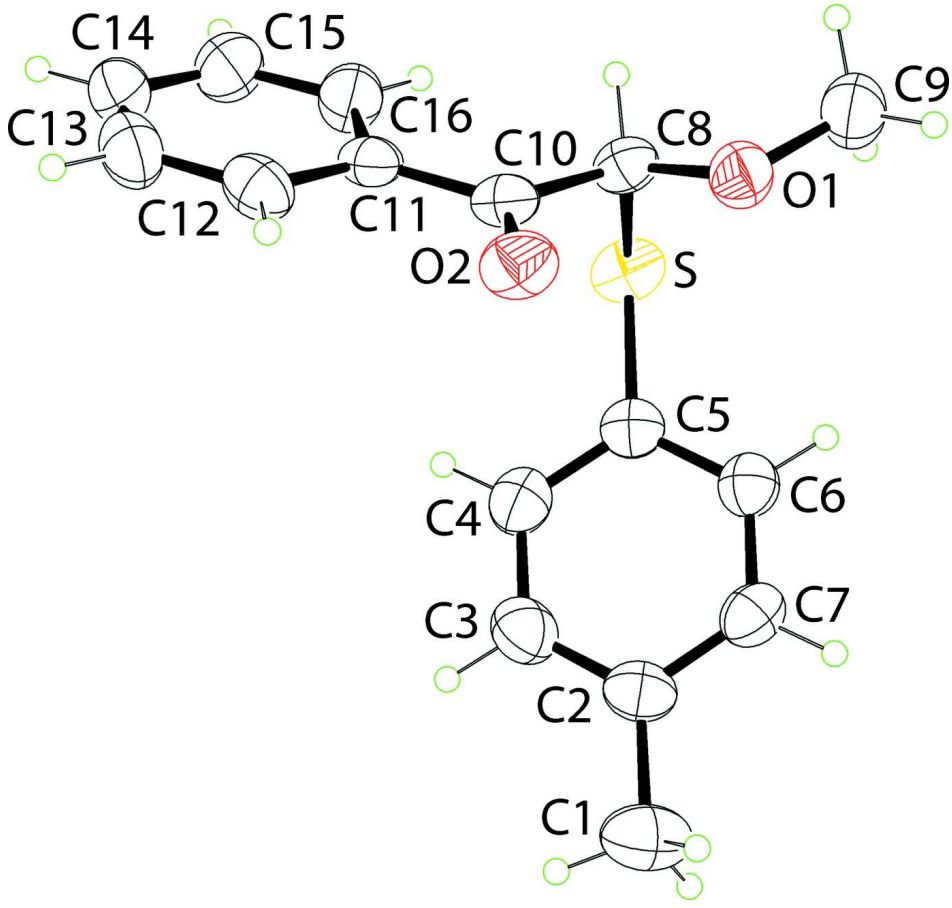

Figure 1

The molecular structure of the title compound showing the atom-labelling scheme and displacement ellipsoids at the 35% probability level.

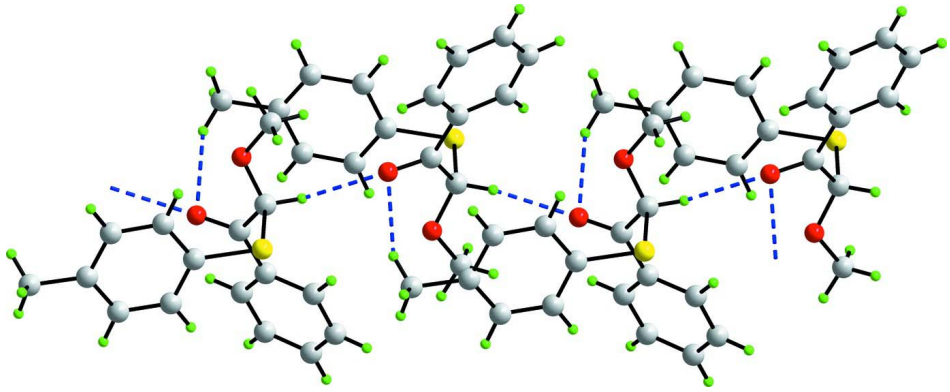

Figure 2

A view of the supramolecular chain along the *c* axis mediated by C—H···O interactions (bluee dashed lines).

