



## 2-[(4-Chlorophenyl)sulfanyl]-2-methoxy-1-phenylethan-1-one: crystal structure and Hirshfeld surface analysis

**Ignéz Caracelli, Julio Zukerman-Schpector, Henrique J. Traesel, Paulo R. Olivato, Mukesh M. Jotani and Edward R. T. Tiekink**

*Acta Cryst.* (2018). **E74**, 703–708



**IUCr Journals**

CRYSTALLOGRAPHY JOURNALS ONLINE

This open-access article is distributed under the terms of the Creative Commons Attribution Licence <http://creativecommons.org/licenses/by/2.0/uk/legalcode>, which permits unrestricted use, distribution, and reproduction in any medium, provided the original authors and source are cited.





# 2-[(4-Chlorophenyl)sulfanyl]-2-methoxy-1-phenyl-ethan-1-one: crystal structure and Hirshfeld surface analysis

Ignez Caracelli,<sup>a</sup> Julio Zukerman-Schpector,<sup>b\*</sup> Henrique J. Traesel,<sup>c</sup> Paulo R. Olivato,<sup>c</sup> Mukesh M. Jotani<sup>d</sup> and Edward R. T. Tiekink<sup>e‡</sup>

Received 17 April 2018

Accepted 20 April 2018

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

‡ Additional correspondence author, e-mail: edwardt@sunway.edu.my.

**Keywords:** crystal structure; sulfanyl; phenyl-ethanone; Hirshfeld surface analysis; NCI plots.

**CCDC reference:** 1838590

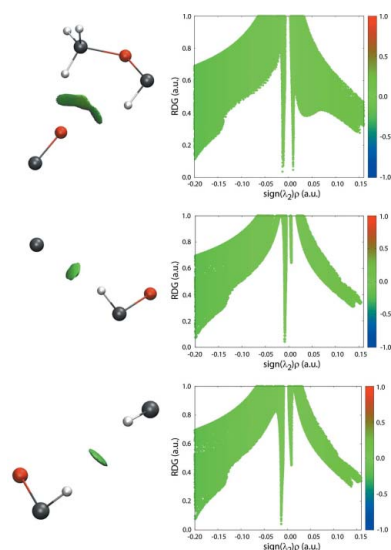
**Supporting information:** this article has supporting information at journals.iucr.org/e

<sup>a</sup>Departamento de Física, Universidade Federal de São Carlos, 13565-905 São Carlos, SP, Brazil, <sup>b</sup>Departamento de Química, Universidade Federal de São Carlos, 13565-905 São Carlos, SP, Brazil, <sup>c</sup>Instituto de Química, Universidade de São Paulo, 05508-000 São Paulo, SP, Brazil, <sup>d</sup>Department of Physics, Bhavan's Sheth R. A. College of Science, Ahmedabad, Gujarat 380001, India, and <sup>e</sup>Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia. \*Correspondence e-mail: julio@power.ufscar.br

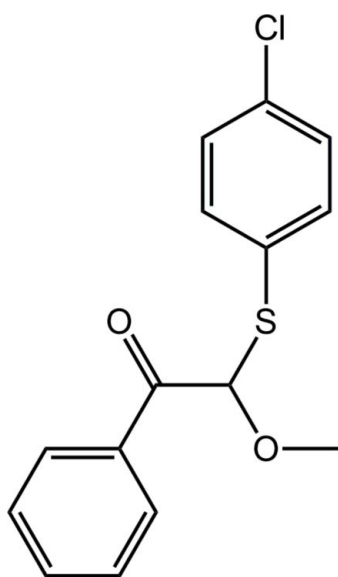
The title compound, C<sub>15</sub>H<sub>13</sub>ClO<sub>2</sub>S, comprises (4-chlorophenyl)sulfanyl, benzaldehyde and methoxy residues linked at a chiral methine-C atom (the crystal is racemic). A twist in the methine-C—C(carbonyl) bond [O—C—C—O torsion angle = 19.3 (7)°] leads to a dihedral angle of 22.2 (5)° between the benzaldehyde and methine+methoxy residues. The chlorobenzene ring is folded to lie over the O atoms, with the dihedral angle between the benzene rings being 42.9 (2)°. In the crystal, the carbonyl-O atom accepts two C—H...O interactions with methyl- and methine-C—H atoms being the donors. The result is an helical supramolecular chain aligned along the *c* axis; chains pack with no directional interactions between them. An analysis of the Hirshfeld surface points to the important contributions of weak H...H and C...C contacts to the molecular packing.

## 1. Chemical context

As part of our ongoing studies on the conformational and electronic characteristics of some  $\beta$ -thiocarbonyl,  $\beta$ -bis-thiocarbonyl and  $\beta$ -thio- $\beta$ -oxacarbonyl compounds, *e.g.* *N,N*-diethyl-2-[(4'-substituted)phenylthio]acetamides (Vinhato *et al.*, 2013), 1-methyl-3-phenylsulfonyl-2-piperidones (Zukerman-Schpector *et al.*, 2008), 3,3-bis[(4'-substituted) phenylsulfanyl]-1-methyl-2-piperidones (Olivato *et al.*, 2013), 2-alkylthio-2-alkylsulfanyl-acetophenones and 2-alkylthio-2-phenylsulfonyl-acetophenones, 2-alkylsulfanyl-2-alkylsulfonyl-acetophenones (Distefano *et al.*, 1996), 2-methoxy-2-[(4'-substituted) phenylsulfanyl]-acetophenones (Zukerman-Schpector *et al.*, 2015; Caracelli *et al.*, 2015) and 2-methoxy-2-(phenylselenanyl)-(4'-substituted)acetophenones (Traesel *et al.*, 2018), utilizing infrared spectroscopy, computational chemistry and X-ray diffraction methods, the title compound (I) was synthesized and characterized. The primary motivation behind this work is the search for selenium/sulfur-containing compounds with anti-inflammatory activity that could be selective COX-2 inhibitors (Cerqueira *et al.*, 2015, 2017). Molecular docking studies have also been conducted in order to understand the mechanism of inhibition (Baptistini, 2015). Herein, the crystal and molecular structures of (I) are described along with an analysis of the calculated Hirshfeld surfaces and non-covalent interaction plots for selected interactions.

