IUCrData

ISSN 2414-3146

(*Z*)-1,4-Bis(2-chlorophenyl)-2-(methylsulfanyl)but-2-ene-1,4-dione

A. J. Ravi,[a] A. C. Vinayaka,[b] K. R. Roopashree,[a] M. P. Sadashiva[b] and H. C. Devarajegowda.[a]*

[a]Department of Physics, Yuvaraja's College (Constituent College), University of Mysore, Mysore 570 005, Karnataka, India, and [b]Department of Studies in Chemistry, Manasagangotri, University of Mysore, Mysore 570 006, India. *Correspondence e-mail: devarajegowda@yahoo.com

Received 18 December 2016
Accepted 23 December 2016

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

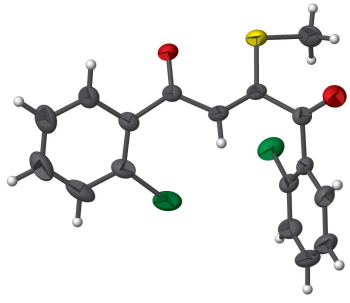
Keywords: crystal structure; 1,4-ene-diones; C—H···O hydrogen bonds.

CCDC reference: 1524322

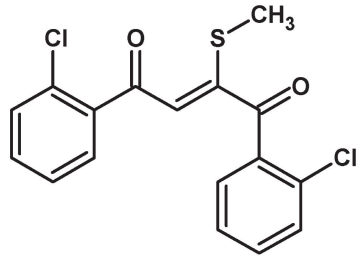
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{17}H_{12}Cl_2O_2S$, the benzene rings are inclined to one another by 84.59 (16)°. The enaminone group is present in a synclinal conformation with respect to the chlorobenzene moiety. The configuration of the C=C bond is *Z*. There is a short intramolecular C—H···O contact present forming an *S*(6) ring motif. In the crystal, molecules are linked by C—H···O hydrogen bonds, forming layers lying parallel to the $(10\bar{1})$ plane.

3D view



Chemical scheme



Structure description

The 2-methylthio-1,4-ene-dione unit is an important building block in synthetic chemistry. The Paal–Knorr selective reduction of double bonds, condensation, and domino reactions of 2-methylthio-1,4-en-diones leads to the formation of biologically and medicinally important heterocyclic compounds such as furan (Yin *et al.*, 2008), pyridazine (Wu *et al.*, 2012), indole-furan (Yang *et al.*, 2011), 1,2-dihydroquinoxaline (Zhang *et al.*, 2013) and beta-enaminones (Vinayaka *et al.*, 2016). The synthesis of these intermediates involves the self-sorting tandem reactions of aryl/heteroaryl methyl ketones, which form a mixture of *E*/*Z* products in different ratios. Due to the importance of 1,4-ene-dione derivatives and as part of our ongoing studies in this area, we have synthesized the title compound and report herein on its crystal structure.

The molecular structure of the title compound is illustrated in Fig. 1. The benzene rings are inclined to one another by 84.59 (16)°. The enaminone group is present in a *syn-clinal* conformation with respect to the chlorobenzene moiety. The configuration about the C13=C15 bond is *Z*. There is a short intramolecular C—H···O contact present forming an S(6) ring motif (Table 1).

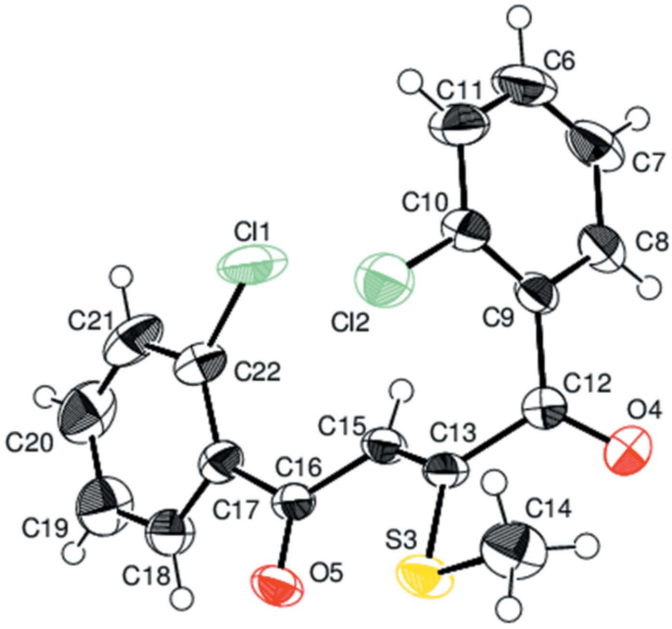


Figure 1
The molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

In the crystal, molecules are linked by C—H···O hydrogen bonds (Table 1), forming layers lying parallel to plane (10$\bar{1}$), as shown in Fig. 2.

