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ISSN 2414-3146

3-(4-Chlorophenyl)-4-phenylthiosydnone

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Received 21 September 2016
Accepted 7 October 2016

Edited by J. Simpson, University of Otago, New Zealand

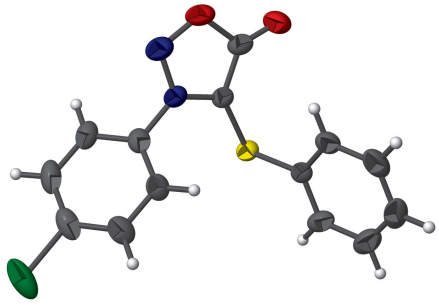
Keywords: crystal structure; sydnone; hydrogen bonds; *X*—π interactions *X* = O; S.

CCDC reference: 1508848

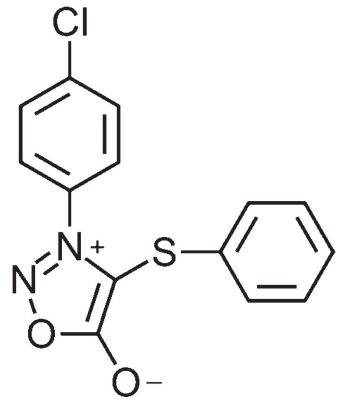
Structural data: full structural data are available from iucrdata.iucr.org

In the structure of $C_{14}H_9ClN_2O_2S$ [systematic name: 3-(4-chlorophenyl)-4-(phenylsulfanyl)-1,2,3λ^5-oxadiazol-3-ylium-5-olate], the central sydnone ring is inclined at angles of 67.49 (10)° to the phenyl ring of the thiophenyl substituent and 52.61 (10)° to the chlorophenyl ring. The compound crystallizes utilizing a network of weak S and Cl-based hydrogen bonds, together with S···π, O···π and C—H···π interactions, forming a three-dimensional structure. In spite of having three planar rings, no π–π interactions are found.

3D view



Chemical scheme



Structure description

The title compound was prepared as part of a project exploring the lithiation chemistry of substituted arylsydnones with the expectation that improved avenues to otherwise difficultly accessible sydnones would result (Grossie, *et al.*, 2007; Turnbull & Krein, 1997; Turnbull *et al.*, 1998). The sydnone and phenyl rings in the title molecule, Fig. 1, are each planar with a maximum r.m.s. deviation of less than 0.01 Å found for all three rings. None of the three rings are coplanar with each other nor are they in close face-to-face proximity. Relative to the sydnone ring, the phenyl ring of the thiophenyl substituent is inclined at an angle of 67.49 (10)° while the sydnone and chlorophenyl rings are rotated by 52.61 (10)° to one another.

In the crystal, no classical hydrogen bonds are found; however, non-classical hydrogen bonds are present involving sulfur and chlorine as the hydrogen-bond acceptor and carbon as the hydrogen-bond donor. A C—H···π hydrogen bond is also found, Table 1. In addition there are S···π and O···π, contacts, Fig. 2, with distance and angle data detailed in Table 2 and 3. Molecules are also linked into sets of three, on one side by C—H···Cl hydrogen bonds and on the other by O···π interactions. These trimers are interconnected by a C32—H32···S1 hydrogen bond forming a chain of molecules approximately along the *bc* diagonal, Fig. 3. Overall these contacts combine to generate an extensive three-dimensional network.

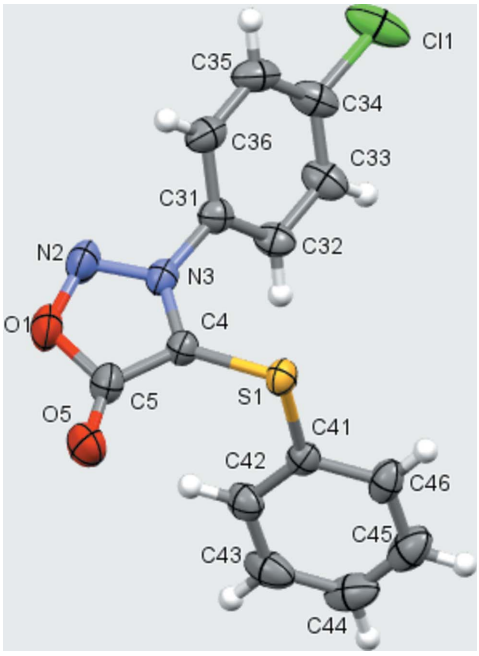


Figure 1
The molecular structure of the title compound with ellipsoids drawn at the 50% probability level.