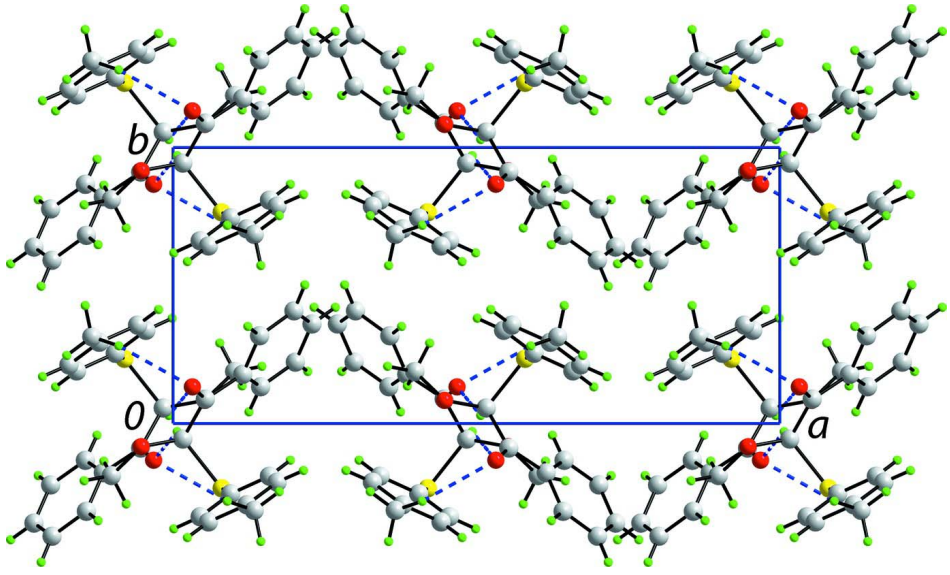

Figure 3

A view in projection down the *c* axis of the unit-cell contents. The C—H···O interactions are shown as blue dashed lines.

(I)

Crystal data

$C_{16}H_{16}O_2S$
$M_r = 272.35$
Orthorhombic, $Pca2_1$
$a = 17.8579\ (9)$ Å
$b = 8.1257\ (4)$ Å
$c = 9.8317\ (5)$ Å
$V = 1426.66\ (12)$ Å^3
$Z = 4$
$F(000) = 576$
$D_x = 1.268$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1023 reflections
$\theta = 3.1$–$18.7°$
$\mu = 0.22$ mm^{-1}
$T = 293$ K
Irregular, colourless
0.41 × 0.14 × 0.08 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.690, T_{max} = 0.745
5399 measured reflections
2337 independent reflections
1648 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 25.4°, θ_{min} = 2.8°
h = −21→21
k = −9→9
l = −10→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.090
S = 1.02
2337 reflections
174 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0294P)^2 + 0.2164P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}
Absolute structure: Flack x determined using 552 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.02 (6)

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.

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

	x	y	z	U_{iso}*/U_{eq}
C1	0.3662 (3)	0.6856 (7)	1.3764 (5)	0.0916 (18)
H1A	0.3249	0.7532	1.4046	0.137*
H1B	0.4106	0.7185	1.4243	0.137*
H1C	0.3553	0.5725	1.3964	0.137*
C2	0.3784 (3)	0.7055 (6)	1.2258 (5)	0.0642 (13)
C3	0.3285 (3)	0.7876 (6)	1.1440 (6)	0.0737 (14)
H3	0.2850	0.8300	1.1823	0.088*
C4	0.3411 (3)	0.8094 (6)	1.0061 (5)	0.0683 (13)
H4	0.3066	0.8670	0.9537	0.082*
C5	0.4049 (2)	0.7455 (5)	0.9462 (5)	0.0564 (11)
C6	0.4553 (2)	0.6622 (5)	1.0273 (5)	0.0615 (12)
H6	0.4987	0.6186	0.9893	0.074*
C7	0.4416 (3)	0.6434 (5)	1.1643 (5)	0.0635 (13)
H7	0.4763	0.5868	1.2171	0.076*
C8	0.4839 (2)	0.9437 (5)	0.7603 (5)	0.0576 (10)
H8	0.4930	0.9708	0.6646	0.069*
C9	0.6015 (3)	0.8116 (6)	0.7474 (6)	0.0834 (15)
H9A	0.6139	0.8637	0.6627	0.125*
H9B	0.5771	0.7085	0.7299	0.125*