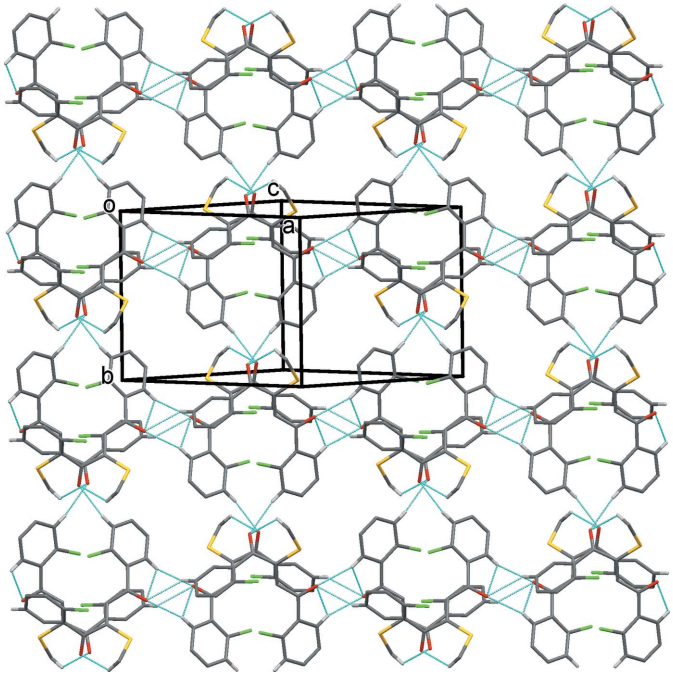


Figure 2
A view normal to plane (10$\bar{1}$) of the crystal packing of the title compound. The hydrogen bonds are shown as dashed lines (see Table 1). For clarity, only the H atoms involved in the C—H···O hydrogen bonds have been included.

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

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14B···O4	0.96	2.39	3.016 (5)	122
C7—H7···O5^{i}	0.93	2.50	3.302 (4)	145
C18—H18···O5^{ii}	0.93	2.54	3.444 (3)	163
C21—H21···O4^{iii}	0.93	2.47	3.393 (4)	170

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{17}H_{12}Cl_2O_2S$
M_r	351.23
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	296
a, b, c (Å)	19.3473 (8), 9.9623 (4), 18.5845 (7)
β (°)	116.194 (2)
V (Å^3)	3214.2 (2)
Z	8
Radiation type	Cu $K\alpha$
μ (mm^{-1})	4.88
Crystal size (mm)	0.24 × 0.20 × 0.12
Data collection	
Diffractometer	Bruker SMART CCD area-detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2009)
T_{min}, T_{max}	0.770, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13526, 2651, 2512
R_{int}	0.058
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.584
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.052, 0.141, 1.08
No. of reflections	2651
No. of parameters	199
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.50, −0.35

Computer programs: *SMART* and *SAINT* (Bruker, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009).

Synthesis and crystallization

A solution of 1-(2-chlorophenyl)ethanone (6.4 mmol), iodine (16.1 mmol) and copper oxide (16.1 mmol) in dimethyl sulfoxide (15 ml) was heated at 333 K for 5 h. After completion of the reaction (monitored by TLC), the reaction mixture was filtered. The obtained organic layer was washed first with sodium thiosulfate solution and then diluted with ethyl acetate and washed with sodium hydroxide and water. The solvent was dried over anhydrous sodium sulfate and removed under reduced pressure. The crude product was purified through silica gel column chromatography. Yellow prismatic crystals of the title compound were obtained from an ethyl acetate–hexane solution by slow evaporation at room temperature.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

The authors thank the Sophisticated Instrumental Centre, of the University of Mysore, Mysuru, for the CCD X-ray facilities.