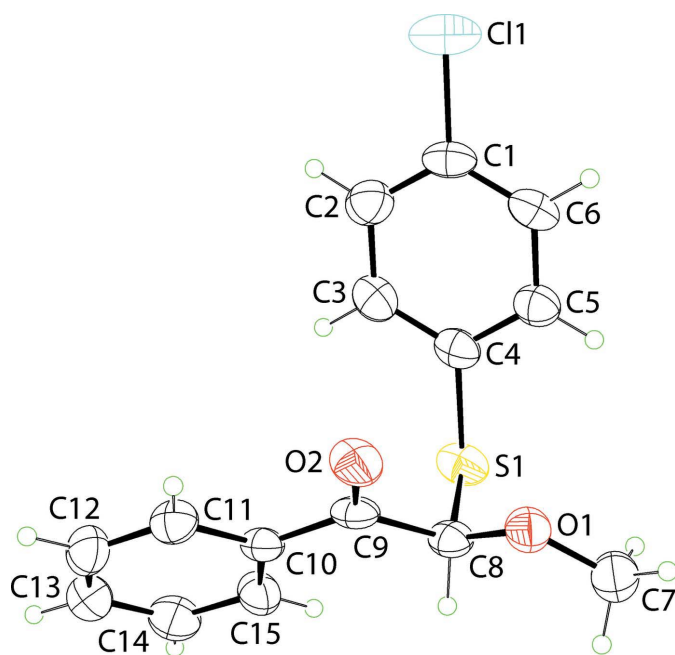


OPEN ACCESS



## 2. Structural commentary

The molecular structure of (I) sees (4-chlorophenyl)sulfanyl, phenylethanone and methoxy groups linked at the chiral methine-C8 atom, Fig. 1. In the arbitrarily chosen asymmetric molecule, C8 has an *R* configuration, but crystal symmetry generates a racemic mixture. The base of the molecule is defined by the phenylethanone [r.m.s. deviation of the eight non-hydrogen atoms = 0.0134 Å] and methoxy groups. These residues are not co-planar, with the dihedral angle between



**Figure 1**

The molecular structure of (I), showing the atom-labelling scheme and displacement ellipsoids at the 35% probability level.

**Table 1**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C7—H7A...O2 <sup>i</sup>	0.96	2.53	3.297 (9)	137
C8—H8...O2 <sup>i</sup>	0.98	2.42	3.305 (8)	150

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

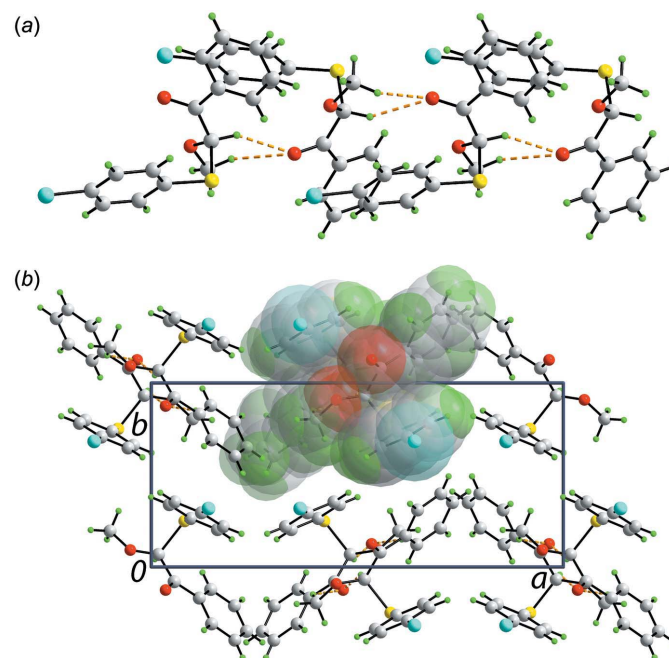
the two planes being 22.2 (5)° owing to the twist about the C8—C9 bond as seen in the value of the O1—C8—C9—O2 torsion angle of 19.3 (7)°. The 4-chlorophenyl group is orientated so that the ring lies over the oxygen atoms with the dihedral angle between the benzene rings being 42.9 (2)°.

## 3. Supramolecular features

The molecular packing of (I) features C—H...O interactions where the donors are methyl-C7 and methine-C8 H atoms, and the acceptor is the carbonyl-O2 atom, Table 1. These interactions combine to sustain a supramolecular chain along [001] with an helical topology as it is propagated by 2<sub>1</sub> symmetry, Fig. 2*a*. Chains assemble into the three-dimensional architecture without directional interactions between them, Fig. 2*b*.

## 4. Hirshfeld surface analysis

The Hirshfeld surface calculations for (I) were performed as per a recent study (Zukerman-Schpector *et al.*, 2017) and serve to provide additional information on the molecular packing, in



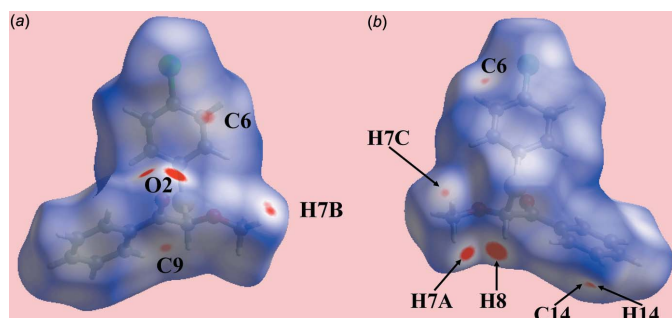
**Figure 2**

Molecular packing in (I): (a) view of the supramolecular chain parallel to the *c* axis and (b) view of the unit-cell contents shown in projection down the *b* axis; one chain is highlighted in space-filling mode. The C—H...O contacts are shown as orange dashed lines.