H9C	0.6465	0.7927	0.7987	0.125*
C10	0.4468 (2)	1.0888 (5)	0.8275 (5)	0.0559 (11)
C11	0.3852 (2)	1.1782 (5)	0.7587 (5)	0.0539 (10)
C12	0.3573 (2)	1.3181 (5)	0.8205 (5)	0.0674 (13)
H12	0.3767	1.3519	0.9037	0.081*
C13	0.3007 (3)	1.4083 (5)	0.7595 (7)	0.0793 (14)
H13	0.2828	1.5027	0.8021	0.095*
C14	0.2709 (3)	1.3608 (6)	0.6381 (7)	0.0781 (14)
H14	0.2325	1.4212	0.5983	0.094*
C15	0.2984 (3)	1.2225 (7)	0.5754 (5)	0.0840 (16)
H15	0.2780	1.1887	0.4930	0.101*
C16	0.3556 (3)	1.1333 (6)	0.6325 (5)	0.0736 (13)
H16	0.3748	1.0423	0.5868	0.088*
O1	0.55239 (15)	0.9162 (4)	0.8235 (3)	0.0666 (9)
O2	0.46803 (18)	1.1328 (4)	0.9400 (3)	0.0727 (9)
S	0.41986 (7)	0.76542 (13)	0.76791 (16)	0.0711 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.090 (4)	0.115 (5)	0.070 (4)	−0.030 (3)	0.006 (3)	0.005 (3)
C2	0.065 (3)	0.064 (3)	0.064 (4)	−0.020 (2)	0.006 (3)	0.000 (3)
C3	0.061 (3)	0.077 (3)	0.084 (4)	−0.004 (3)	0.011 (3)	0.002 (3)
C4	0.064 (3)	0.064 (3)	0.077 (4)	−0.001 (2)	−0.007 (3)	0.006 (3)
C5	0.061 (3)	0.048 (2)	0.060 (3)	−0.011 (2)	−0.001 (2)	−0.003 (2)
C6	0.061 (3)	0.056 (3)	0.067 (3)	0.000 (2)	−0.001 (2)	−0.001 (3)
C7	0.066 (3)	0.058 (3)	0.066 (4)	−0.006 (2)	−0.008 (3)	0.009 (3)
C8	0.070 (3)	0.058 (2)	0.045 (2)	−0.0025 (19)	−0.003 (3)	0.003 (3)
C9	0.084 (3)	0.095 (3)	0.072 (4)	0.024 (3)	−0.003 (3)	0.000 (4)
C10	0.070 (3)	0.052 (3)	0.046 (3)	−0.009 (2)	0.007 (2)	0.002 (2)
C11	0.061 (2)	0.051 (2)	0.049 (3)	−0.0077 (18)	0.012 (3)	0.003 (3)
C12	0.066 (3)	0.065 (3)	0.071 (3)	−0.009 (2)	0.012 (3)	−0.013 (3)
C13	0.069 (3)	0.065 (3)	0.104 (4)	0.006 (2)	0.013 (4)	−0.008 (4)
C14	0.064 (3)	0.077 (3)	0.094 (4)	0.009 (3)	0.013 (3)	0.013 (3)
C15	0.085 (3)	0.102 (4)	0.065 (4)	0.014 (3)	−0.011 (3)	0.010 (3)
C16	0.090 (3)	0.078 (3)	0.053 (3)	0.017 (3)	−0.004 (3)	−0.007 (3)
O1	0.0665 (18)	0.077 (2)	0.057 (2)	0.0086 (16)	−0.0038 (16)	−0.0012 (16)
O2	0.094 (2)	0.076 (2)	0.048 (2)	−0.0017 (17)	−0.0047 (18)	−0.0078 (19)
S	0.0948 (8)	0.0600 (6)	0.0583 (7)	−0.0129 (6)	−0.0079 (8)	−0.0055 (8)

Geometric parameters (Å, º)

C1—C2	1.505 (7)	C8—H8	0.9800
C1—H1A	0.9600	C9—O1	1.432 (5)
C1—H1B	0.9600	C9—H9A	0.9600
C1—H1C	0.9600	C9—H9B	0.9600
C2—C3	1.373 (7)	C9—H9C	0.9600
C2—C7	1.376 (6)	C10—O2	1.224 (5)