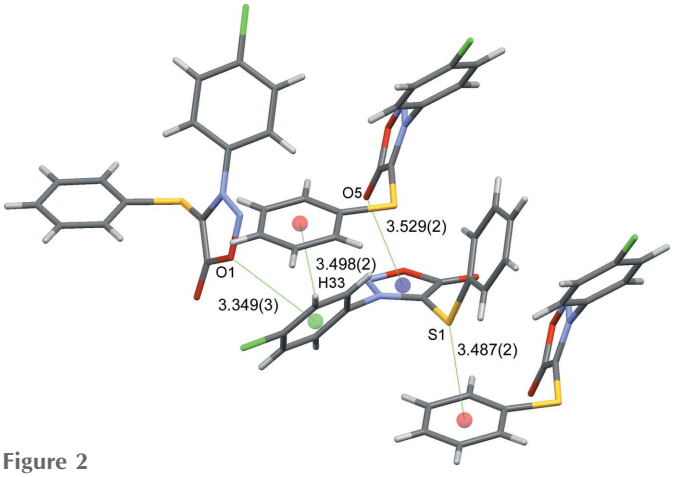


Figure 2
C—H···π and X···π contacts.

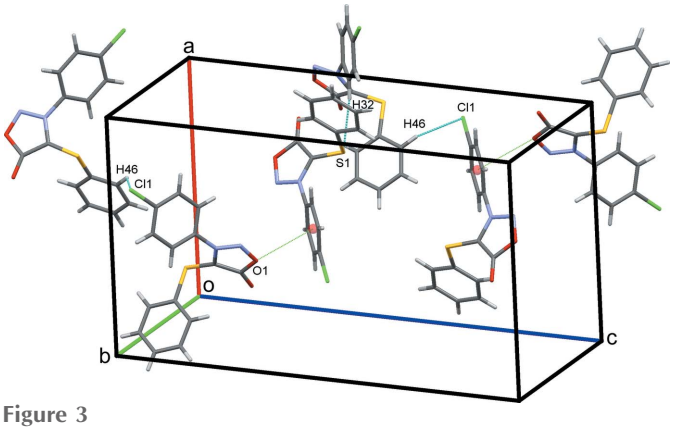


Figure 3
Chains of molecules along the *bc* diagonal.

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

*Cg*1 is the centroid of the C41–C46 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C46—H46···Cl1^{i}	0.93	2.96	3.388 (2)	109
C32—H32···S1^{ii}	0.93	2.99	3.797 (2)	146
C33—H33···*Cg*1^{iii}	0.93	2.74	3.498 (2)	140

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+\frac{3}{2}, y+\frac{1}{2}, z$; (iii) $x+1, -y-\frac{3}{2}, z-\frac{1}{2}$.

Table 2
Analysis of Y—X···Cg(π-ring) interactions (Å, °).

Gamma is the angle between the *Cg*–H vector and the normal to the ring. *Cg*2 is the centroid of the O1/N2/N3/C4/C5 ring.

Y—X···Cg	X···Cg	X-Perp	Gamma	Y—X···Cg
C5—O5···*Cg*2^{ii}	3.529 (2)	3.261	22.45	140.29 (14)

Symmetry code: (ii) $-x+\frac{3}{2}, y+\frac{1}{2}, z$.

Table 3
Analysis of lone pair–π ring [X···Cg(π-ring)] interactions (Å, °).

*Cg*1 and *Cg*3 are the centroids of the C41–C46 and C31–C36 rings, respectively.

X···Cg	X···Cg	Y—X···Cg	X-Perp	Gamma
S1···*Cg*1	3.487 (2)	95.73	3.447	8.69
O1···*Cg*3	3.349 (3)	118.55	3.188	17.84

Symmetry codes: (iii) $-x+\frac{3}{2}, y-\frac{1}{2}, z$; (iv) $-x+1$, y- 1/2, $-z+\frac{1}{2}$.

Table 4
Experimental details.

Crystal data	
Chemical formula	$C_{14}H_9ClN_2O_2S$
M_r	304.74
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	173
a, *b*, *c* (Å)	12.5782 (11), 9.7406 (9), 22.2168 (19)
V (Å^3)	2722.0 (4)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.44
Crystal size (mm)	0.7 × 0.7 × 0.6
Data collection	
Diffractometer	Bruker Smart X2S
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.904, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	33900, 2973, 2413
R_{int}	0.048
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.639
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.091, 1.04
No. of reflections	2973
No. of parameters	181
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.38, −0.47

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009), *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008)'.