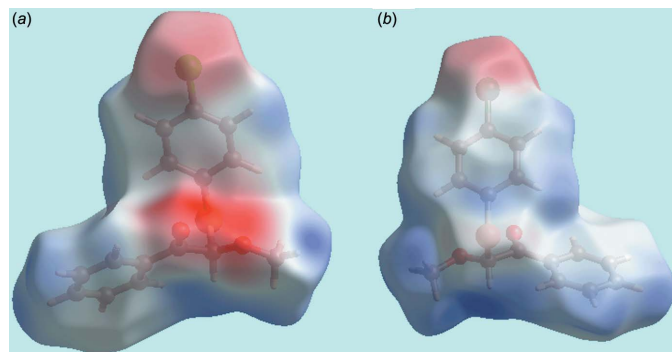
**Table 2**  
Summary of short interatomic contacts (Å) in (I).

Contact	Distance	Symmetry operation
H7B...H14	2.10	$1 - x, -y, \frac{1}{2} + z$
H7B...C14	2.76	$1 - x, -y, \frac{1}{2} + z$
H7C...C6	2.73	$1 - x, 1 - y, \frac{1}{2} + z$
C6...C9	3.33	$1 - x, -y, \frac{1}{2} + z$

particular the weaker interactions between molecules. In addition to bright-red spots near the methyl-H7A and methine-H8 atoms, a pair near the carbonyl-O2 atom arise as a result of the C—H...O interactions leading to the supra-molecular chain discussed above, Table 1. The presence of diminutive and faint-red spots on the Hirshfeld surfaces illustrated in Fig. 3 indicate the influence of short interatomic contacts on the molecular packing in the crystal, Table 2. Thus, the C...C and C...H/H...C contacts involving chlorobenzene-C6, carbonyl-C9 and methyl-H7C atoms are viewed as the pair of diminutive and faint-red spots near these atoms in Fig. 3, whereas similar features near the methyl-H7B, phenyl-C14 and -H14 atoms represent H7B...H14 and C...H/H...C contacts. Views of the Hirshfeld surfaces mapped over electrostatic potential are shown in Fig. 4 and also indicate the donors and acceptors of the C—H...O interactions through the appearance of intense-blue and -red regions around the



**Figure 3**  
Two views of the Hirshfeld surface for (I) mapped over  $d_{\text{norm}}$  in the range  $-0.073$  to  $+1.389$  au.



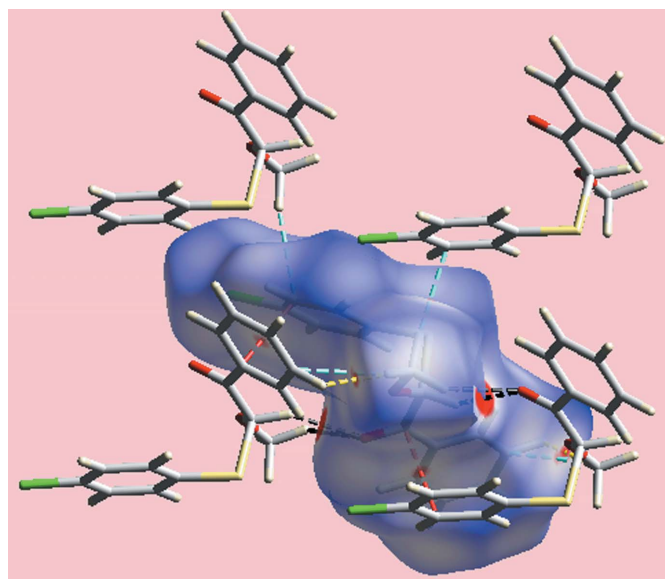
**Figure 4**  
Two views of the Hirshfeld surfaces mapped over the electrostatic potential in the range  $-0.073$  to  $+0.056$  au. The red and blue regions represent negative and positive electrostatic potentials, respectively.

**Table 3**  
Percentage contributions of interatomic contacts to the Hirshfeld surface for (I).

Contact	Percentage contribution
H...H	39.3
C...H/H...C	23.2
Cl...H/H...Cl	12.8
O...H/H...O	11.0
S...H/H...S	4.4
Cl...S/S...Cl	2.1
Cl...O/O...Cl	2.1
C...O/O...C	1.5
C...Cl/Cl...C	1.5
C...S/S...C	1.2
C...C	0.6

participating atoms. Fig. 5 illustrates the environment around a reference molecule within the  $d_{\text{norm}}$ -mapped Hirshfeld surface and highlight the intermolecular C—H...O interactions and short interatomic H...H, C...H/H...C and C...C contacts.

The non-symmetric molecular geometry in (I) results in an asymmetric distribution of points in its overall two-dimensional fingerprint plot shown in Fig. 6 and also in those delineated into H...H, C...H/H...C, Cl...H/H...Cl, O...H/H...O and C...C contacts (McKinnon *et al.*, 2007), also illustrated in Fig. 6. The major percentage contributions to the Hirshfeld surface are from (in descending order) H...H, C...H/H...C, Cl...H/H...Cl, O...H/H...O and S...H/H...S contacts along with a small, *i.e.* 0.6%, contribution from C...C contacts as summarized in Table 3. These interactions result in distinctive features in their respective delineated fingerprint plots. The short interatomic H...H and C...H/H...C contacts are characterized as a pair of beak-shape tips at  $d_e + d_i \sim 2.1$  Å



**Figure 5**  
A view of the Hirshfeld surface mapped over  $d_{\text{norm}}$  in the range  $-0.073$  to  $+1.389$  au highlighting intermolecular C—H...O, C...C, H...H and C...H/H...C contacts by black, red, yellow and sky-blue dashed lines, respectively.