References

Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Vinayaka, A. C., Swaroop, T. R., Chikkade, P. K., Rangappa, K. S. & Sadashiva, M. P. (2016). *RSC Adv.* **6**, 11528–11535.
Wu, L., Yang, Y., Gao, M., Zhang, D., Shu, W., Zhu, Y. & Wu, A. (2012). *Synlett*, **23**, 2137–2141.
Yang, Y., Gao, M., Wu, L.-M., Deng, C., Zhang, D.-X., Gao, Y., Zhu, Y.-P. & Wu, A.-X. (2011). *Tetrahedron*, **67**, 5142–5149.
Yin, G., Wang, Z., Chen, A., Gao, M., Wu, A. & Pan, Y. (2008). *J. Org. Chem.* **73**, 3377–3383.
Zhang, D., Yang, Y., Gao, M., Shu, W., Wu, L., Zhu, Y. & Wu, A. (2013). *Tetrahedron*, **69**, 1849–1856.

full crystallographic data

IUCrData (2017). **2**, x162047 [https://doi.org/10.1107/S2414314616020472]

(*Z*)-1,4-Bis(2-chlorophenyl)-2-(methylsulfanyl)but-2-ene-1,4-dione

A. J. Ravi, A. C. Vinayaka, K. R. Roopashree, M. P. Sadashiva and H. C. Devarajegowda.

(*Z*)-1,4-Bis(2-chlorophenyl)-2-(methylsulfanyl)but-2-ene-1,4-dione

Crystal data

$C_{17}H_{12}Cl_2O_2S$
M_r = 351.23
Monoclinic, $C2/c$
a = 19.3473 (8) Å
b = 9.9623 (4) Å
c = 18.5845 (7) Å
β = 116.194 (2)°
V = 3214.2 (2) Å^3
Z = 8
$F(000)$ = 1440
D_x = 1.452 Mg m^{-3}
Melting point: 378 K
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 2651 reflections
θ = 5.1–64.3°
μ = 4.88 mm^{-1}
T = 296 K
Prism, colourless
0.24 × 0.20 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (SADABS; Bruker, 2009)
T_{min} = 0.770, T_{max} = 1.000
13526 measured reflections
2651 independent reflections
2512 reflections with $I > 2\sigma(I)$
R_{int} = 0.058
θ_{max} = 64.3°, θ_{min} = 5.1°
h = −19→22
k = −11→11
l = −21→21

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.141
S = 1.08
2651 reflections
199 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
$w = 1/[\sigma^2(F_o^2) + (0.0864P)^2 + 3.2646P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.42143 (6)	0.48209 (8)	0.30724 (5)	0.0691 (3)
Cl2	0.35016 (4)	0.17073 (8)	0.40050 (4)	0.0568 (3)
S3	0.29130 (4)	−0.01014 (6)	0.19937 (4)	0.0438 (2)
O4	0.46266 (12)	−0.10000 (19)	0.31873 (12)	0.0561 (5)
O5	0.28248 (10)	0.21333 (17)	0.10972 (10)	0.0443 (5)
C6	0.5719 (2)	0.2545 (3)	0.52831 (17)	0.0598 (8)
H6	0.6014	0.3101	0.5711	0.072*
C7	0.60755 (17)	0.1725 (3)	0.49585 (17)	0.0551 (8)
H7	0.6610	0.1706	0.5176	0.066*
C8	0.56390 (15)	0.0925 (3)	0.43058 (15)	0.0424 (6)
H8	0.5883	0.0366	0.4088	0.051*
C9	0.48418 (14)	0.0949 (2)	0.39747 (13)	0.0342 (5)
C10	0.44942 (15)	0.1751 (2)	0.43308 (14)	0.0402 (6)
C11	0.49297 (19)	0.2556 (3)	0.49832 (16)	0.0546 (7)
H11	0.4691	0.3096	0.5215	0.066*
C12	0.44141 (14)	0.0122 (2)	0.32400 (14)	0.0345 (5)
C13	0.37629 (13)	0.0776 (2)	0.25295 (12)	0.0318 (5)
C14	0.29307 (19)	−0.1364 (3)	0.26996 (19)	0.0558 (7)
H14A	0.2477	−0.1911	0.2457	0.084*
H14B	0.3380	−0.1916	0.2849	0.084*
H14C	0.2945	−0.0936	0.3169	0.084*
C15	0.39188 (13)	0.1990 (2)	0.23167 (13)	0.0324 (5)
H15	0.4391	0.2385	0.2639	0.039*
C16	0.33863 (13)	0.2718 (2)	0.16073 (13)	0.0317 (5)
C17	0.35056 (14)	0.4165 (2)	0.14718 (14)	0.0364 (5)
C18	0.32058 (16)	0.4572 (3)	0.06691 (16)	0.0447 (6)
H18	0.2958	0.3944	0.0266	0.054*
C19	0.3268 (2)	0.5872 (3)	0.0463 (2)	0.0627 (8)
H19	0.3059	0.6113	−0.0075	0.075*
C20	0.3635 (2)	0.6815 (3)	0.1040 (2)	0.0684 (9)
H20	0.3680	0.7692	0.0894	0.082*
C21	0.3937 (2)	0.6466 (3)	0.1835 (2)	0.0623 (9)
H21	0.4187	0.7107	0.2229	0.075*
C22	0.38701 (17)	0.5146 (3)	0.20539 (17)	0.0448 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0952 (7)	0.0602 (5)	0.0431 (4)	−0.0172 (4)	0.0225 (4)	−0.0233 (3)
Cl2	0.0457 (4)	0.0747 (5)	0.0494 (4)	0.0085 (3)	0.0205 (3)	−0.0109 (3)
S3	0.0409 (4)	0.0427 (4)	0.0353 (4)	−0.0140 (2)	0.0055 (3)	−0.0027 (2)
O4	0.0600 (12)	0.0403 (10)	0.0521 (11)	0.0109 (9)	0.0103 (9)	−0.0100 (8)
O5	0.0434 (10)	0.0386 (9)	0.0335 (9)	−0.0088 (7)	0.0011 (8)	−0.0009 (7)
C6	0.066 (2)	0.0596 (18)	0.0335 (14)	−0.0175 (15)	0.0037 (13)	−0.0097 (13)
C7	0.0412 (15)	0.0619 (18)	0.0408 (15)	−0.0125 (13)	−0.0015 (12)	0.0058 (13)