C3—C4	1.385 (7)	C10—C11	1.480 (6)
C3—H3	0.9300	C11—C12	1.382 (6)
C4—C5	1.383 (6)	C11—C16	1.398 (7)
C4—H4	0.9300	C12—C13	1.384 (6)
C5—C6	1.379 (6)	C12—H12	0.9300
C5—S	1.781 (5)	C13—C14	1.363 (8)
C6—C7	1.378 (6)	C13—H13	0.9300
C6—H6	0.9300	C14—C15	1.373 (6)
C7—H7	0.9300	C14—H14	0.9300
C8—O1	1.390 (4)	C15—C16	1.372 (6)
C8—C10	1.505 (5)	C15—H15	0.9300
C8—S	1.847 (4)	C16—H16	0.9300
C2—C1—H1A	109.5	O1—C9—H9A	109.5
C2—C1—H1B	109.5	O1—C9—H9B	109.5
H1A—C1—H1B	109.5	H9A—C9—H9B	109.5
C2—C1—H1C	109.5	O1—C9—H9C	109.5
H1A—C1—H1C	109.5	H9A—C9—H9C	109.5
H1B—C1—H1C	109.5	H9B—C9—H9C	109.5
C3—C2—C7	116.9 (5)	O2—C10—C11	120.0 (4)
C3—C2—C1	122.3 (5)	O2—C10—C8	119.2 (4)
C7—C2—C1	120.8 (5)	C11—C10—C8	120.7 (4)
C2—C3—C4	122.0 (5)	C12—C11—C16	117.9 (4)
C2—C3—H3	119.0	C12—C11—C10	118.1 (4)
C4—C3—H3	119.0	C16—C11—C10	123.9 (4)
C5—C4—C3	120.2 (5)	C11—C12—C13	120.6 (5)
C5—C4—H4	119.9	C11—C12—H12	119.7
C3—C4—H4	119.9	C13—C12—H12	119.7
C6—C5—C4	118.4 (5)	C14—C13—C12	120.9 (5)
C6—C5—S	121.0 (4)	C14—C13—H13	119.5
C4—C5—S	120.6 (4)	C12—C13—H13	119.5
C7—C6—C5	120.2 (5)	C13—C14—C15	119.0 (5)
C7—C6—H6	119.9	C13—C14—H14	120.5
C5—C6—H6	119.9	C15—C14—H14	120.5
C2—C7—C6	122.3 (5)	C16—C15—C14	121.0 (5)
C2—C7—H7	118.8	C16—C15—H15	119.5
C6—C7—H7	118.8	C14—C15—H15	119.5
O1—C8—C10	108.5 (4)	C15—C16—C11	120.4 (5)
O1—C8—S	113.6 (3)	C15—C16—H16	119.8
C10—C8—S	108.9 (3)	C11—C16—H16	119.8
O1—C8—H8	108.6	C8—O1—C9	113.7 (3)
C10—C8—H8	108.6	C5—S—C8	101.8 (2)
S—C8—H8	108.6		
C7—C2—C3—C4	−0.8 (7)	O2—C10—C11—C16	−177.7 (4)
C1—C2—C3—C4	178.2 (4)	C8—C10—C11—C16	2.3 (6)
C2—C3—C4—C5	1.0 (7)	C16—C11—C12—C13	1.2 (6)
C3—C4—C5—C6	−0.7 (6)	C10—C11—C12—C13	178.7 (4)

C3—C4—C5—S	177.5 (4)	C11—C12—C13—C14	0.5 (7)
C4—C5—C6—C7	0.3 (6)	C12—C13—C14—C15	−0.8 (7)
S—C5—C6—C7	−177.9 (4)	C13—C14—C15—C16	−0.6 (8)
C3—C2—C7—C6	0.3 (7)	C14—C15—C16—C11	2.4 (8)
C1—C2—C7—C6	−178.7 (4)	C12—C11—C16—C15	−2.7 (7)
C5—C6—C7—C2	0.0 (7)	C10—C11—C16—C15	180.0 (4)
O1—C8—C10—O2	−18.2 (5)	C10—C8—O1—C9	−164.3 (3)
S—C8—C10—O2	105.9 (4)	S—C8—O1—C9	74.4 (4)
O1—C8—C10—C11	161.7 (3)	C6—C5—S—C8	−83.1 (4)
S—C8—C10—C11	−74.1 (4)	C4—C5—S—C8	98.8 (4)
O2—C10—C11—C12	4.9 (6)	O1—C8—S—C5	63.2 (4)
C8—C10—C11—C12	−175.0 (4)	C10—C8—S—C5	−57.9 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*B*···O2^{i}	0.96	2.49	3.366 (6)	152
C8—H8···O2^{ii}	0.98	2.46	3.323 (6)	146

Symmetry codes: (i) −*x*+1, −*y*+2, *z*+1/2; (ii) −*x*+1, −*y*+2, *z*−1/2.