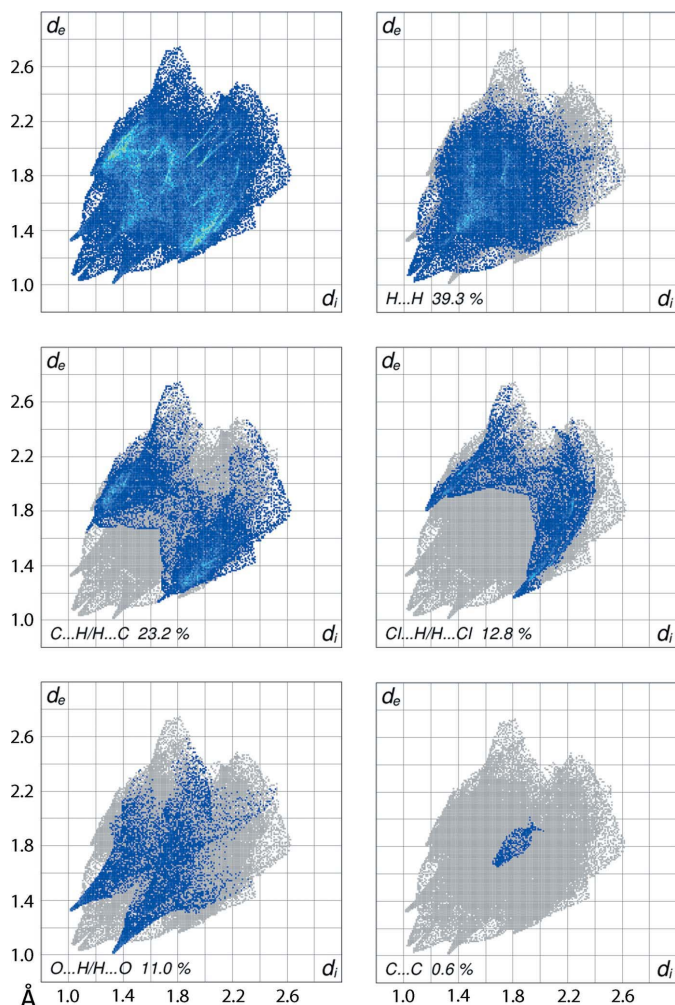


Figure 6

The full two-dimensional fingerprint plot for (I) and those delineated into H...H, C...H/H...C, Cl...H/H...Cl, O...H/H...O and C...C contacts.

and the pair of parabolic distributions of points at around  $d_e + d_i < 2.8$  Å in their respective delineated fingerprint plots. The short interatomic C...H/H...C contacts in the crystal, Table 2, appear as a pair of thin tips at  $d_e + d_i \sim 2.7$  Å attached to the aforementioned parabolic distribution. The interatomic Cl...H/H...Cl contacts, making the next most significant contribution to the Hirshfeld surface, *i.e.* 12.8%, are at van der Waals separations. The C—H...O contacts, involving the carbonyl-O2 with methyl-C7 H and methine-C8 H atoms, Table 1, are evident as a pair of spikes with tips at  $d_e + d_i \sim 2.3$  Å. The vase-shaped distribution of points beginning at  $d_e + d_i \sim 3.3$  Å in the fingerprint plot delineated into C...C contacts results from the contacts highlighted in Fig. 5 and Table 2. The small contribution from other remaining interatomic contacts summarized in Table 3 have a negligible influence upon the molecular packing.

## 5. Non-covalent interaction plots

Non-covalent interaction plots are a convenient means by which the nature of a specified intermolecular interaction may

be assessed in terms of it being attractive or otherwise (Johnson *et al.*, 2010; Contreras-García *et al.*, 2011). If a specified interaction is attractive, the isosurface will be blue in appearance whereas a repulsive interaction will result in a red isosurface. On the other hand, a weakly attractive interaction will appear green. The isosurfaces for the interactions between the methyl-C7 and methine-C H atoms and the carbonyl-O2 atom are shown in Fig. 7a, clearly indicating their weakly attractive nature. Similarly, the interactions between the chlorobenzene-C6 and methyl-H7C atoms, Fig. 7b, and between the methyl-H7B and phenyl-H14 atoms, Fig. 7c, are weakly attractive.

## 6. Database survey

There are two closely related literature precedents for (I), namely the S-bound 4-methoxybenzene [(II); Caracelli *et al.*, 2015] and 4-tolyl [(III); Zukerman-Schpector *et al.*, 2015] derivatives. The three compounds crystallize in the same *Pca*2<sub>1</sub> space group and present similar unit-cell dimensions. An