Synthesis and crystallization

The title compound was prepared from 3-(4-chlorophenyl)-sydnone by treatment with *n*-BuLi (1.7 equivalents) at −40°C followed by addition of diphenyl disulfide (1.1 equivalents). Column chromatography on silica gel using dichloromethane as eluent and subsequent recrystallization from dichloromethane solution afforded the product as colorless needles in 57% yield (Dossa, 2006).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4.

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full crystallographic data

IUCrData (2016). **1**, x161586 [https://doi.org/10.1107/S2414314616015868]

3-(4-Chlorophenyl)-4-phenylthiosydnone

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3-(4-Chlorophenyl)-4-(phenylsulfanyl)-1,2,3λ^5-oxadiazol-3-ylium-5-olate

Crystal data

$C_{14}H_9ClN_2O_2S$
M_r = 304.74
Orthorhombic, *Pbca*
a = 12.5782 (11) Å
b = 9.7406 (9) Å
c = 22.2168 (19) Å
V = 2722.0 (4) Å^3
Z = 8
F(000) = 1248
D_x = 1.487 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7304 reflections
θ = 2.4–23.9°
μ = 0.44 mm^{-1}
T = 173 K
Block, yellow
0.7 × 0.7 × 0.6 mm

Data collection

Bruker Smart X2S diffractometer
Radiation source: Incoatec Microfocus Source
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2014)
T_{min} = 0.904, T_{max} = 1.000
33900 measured reflections
2973 independent reflections
2413 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 27.0°, θ_{min} = 2.8°
h = −16→15
k = −11→12
l = −28→28

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.091
S = 1.04
2973 reflections
181 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 1.677P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 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.
Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane)
Ring 1 7.261 (10) x + 7.749 (6) y + -4.09 (2) z = 4.563 (9)
* 0.007 (2) O(1) * -0.003 (2) N(2) * -0.003 (2) N(3) * 0.007 (2) C(4) * -0.008 (2) C(5)
Ring 2 0.671 (11) x + -6.051 (6) y + 17.371 (11) z = 4.516 (8)
* -0.005 (2) C(31) * -0.002 (2) C(32) * 0.007 (2) C(33) * -0.006 (2) C(34) * 0.000 (2) C(35) * 0.006 (2) C(36)
Ring 3 -6.513 (9) x + 8.333 (4) y + -0.141 (19) z = -3.552 (12)
* -0.008 (2) C(41) * 0.000 (2) C(42) * 0.007 (2) C(43) * -0.006 (2) C(44) * -0.003 (2) C(45) * 0.010 (2) C(46)
Ring Ring Angle
1 2 52.61 (10) 1 3 67.49 (10) 2 3 55.67 (10)