C8	0.0375 (13)	0.0458 (14)	0.0360 (13)	0.0008 (11)	0.0090 (11)	0.0063 (11)
C9	0.0359 (12)	0.0335 (11)	0.0255 (11)	−0.0010 (9)	0.0066 (9)	0.0037 (9)
C10	0.0443 (14)	0.0416 (13)	0.0286 (12)	0.0010 (11)	0.0105 (10)	−0.0011 (10)
C11	0.071 (2)	0.0534 (16)	0.0335 (14)	−0.0029 (14)	0.0180 (14)	−0.0105 (11)
C12	0.0358 (12)	0.0333 (12)	0.0318 (12)	0.0001 (9)	0.0126 (10)	−0.0022 (9)
C13	0.0331 (11)	0.0350 (12)	0.0240 (10)	−0.0022 (9)	0.0096 (9)	−0.0070 (9)
C14	0.0579 (17)	0.0525 (16)	0.0538 (17)	−0.0186 (13)	0.0217 (14)	0.0023 (13)
C15	0.0297 (11)	0.0356 (11)	0.0265 (11)	−0.0041 (9)	0.0074 (9)	−0.0055 (9)
C16	0.0335 (12)	0.0314 (11)	0.0282 (11)	−0.0026 (9)	0.0118 (9)	−0.0049 (9)
C17	0.0382 (12)	0.0316 (12)	0.0401 (13)	−0.0029 (10)	0.0177 (11)	−0.0040 (10)
C18	0.0524 (15)	0.0383 (12)	0.0405 (13)	−0.0026 (11)	0.0180 (12)	0.0021 (11)
C19	0.084 (2)	0.0452 (16)	0.0621 (19)	−0.0030 (15)	0.0346 (17)	0.0136 (14)
C20	0.094 (3)	0.0368 (15)	0.082 (2)	−0.0051 (15)	0.047 (2)	0.0071 (15)
C21	0.075 (2)	0.0358 (14)	0.083 (2)	−0.0157 (14)	0.0408 (19)	−0.0232 (15)
C22	0.0510 (15)	0.0384 (13)	0.0460 (16)	−0.0079 (11)	0.0222 (13)	−0.0116 (11)

Geometric parameters (Å, º)

Cl1—C22	1.737 (3)	C13—C15	1.348 (3)
Cl2—C10	1.741 (3)	C14—H14A	0.9600
S3—C13	1.736 (2)	C14—H14B	0.9600
S3—C14	1.807 (3)	C14—H14C	0.9600
O4—C12	1.210 (3)	C15—C16	1.458 (3)
O5—C16	1.228 (3)	C15—H15	0.9300
C6—C7	1.368 (5)	C16—C17	1.499 (3)
C6—C11	1.376 (5)	C17—C22	1.396 (3)
C6—H6	0.9300	C17—C18	1.401 (4)
C7—C8	1.384 (4)	C18—C19	1.371 (4)
C7—H7	0.9300	C18—H18	0.9300
C8—C9	1.386 (4)	C19—C20	1.365 (5)
C8—H8	0.9300	C19—H19	0.9300
C9—C10	1.386 (4)	C20—C21	1.373 (5)
C9—C12	1.493 (3)	C20—H20	0.9300
C10—C11	1.386 (4)	C21—C22	1.399 (4)
C11—H11	0.9300	C21—H21	0.9300
C12—C13	1.512 (3)		
C13—S3—C14	102.97 (12)	S3—C14—H14C	109.5
C7—C6—C11	120.7 (3)	H14A—C14—H14C	109.5
C7—C6—H6	119.6	H14B—C14—H14C	109.5
C11—C6—H6	119.6	C13—C15—C16	123.5 (2)
C6—C7—C8	119.9 (3)	C13—C15—H15	118.3
C6—C7—H7	120.0	C16—C15—H15	118.3
C8—C7—H7	120.0	O5—C16—C15	119.6 (2)
C7—C8—C9	120.5 (3)	O5—C16—C17	118.4 (2)
C7—C8—H8	119.7	C15—C16—C17	122.02 (19)
C9—C8—H8	119.7	C22—C17—C18	116.9 (2)
C8—C9—C10	118.5 (2)	C22—C17—C16	127.3 (2)