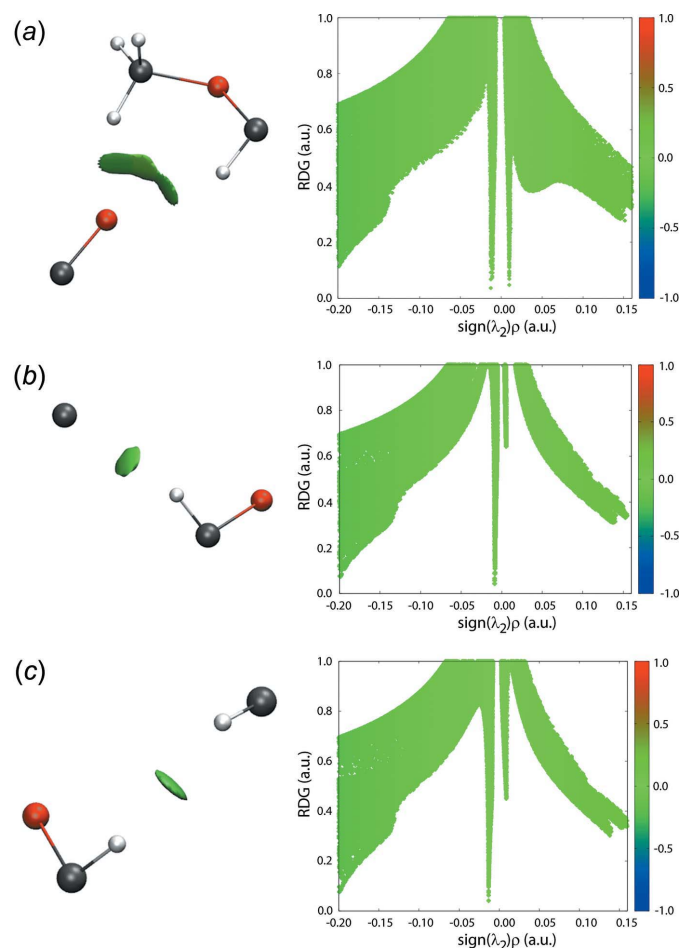
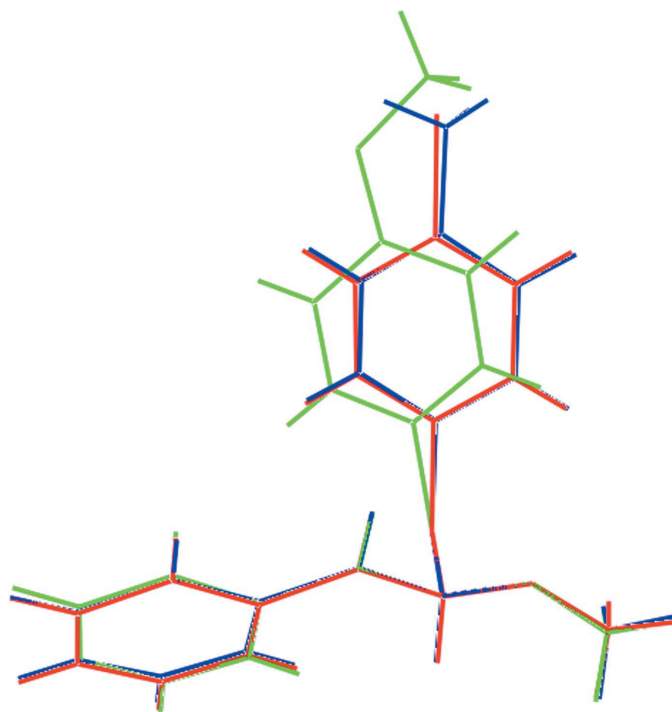


Figure 7

Non-covalent interaction plots for intermolecular interactions between (a) methyl-C7- and methine-C—H atoms, and the carbonyl-O2 atom, (b) chlorobenzene-C6 and methyl-H7C atoms and (c) methyl-H7B and phenyl-H14 atoms.



**Figure 8**  
Overlay diagram of (a) (I), red image, (b) (II), green and (c) (III), blue.

overlay diagram for (I)–(III) is shown in Fig. 8 from which it can be noted there is a high degree of concordance for (I) and (III). The molecule in (II) is coincident with (I) and (III) except for the relative disposition of the S-bound methoxybenzene ring. This difference arises as a result of a twist about the C8–S1 bond as seen in the C4–S1–C8–C9 torsion angles of 57.3 (5), 46.6 (3) and 57.9 (3)° for (I)–(III), respectively. Despite this difference, the angles between the S-bound benzene rings and the phenyl rings in (I)–(III) are relatively constant at 42.9 (2), 40.11 (16) and 44.03 (16)°, respectively.

## 7. Synthesis and crystallization

The 4'-chlorophenyl disulfide precursor was prepared as previously described (Ali & McDermott, 2002) through the oxidation of 4'-chlorothiophenol by bromine. A solution of 2-methoxy acetophenone (0.70 ml, 5.08 mmol, Sigma–Aldrich) in THF (15 ml), was added dropwise to a cooled (195 K) solution of diisopropylamine (0.78 ml, 5.59 mmol) and *n*-butyllithium (3.76 ml, 5.08 mmol) in THF (25 ml). After 30 min., a solution of 4'-chlorophenyl disulfide (1.61 g, 5.08 mmol) with hexamethylphosphoramide (HMPA) (0.90 ml, *ca* 5.08 mmol) dissolved in THF (15 ml) was added dropwise 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 solvent. Purification through flash chromatography with *n*-hexane was used in order to remove the non-polar reactant

**Table 4**  
Experimental details.

Crystal data	
Chemical formula	C <sub>15</sub> H <sub>13</sub> ClO <sub>2</sub> S
<i>M<sub>r</sub></i>	292.76
Crystal system, space group	Orthorhombic, <i>Pca</i> 2 <sub>1</sub>
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	17.964 (3), 8.0234 (15), 9.7761 (19)
<i>V</i> (Å <sup>3</sup> )	1409.0 (5)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
<i>μ</i> (mm <sup>−1</sup> )	0.41
Crystal size (mm)	0.42 × 0.21 × 0.12
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Sheldrick, 1996)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.365, 0.745
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	5010, 2081, 1505
<i>R<sub>int</sub></i>	0.049
(sin θ/λ) <sub>max</sub> (Å <sup>−1</sup> )	0.594
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.048, 0.116, 1.04
No. of reflections	2081
No. of parameters	173
No. of restraints	1
H-atom treatment	H-atom parameters constrained
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>−3</sup> )	0.28, −0.18
Absolute structure	Flack <i>x</i> determined using 465 quotients [( <i>I</i> <sup>+</sup> ) − ( <i>I</i> <sup>−</sup> )]/[( <i>I</i> <sup>+</sup> ) + ( <i>I</i> <sup>−</sup> )] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.06 (9)

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SIR2014* (Burla *et al.*, 2015), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *DIAMOND* (Brandenburg, 2006), *MarvinSketch* (ChemAxon, 2010) and *publCIF* (Westrip, 2010).