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.70839 (4)	0.11292 (5)	0.39942 (2)	0.03326 (13)
Cl1	0.28185 (5)	0.54265 (6)	0.43739 (4)	0.0711 (2)
O1	0.64891 (13)	0.10104 (17)	0.22602 (6)	0.0549 (4)
N3	0.58757 (12)	0.19843 (16)	0.30413 (6)	0.0346 (3)
O5	0.79114 (13)	−0.01484 (17)	0.26453 (6)	0.0563 (4)
N2	0.56899 (15)	0.18549 (19)	0.24655 (8)	0.0509 (5)
C31	0.51284 (15)	0.28083 (19)	0.33771 (8)	0.0349 (4)
C4	0.67396 (15)	0.12955 (18)	0.32453 (8)	0.0325 (4)
C41	0.82162 (15)	0.22185 (18)	0.40756 (8)	0.0324 (4)
C5	0.71701 (17)	0.0605 (2)	0.27391 (8)	0.0422 (5)
C32	0.55037 (16)	0.38634 (19)	0.37319 (9)	0.0390 (4)
H32	0.6229	0.4035	0.3762	0.047*
C46	0.85093 (17)	0.2479 (2)	0.46683 (9)	0.0433 (5)
H46	0.8082	0.2174	0.4983	0.052*
C36	0.40563 (15)	0.2517 (2)	0.33229 (9)	0.0427 (5)
H36	0.3824	0.1791	0.3085	0.051*
C42	0.88276 (15)	0.2698 (2)	0.36062 (9)	0.0408 (4)
H42	0.8627	0.2534	0.3210	0.049*
C34	0.37116 (16)	0.4392 (2)	0.39826 (10)	0.0447 (5)
C33	0.47785 (17)	0.4662 (2)	0.40430 (9)	0.0447 (5)
H33	0.5010	0.5372	0.4290	0.054*
C35	0.33365 (16)	0.3330 (2)	0.36306 (10)	0.0478 (5)
H35	0.2610	0.3163	0.3601	0.057*
C43	0.97527 (17)	0.3432 (2)	0.37342 (11)	0.0537 (6)
H43	1.0170	0.3769	0.3422	0.064*
C44	1.00502 (18)	0.3659 (2)	0.43267 (13)	0.0599 (7)
H44	1.0674	0.4134	0.4410	0.072*
C45	0.9434 (2)	0.3189 (2)	0.47894 (11)	0.0568 (6)
H45	0.9638	0.3348	0.5186	0.068*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0378 (3)	0.0360 (2)	0.0261 (2)	−0.00063 (19)	−0.00220 (18)	0.00344 (18)
Cl1	0.0543 (4)	0.0476 (3)	0.1115 (5)	0.0168 (3)	0.0348 (3)	0.0146 (3)
O1	0.0634 (10)	0.0715 (11)	0.0299 (7)	0.0099 (8)	−0.0076 (6)	−0.0115 (7)
N3	0.0378 (9)	0.0376 (8)	0.0283 (7)	−0.0029 (7)	−0.0045 (6)	0.0009 (6)
O5	0.0579 (10)	0.0635 (10)	0.0476 (9)	0.0153 (8)	0.0020 (7)	−0.0154 (8)
N2	0.0561 (11)	0.0646 (12)	0.0319 (8)	0.0078 (9)	−0.0108 (8)	−0.0033 (8)
C31	0.0343 (10)	0.0358 (10)	0.0345 (9)	0.0007 (8)	−0.0003 (7)	0.0078 (8)
C4	0.0345 (10)	0.0343 (9)	0.0288 (8)	0.0002 (8)	−0.0026 (7)	−0.0001 (7)
C41	0.0346 (9)	0.0278 (9)	0.0349 (9)	0.0067 (7)	−0.0034 (7)	−0.0040 (7)
C5	0.0474 (12)	0.0477 (11)	0.0315 (9)	−0.0012 (10)	−0.0035 (8)	−0.0051 (8)
C32	0.0335 (10)	0.0353 (10)	0.0482 (11)	−0.0051 (8)	0.0052 (8)	0.0025 (8)
C46	0.0562 (13)	0.0364 (10)	0.0374 (10)	0.0060 (10)	−0.0103 (9)	−0.0066 (8)
C36	0.0357 (11)	0.0458 (11)	0.0464 (11)	−0.0044 (9)	−0.0083 (9)	0.0088 (9)
C42	0.0412 (11)	0.0377 (10)	0.0435 (10)	0.0002 (9)	0.0055 (9)	−0.0103 (9)
C34	0.0379 (11)	0.0353 (10)	0.0610 (13)	0.0077 (9)	0.0142 (9)	0.0187 (10)
C33	0.0447 (12)	0.0323 (10)	0.0570 (12)	−0.0033 (9)	0.0127 (10)	0.0022 (9)
C35	0.0287 (10)	0.0526 (13)	0.0623 (13)	−0.0004 (9)	−0.0012 (9)	0.0196 (11)
C43	0.0427 (12)	0.0421 (12)	0.0763 (16)	−0.0027 (10)	0.0171 (11)	−0.0167 (11)
C44	0.0400 (12)	0.0426 (12)	0.0972 (19)	0.0029 (10)	−0.0145 (13)	−0.0307 (13)
C45	0.0610 (15)	0.0480 (13)	0.0615 (14)	0.0078 (11)	−0.0218 (12)	−0.0191 (11)

Geometric parameters (Å, º)

S1—C4	1.7268 (17)	C46—H46	0.9300
S1—C41	1.7852 (19)	C46—C45	1.380 (3)
Cl1—C34	1.742 (2)	C36—H36	0.9300
O1—N2	1.377 (2)	C36—C35	1.383 (3)
O1—C5	1.422 (2)	C42—H42	0.9300
N3—N2	1.307 (2)	C42—C43	1.395 (3)
N3—C31	1.444 (2)	C34—C33	1.374 (3)
N3—C4	1.355 (2)	C34—C35	1.380 (3)
O5—C5	1.205 (2)	C33—H33	0.9300
C31—C32	1.379 (3)	C35—H35	0.9300
C31—C36	1.383 (3)	C43—H43	0.9300
C4—C5	1.418 (3)	C43—C44	1.386 (3)
C41—C46	1.391 (2)	C44—H44	0.9300
C41—C42	1.377 (3)	C44—C45	1.366 (4)
C32—H32	0.9300	C45—H45	0.9300
C32—C33	1.384 (3)		
C4—S1—C41	104.00 (9)	C31—C36—H36	120.7
N2—O1—C5	110.98 (14)	C31—C36—C35	118.5 (2)
N2—N3—C31	116.30 (15)	C35—C36—H36	120.7
N2—N3—C4	115.04 (16)	C41—C42—H42	120.5
C4—N3—C31	128.65 (14)	C41—C42—C43	119.01 (19)