C8—C9—C12	117.1 (2)	C18—C17—C16	115.8 (2)
C10—C9—C12	124.4 (2)	C19—C18—C17	121.7 (3)
C11—C10—C9	121.0 (3)	C19—C18—H18	119.2
C11—C10—Cl2	118.1 (2)	C17—C18—H18	119.2
C9—C10—Cl2	120.83 (18)	C20—C19—C18	120.6 (3)
C6—C11—C10	119.2 (3)	C20—C19—H19	119.7
C6—C11—H11	120.4	C18—C19—H19	119.7
C10—C11—H11	120.4	C19—C20—C21	119.9 (3)
O4—C12—C9	120.8 (2)	C19—C20—H20	120.1
O4—C12—C13	120.6 (2)	C21—C20—H20	120.1
C9—C12—C13	118.24 (18)	C20—C21—C22	120.0 (3)
C15—C13—C12	115.8 (2)	C20—C21—H21	120.0
C15—C13—S3	124.17 (17)	C22—C21—H21	120.0
C12—C13—S3	119.83 (17)	C17—C22—C21	120.9 (3)
S3—C14—H14A	109.5	C17—C22—Cl1	122.2 (2)
S3—C14—H14B	109.5	C21—C22—Cl1	116.8 (2)
H14A—C14—H14B	109.5		

C11—C6—C7—C8	2.0 (5)	C14—S3—C13—C12	21.4 (2)
C6—C7—C8—C9	0.2 (4)	C12—C13—C15—C16	174.5 (2)
C7—C8—C9—C10	−2.5 (4)	S3—C13—C15—C16	0.2 (3)
C7—C8—C9—C12	176.1 (2)	C13—C15—C16—O5	−12.9 (4)
C8—C9—C10—C11	2.6 (4)	C13—C15—C16—C17	167.8 (2)
C12—C9—C10—C11	−175.9 (2)	O5—C16—C17—C22	151.3 (3)
C8—C9—C10—Cl2	−173.85 (18)	C15—C16—C17—C22	−29.4 (4)
C12—C9—C10—Cl2	7.6 (3)	O5—C16—C17—C18	−27.7 (3)
C7—C6—C11—C10	−1.8 (5)	C15—C16—C17—C18	151.6 (2)
C9—C10—C11—C6	−0.5 (4)	C22—C17—C18—C19	0.2 (4)
Cl2—C10—C11—C6	176.0 (2)	C16—C17—C18—C19	179.3 (3)
C8—C9—C12—O4	42.4 (3)	C17—C18—C19—C20	0.6 (5)
C10—C9—C12—O4	−139.1 (3)	C18—C19—C20—C21	−0.7 (6)
C8—C9—C12—C13	−131.0 (2)	C19—C20—C21—C22	0.0 (6)
C10—C9—C12—C13	47.5 (3)	C18—C17—C22—C21	−0.8 (4)
O4—C12—C13—C15	−126.1 (3)	C16—C17—C22—C21	−179.8 (3)
C9—C12—C13—C15	47.3 (3)	C18—C17—C22—Cl1	175.7 (2)
O4—C12—C13—S3	48.5 (3)	C16—C17—C22—Cl1	−3.3 (4)
C9—C12—C13—S3	−138.11 (19)	C20—C21—C22—C17	0.8 (5)
C14—S3—C13—C15	−164.5 (2)	C20—C21—C22—Cl1	−176.0 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14*B*···O4	0.96	2.39	3.016 (5)	122
C7—H7···O5^{i}	0.93	2.50	3.302 (4)	145
C18—H18···O5^{ii}	0.93	2.54	3.444 (3)	163
C21—H21···O4^{iii}	0.93	2.47	3.393 (4)	170

Symmetry codes: (i) $x+1/2, -y+1/2, z+1/2$; (ii) $-x+1/2, -y+1/2, -z$; (iii) $x, y+1, z$.