(disulfide), then with dry acetone to give a mixture of both acetophenones (product and reactant). Crystallization was performed by vapour diffusion of *n*-hexane into a chloroform solution held at 283 K to give pure product (0.4 g, yield = 60%). Irregular colourless crystals for X-ray diffraction of (I) were obtained by the same pathway. M.p. 358.2–358.8 K. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ ppm): 3.67 (s, 3H), 5.86 (s, 1H), 7.24–7.29 (m, 4H), 7.44–7.47 (m, 2H), 7.57–7.60 (m, 1H), 7.93–7.95 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, δ p.p.m.): 190.20, 135.60, 135.25, 134.23, 133.55, 129.22, 128.84, 128.59, 89.37, 56.13. Microanalysis calculated for C<sub>15</sub>H<sub>13</sub>ClO<sub>2</sub>S (%): C 61.53, H 4.48. Found (%): C 61.47, H 4.55. High-resolution MS [*M*<sup>+</sup>, *M*<sup>2+</sup>] calculated: 292.0325, 294.0295; found: 292.0324, 294.0296.

## 8. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 4. The carbon-bound H atoms were placed in calculated positions (C–H = 0.93–0.98 Å) and were included in the refinement in the riding-model approximation, with *U*<sub>iso</sub>(H) set to 1.2–1.5*U*<sub>eq</sub>(C).

## Funding information

The Brazilian agency the São Paulo Research Foundation (FAPESP) is thanked for financial support of this research, the

Coordination for the Improvement of Higher Education Personnel for a scholarship (CAPES 3300201191P0 to HJT) and the National Council for Scientific and Technological Development for fellowships (CNPq: 308480/2016–3 to IC; 303207/2017–5 to JZ-S; 301180/2013–0 to PRO). Funding for this research was provided by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (awards No. 457255/2014–5 and 301180/2013–0).

## References

- Ali, M. H. & McDermott, M. (2002). *Tetrahedron Lett.* **43**, 6271–6273.
- Baptistini, N. (2015). Ph. D. Thesis, Federal University of São Carlos, São Carlos, Brazil. available online at: <https://repositorio.ufscar.br/handle/ufscar/7554>.
- Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Bruker (2009). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Burla, M. C., Caliendo, R., Carrozzini, B., Cascarano, G. L., Cuocci, C., Giacovazzo, C., Mallamo, M., Mazzzone, A. & Polidori, G. (2015). *J. Appl. Cryst.* **48**, 306–309.
- Caracelli, I., Olivato, P. R., Traesel, H. J., Valença, J., Rodrigues, D. N. S. & Tiekink, E. R. T. (2015). *Acta Cryst. E* **71**, o657–o658.
- Cerqueira, C. R., Olivato, P. R. & Dal Colle, M. (2015). *Spectrochim. Acta A*, **139**, 495–504.
- Cerqueira, C. R., Olivato, P. R., Rodrigues, D. N. S., Zukerman-Schpector, J., Tiekink, E. R. T. & Dal Colle, M. (2017). *J. Mol. Struct.* **1133**, 49–65.
- ChemAxon (2010). *Marvinsketch*. <http://www.chemaxon.com>.
- Contreras-García, J., Johnson, E. R., Keinan, S., Chaudret, R., Piquemal, J.-P., Beratan, D. N. & Yang, W. (2011). *J. Chem. Theory Comput.* **7**, 625–632.
- Distefano, G., Dal Colle, M., de Palo, M., Jones, D., Bombieri, G., Del Pra, A., Olivato, P. R. & Mondino, M. (1996). *J. Chem. Soc. Perkin Trans. 2*, pp. 1661–1669.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Johnson, E. R., Keinan, S., Mori-Sánchez, P., Contreras-García, J., Cohen, A. J. & Yang, W. (2010). *J. Am. Chem. Soc.* **132**, 6498–6506.
- McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.
- Olivato, P. R., Cerqueira, C. Jr, Contieri, B., Santos, J. M. M. & Zukerman-Schpector, J. (2013). *J. Sulfur Chem.* **34**, 617–626.
- Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst. B* **69**, 249–259.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2015). *Acta Cryst. C* **71**, 3–8.
- Traesel, H. J., Olivato, P. R., Valença, J., Rodrigues, D. N. S., Zukerman-Schpector, J. & Colle, M. D. (2018). *J. Mol. Struct.* **1157**, 29–39.
- Vinhato, E., Olivato, P. R., Zukerman-Schpector, J. & Dal Colle, M. (2013). *Spectrochim. Acta Part A*, **115**, 738–746.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Zoretic, P. A. & Soja, P. (1976). *J. Org. Chem.* **41**, 3587–3589.
- Zukerman-Schpector, J., Olivato, P. R., Cerqueira, C. R. Jr, Vinhato, E. & Tiekink, E. R. T. (2008). *Acta Cryst. E* **64**, o835–o836.
- Zukerman-Schpector, J., Olivato, P. R., Traesel, H. J., Valença, J., Rodrigues, D. N. S. & Tiekink, E. R. T. (2015). *Acta Cryst. E* **71**, o3–o4.
- Zukerman-Schpector, J., Sugiyama, F. H., Garcia, A. L. L., Correia, C. R. D., Jotani, M. M. & Tiekink, E. R. T. (2017). *Acta Cryst. E* **73**, 1218–1222.

## supporting information

*Acta Cryst.* (2018). E74, 703-708 [https://doi.org/10.1107/S2056989018006072]

## 2-[(4-Chlorophenyl)sulfanyl]-2-methoxy-1-phenylethan-1-one: crystal structure and Hirshfeld surface analysis

**Ignez Caracelli, Julio Zukerman-Schpector, Henrique J. Traesel, Paulo R. Olivato, Mukesh M. Jotani and Edward R. T. Tiekink**

### Computing details

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT* (Bruker, 2009); program(s) used to solve structure: *SIR2014* (Burla *et al.*, 2015); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); 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).