N3—N2—O1	104.56 (15)	C43—C42—H42	120.5
C32—C31—N3	119.14 (16)	C33—C34—Cl1	118.05 (18)
C32—C31—C36	122.44 (19)	C33—C34—C35	122.20 (19)
C36—C31—N3	118.42 (17)	C35—C34—Cl1	119.75 (16)
N3—C4—S1	124.74 (13)	C32—C33—H33	120.4
N3—C4—C5	106.01 (15)	C34—C33—C32	119.2 (2)
C5—C4—S1	128.61 (15)	C34—C33—H33	120.4
C46—C41—S1	114.58 (15)	C36—C35—H35	120.5
C42—C41—S1	124.76 (14)	C34—C35—C36	119.03 (19)
C42—C41—C46	120.47 (19)	C34—C35—H35	120.5
O5—C5—O1	120.41 (17)	C42—C43—H43	120.0
O5—C5—C4	136.19 (19)	C44—C43—C42	120.0 (2)
C4—C5—O1	103.40 (17)	C44—C43—H43	120.0
C31—C32—H32	120.7	C43—C44—H44	119.7
C31—C32—C33	118.61 (18)	C45—C44—C43	120.5 (2)
C33—C32—H32	120.7	C45—C44—H44	119.7
C41—C46—H46	120.0	C46—C45—H45	120.0
C45—C46—C41	120.0 (2)	C44—C45—C46	120.0 (2)
C45—C46—H46	120.0	C44—C45—H45	120.0

S1—C4—C5—O1	172.40 (14)	C31—C36—C35—C34	−0.5 (3)
S1—C4—C5—O5	−8.6 (4)	C4—S1—C41—C46	167.36 (14)
S1—C41—C46—C45	173.35 (16)	C4—S1—C41—C42	−17.73 (18)
S1—C41—C42—C43	−173.76 (15)	C4—N3—N2—O1	0.0 (2)
Cl1—C34—C33—C32	−179.33 (15)	C4—N3—C31—C32	54.0 (3)
Cl1—C34—C35—C36	−179.97 (15)	C4—N3—C31—C36	−126.9 (2)
N3—C31—C32—C33	178.85 (17)	C41—S1—C4—N3	−107.63 (16)
N3—C31—C36—C35	−178.18 (16)	C41—S1—C4—C5	82.94 (19)
N3—C4—C5—O1	1.4 (2)	C41—C46—C45—C44	1.3 (3)
N3—C4—C5—O5	−179.5 (2)	C41—C42—C43—C44	0.6 (3)
N2—O1—C5—O5	179.30 (19)	C5—O1—N2—N3	0.9 (2)
N2—O1—C5—C4	−1.5 (2)	C32—C31—C36—C35	0.9 (3)
N2—N3—C31—C32	−127.57 (19)	C46—C41—C42—C43	0.9 (3)
N2—N3—C31—C36	51.6 (2)	C36—C31—C32—C33	−0.2 (3)
N2—N3—C4—S1	−172.41 (15)	C42—C41—C46—C45	−1.8 (3)
N2—N3—C4—C5	−1.0 (2)	C42—C43—C44—C45	−1.1 (3)
C31—N3—N2—O1	−178.59 (15)	C33—C34—C35—C36	−0.7 (3)
C31—N3—C4—S1	6.0 (3)	C35—C34—C33—C32	1.4 (3)
C31—N3—C4—C5	177.46 (17)	C43—C44—C45—C46	0.2 (3)
C31—C32—C33—C34	−0.9 (3)		

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the C41–C46 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C46—H46···Cl1^{i}	0.93	2.96	3.388 (2)	109

C32—H32···S1^{ii}	0.93	2.99	3.797 (2)	146
C33—H33···*Cg*1^{iii}	0.93	2.74	3.498 (2)	140

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+3/2, *y*+1/2, *z*; (iii) *x*+1, −*y*−3/2, *z*−1/2.