### 2-[(4-Chlorophenyl)sulfanyl]-2-methoxy-1-phenylethan-1-one

#### Crystal data

C<sub>15</sub>H<sub>13</sub>ClO<sub>2</sub>S

$M_r = 292.76$

Orthorhombic, *Pca*2<sub>1</sub>

$a = 17.964$  (3) Å

$b = 8.0234$  (15) Å

$c = 9.7761$  (19) Å

$V = 1409.0$  (5) Å<sup>3</sup>

$Z = 4$

$F(000) = 608$

$D_x = 1.380$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 1839 reflections

$\theta = 2.5\text{--}23.7^\circ$

$\mu = 0.41$  mm<sup>-1</sup>

$T = 293$  K

Irregular, colourless

$0.42 \times 0.21 \times 0.12$  mm

#### Data collection

Bruker APEXII CCD

diffractometer

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.365$ ,  $T_{\max} = 0.745$

5010 measured reflections

2081 independent reflections

1505 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.049$

$\theta_{\max} = 25.0^\circ$ ,  $\theta_{\min} = 2.3^\circ$

$h = -20 \rightarrow 21$

$k = -7 \rightarrow 9$

$l = -11 \rightarrow 8$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.048$

$wR(F^2) = 0.116$

$S = 1.04$

2081 reflections

173 parameters

1 restraint

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.043P)^2 + 0.3264P]$

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

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

$\Delta\rho_{\max} = 0.28$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.18$  e Å<sup>-3</sup>

Absolute structure: Flack  $x$  determined using

465 quotients  $[(I^+) - (I^-)] / [(I^+) + (I^-)]$  (Parsons *et al.*, 2013)

Absolute structure parameter: 0.06 (9)



*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.36121 (11)	0.3177 (3)	1.0687 (2)	0.0916 (7)
S1	0.41934 (10)	0.2492 (2)	0.4390 (2)	0.0646 (5)
O1	0.5511 (2)	0.0919 (5)	0.4909 (4)	0.0616 (11)
O2	0.4654 (2)	−0.1253 (5)	0.6070 (4)	0.0685 (12)
C1	0.3786 (4)	0.2943 (8)	0.8946 (7)	0.0571 (17)
C2	0.3254 (4)	0.2193 (8)	0.8147 (9)	0.069 (2)
H2	0.2812	0.1806	0.8527	0.083*
C3	0.3396 (4)	0.2028 (8)	0.6744 (8)	0.0644 (18)
H3	0.3048	0.1506	0.6186	0.077*
C4	0.4045 (3)	0.2632 (7)	0.6186 (7)	0.0529 (15)
C5	0.4565 (4)	0.3385 (7)	0.7019 (7)	0.0579 (16)
H5	0.5005	0.3793	0.6647	0.069*
C6	0.4432 (4)	0.3534 (8)	0.8404 (7)	0.0593 (18)
H6	0.4784	0.4038	0.8967	0.071*
C7	0.6003 (4)	0.1950 (9)	0.4167 (9)	0.081 (2)
H7A	0.6078	0.1492	0.3271	0.121*
H7B	0.6472	0.2011	0.4637	0.121*
H7C	0.5794	0.3047	0.4090	0.121*
C8	0.4828 (3)	0.0677 (6)	0.4279 (7)	0.0504 (14)
H8	0.4915	0.0421	0.3312	0.060*
C9	0.4447 (3)	−0.0804 (7)	0.4942 (6)	0.0493 (14)
C10	0.3836 (3)	−0.1693 (7)	0.4225 (7)	0.0465 (13)
C11	0.3538 (3)	−0.3095 (7)	0.4869 (7)	0.0577 (16)
H11	0.3719	−0.3431	0.5716	0.069*
C12	0.2974 (3)	−0.3981 (7)	0.4246 (9)	0.0690 (18)
H12	0.2784	−0.4924	0.4674	0.083*
C13	0.2691 (4)	−0.3500 (9)	0.3017 (9)	0.073 (2)
H13	0.2306	−0.4097	0.2613	0.087*
C14	0.2984 (4)	−0.2114 (9)	0.2377 (8)	0.075 (2)
H14	0.2794	−0.1774	0.1537	0.090*
C15	0.3559 (3)	−0.1224 (8)	0.2978 (7)	0.0621 (17)
H15	0.3758	−0.0303	0.2531	0.075*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl1	0.1147 (15)	0.1100 (15)	0.0501 (11)	0.0357 (11)	0.0107 (12)	−0.0064 (10)
S1	0.0977 (11)	0.0519 (8)	0.0441 (8)	0.0100 (8)	−0.0060 (11)	0.0053 (8)
O1	0.072 (3)	0.068 (3)	0.045 (3)	−0.012 (2)	−0.002 (2)	0.001 (2)

O2	0.103 (3)	0.066 (3)	0.037 (3)	−0.010 (2)	−0.008 (3)	0.009 (2)
C1	0.074 (4)	0.054 (4)	0.042 (4)	0.022 (3)	0.005 (4)	−0.003 (3)
C2	0.075 (5)	0.061 (4)	0.071 (5)	0.002 (3)	0.014 (4)	−0.002 (4)
C3	0.073 (4)	0.054 (4)	0.066 (5)	0.000 (3)	−0.005 (4)	−0.006 (3)
C4	0.074 (4)	0.036 (3)	0.048 (4)	0.009 (3)	−0.003 (4)	0.001 (3)
C5	0.068 (4)	0.051 (4)	0.055 (4)	0.005 (3)	0.001 (4)	−0.004 (3)
C6	0.068 (4)	0.058 (4)	0.052 (4)	0.014 (3)	−0.010 (3)	−0.015 (3)
C7	0.087 (5)	0.092 (5)	0.063 (6)	−0.026 (4)	0.004 (5)	−0.004 (5)
C8	0.068 (3)	0.049 (3)	0.034 (3)	0.001 (3)	0.003 (3)	0.003 (3)
C9	0.075 (4)	0.046 (3)	0.028 (3)	0.009 (3)	0.009 (3)	0.002 (3)
C10	0.061 (3)	0.044 (3)	0.035 (3)	0.006 (3)	0.006 (3)	−0.002 (3)
C11	0.067 (4)	0.056 (4)	0.050 (4)	0.005 (3)	0.004 (3)	0.008 (3)
C12	0.073 (4)	0.053 (4)	0.081 (6)	−0.007 (3)	0.012 (5)	0.005 (4)
C13	0.073 (5)	0.076 (5)	0.069 (5)	−0.011 (3)	0.002 (4)	−0.011 (4)
C14	0.088 (5)	0.092 (5)	0.046 (5)	−0.003 (4)	−0.010 (4)	−0.006 (4)
C15	0.082 (4)	0.059 (4)	0.046 (4)	−0.013 (3)	−0.003 (4)	0.001 (3)

*Geometric parameters (Å, °)*

C11—C1	1.741 (7)	C7—H7B	0.9600
S1—C4	1.780 (7)	C7—H7C	0.9600
S1—C8	1.853 (5)	C8—C9	1.517 (7)
O1—C8	1.386 (6)	C8—H8	0.9800
O1—C7	1.412 (8)	C9—C10	1.485 (8)
O2—C9	1.219 (7)	C10—C15	1.370 (9)
C1—C6	1.362 (9)	C10—C11	1.395 (8)
C1—C2	1.372 (10)	C11—C12	1.379 (9)
C2—C3	1.401 (10)	C11—H11	0.9300
C2—H2	0.9300	C12—C13	1.360 (11)
C3—C4	1.376 (9)	C12—H12	0.9300
C3—H3	0.9300	C13—C14	1.380 (9)
C4—C5	1.378 (8)	C13—H13	0.9300
C5—C6	1.381 (9)	C14—C15	1.387 (8)
C5—H5	0.9300	C14—H14	0.9300
C6—H6	0.9300	C15—H15	0.9300
C7—H7A	0.9600		
C4—S1—C8	101.5 (3)	O1—C8—S1	114.1 (4)
C8—O1—C7	114.1 (5)	C9—C8—S1	108.2 (4)
C6—C1—C2	121.6 (7)	O1—C8—H8	108.6
C6—C1—C11	119.7 (6)	C9—C8—H8	108.6
C2—C1—C11	118.6 (6)	S1—C8—H8	108.6
C1—C2—C3	118.2 (7)	O2—C9—C10	120.7 (5)
C1—C2—H2	120.9	O2—C9—C8	118.8 (5)
C3—C2—H2	120.9	C10—C9—C8	120.6 (5)
C4—C3—C2	120.6 (6)	C15—C10—C11	118.9 (6)
C4—C3—H3	119.7	C15—C10—C9	123.8 (5)
C2—C3—H3	119.7	C11—C10—C9	117.3 (5)

C3—C4—C5	119.6 (7)	C12—C11—C10	119.9 (7)
C3—C4—S1	119.7 (5)	C12—C11—H11	120.0
C5—C4—S1	120.6 (5)	C10—C11—H11	120.0
C4—C5—C6	120.0 (6)	C13—C12—C11	121.2 (6)
C4—C5—H5	120.0	C13—C12—H12	119.4
C6—C5—H5	120.0	C11—C12—H12	119.4
C1—C6—C5	119.9 (6)	C12—C13—C14	119.1 (7)
C1—C6—H6	120.1	C12—C13—H13	120.5
C5—C6—H6	120.1	C14—C13—H13	120.5
O1—C7—H7A	109.5	C13—C14—C15	120.5 (7)
O1—C7—H7B	109.5	C13—C14—H14	119.8
H7A—C7—H7B	109.5	C15—C14—H14	119.8
O1—C7—H7C	109.5	C10—C15—C14	120.4 (6)
H7A—C7—H7C	109.5	C10—C15—H15	119.8
H7B—C7—H7C	109.5	C14—C15—H15	119.8
O1—C8—C9	108.6 (5)		
C6—C1—C2—C3	0.8 (9)	O1—C8—C9—O2	19.3 (7)
C11—C1—C2—C3	179.3 (5)	S1—C8—C9—O2	−105.1 (5)
C1—C2—C3—C4	−1.2 (9)	O1—C8—C9—C10	−160.4 (5)
C2—C3—C4—C5	0.9 (9)	S1—C8—C9—C10	75.2 (6)
C2—C3—C4—S1	−177.2 (5)	O2—C9—C10—C15	177.7 (6)
C8—S1—C4—C3	−101.5 (5)	C8—C9—C10—C15	−2.5 (8)
C8—S1—C4—C5	80.5 (5)	O2—C9—C10—C11	−2.9 (8)
C3—C4—C5—C6	−0.2 (8)	C8—C9—C10—C11	176.9 (5)
S1—C4—C5—C6	177.9 (5)	C15—C10—C11—C12	0.0 (9)
C2—C1—C6—C5	0.0 (9)	C9—C10—C11—C12	−179.4 (5)
C11—C1—C6—C5	−178.5 (5)	C10—C11—C12—C13	−1.0 (9)
C4—C5—C6—C1	−0.3 (9)	C11—C12—C13—C14	1.0 (10)
C7—O1—C8—C9	163.9 (5)	C12—C13—C14—C15	0.1 (10)
C7—O1—C8—S1	−75.3 (6)	C11—C10—C15—C14	1.0 (10)
C4—S1—C8—O1	−63.7 (4)	C9—C10—C15—C14	−179.6 (5)
C4—S1—C8—C9	57.3 (5)	C13—C14—C15—C10	−1.1 (10)

## Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C7—H7A $\cdots$ O2 <sup>i</sup>	0.96	2.53	3.297 (9)	137
C8—H8 $\cdots$ O2 <sup>i</sup>	0.98	2.42	3.305 (8)	150

Symmetry code: (i)  $-x+1, -y, z-1/2$ .