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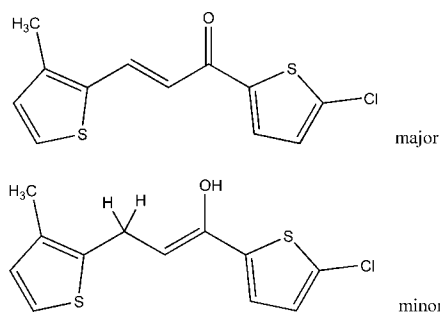
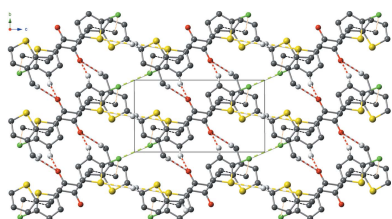
Unexpected formation of a co-crystal containing the chalcone (*E*)-1-(5-chlorothiophen-2-yl)-3-(3-methylthiophen-2-yl)prop-2-en-1-one and the keto–enol tautomer (*Z*)-1-(5-chlorothiophen-2-yl)-3-(3-methylthiophen-2-yl)prop-1-en-1-ol

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The title crystal structure is assembled from the superposition of two molecular structures, (*E*)-1-(5-chlorothiophen-2-yl)-3-(3-methylthiophen-2-yl)prop-2-en-1-one, C₁₂H₉ClOS₂ (93%), and (*Z*)-1-(5-chlorothiophen-2-yl)-3-(3-methylthiophen-2-yl)prop-1-en-1-ol, C₁₂H₁₁ClOS₂ (7%), 0.93C₁₂H₉ClOS₂·0.07C₁₂H₁₁ClOS₂. Both were obtained from the reaction of 3-methylthiophene-2-carbaldehyde and 1-(5-chlorothiophen-2-yl)ethanone. In the extended structure of the major chalcone component, molecules are linked by a combination of C–H···O/S, Cl···Cl, Cl···π and π–π interactions, leading to a compact three-dimensional supramolecular assembly.

1. Chemical context

Chalcones exhibit a wide spectrum of pharmacological activities, including antibacterial (Tran *et al.*, 2012), anticancer (Shin *et al.*, 2013), antifungal (López *et al.*, 2001) and anti-inflammatory properties (Fang *et al.*, 2015). On the other hand, thiophene derivatives display a wide range of biological activities such as antimicrobial (Mishra *et al.*, 2012), anti-allergic (Gillespie *et al.*, 1985), anti-inflammatory (Molvi *et al.*, 2007), antioxidant and antitumor agents (Jarak *et al.*, 2005). Combining thiophenes and chalcones could result in compounds with interesting new structures and properties: Al-Maqtari *et al.* (2015) reported the synthesis of thiophene–chalcones containing two thiophene rings and their antimicrobial and anticancer activities. One of their reported structures is (*E*)-1-(5-chlorothiophen-2-yl)-3-(3-methylthiophen-2-yl)prop-2-en-1-one. However, the crystal structure of this thiophene-based chalcone has not yet been determined.



As a part of our ongoing research in this area (Ibrahim *et al.*, 2019), we report herein the crystal structure of a chalcone containing two terminal-substituted thiophene rings, namely (*E*)-1-(5-chlorothiophen-2-yl)-3-(3-methylthiophen-2-yl)prop-2-en-1-one, which crystallized as a co-crystal in an unexpected superposition with the keto–enol tautomer (*Z*)-1-(5-chlorothiophen-2-yl)-3-(3-methylthiophen-2-yl)prop-1-en-1-ol as a minor component.

2. Structural commentary

The crystal structure (Fig. 1) exhibits two superimposed molecules with occupancies of 93% and 7%: this was surprising since the formation of the minor (enol) component was quite unexpected. A possible mechanism for the formation of this component is shown in Fig. 2. Equilibria between keto and enol isomers are regularly observed in solution but not in crystals. This issue needs a thorough exploration, which is beyond the scope of this report.

The molecular structures show similar conformations but differ in bond lengths and the carbon-atom geometry (hybridization), which we will describe for the major component in more detail. The molecular structure (Fig. 1) is composed of

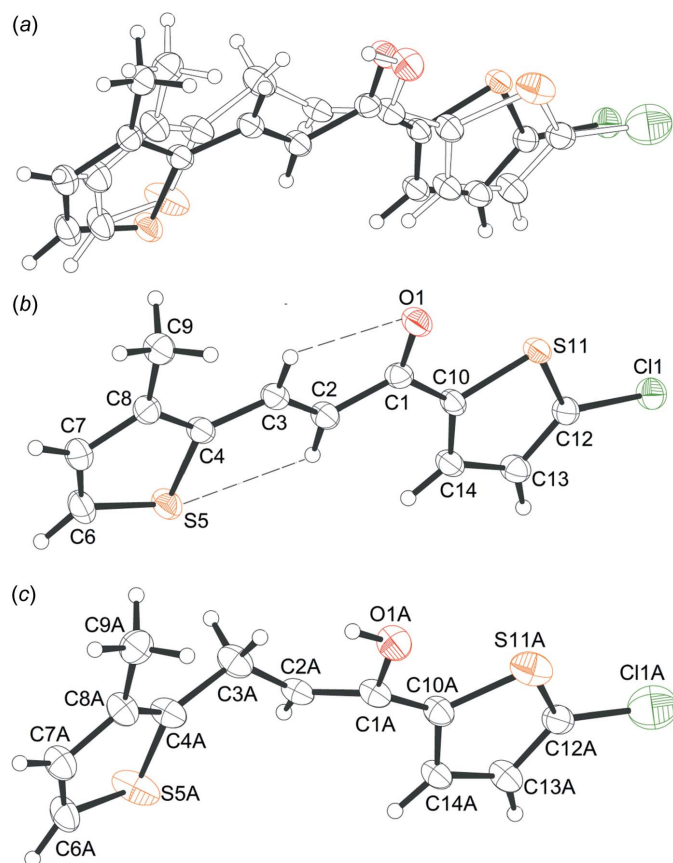


Figure 1
(a) The molecular structure of the title co-crystal showing the superposition of the two components, whose occupancies are 93% (black bonds) and 7% (white bonds), (b) the molecular structure with the atom-labelling scheme of the major component and (c) the minor component. Displacement ellipsoids are drawn at the 50% 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>
C3–H3···O1	0.95	2.48	2.818 (3)	101
C2–H2···S5	0.95	2.80	3.166 (2)	104
C13–H13···O1 ⁱ	0.95	2.35	3.184 (4)	146
C9–H9C···O1 ⁱⁱ	0.98	2.58	3.488 (4)	154
C6–H6···S11 ⁱⁱⁱ	0.95	3.04	3.948 (2)	160

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

two substituted thiophene rings, 5-chlorothiophen-2-yl and 3-methylthiophen-2-yl, which are linked by the central –CO–CH=CH– spacer. The configuration about the C=C bond [1.344 (3) Å] is *E* and the carbonyl group is *syn* with respect to the C=C bond. The molecule is effectively planar as indicated by the torsion angles O1–C1–C10–C14 = 175.0 (3), C2–C1–C10–C14 = –5.2 (3), C10–C1–C2–C3 = 176.41 (19), O1–C1–C2–C3 = –3.8 (3), C1–C2–C3–C4 = 179.37 (19) and C2–C3–C4–C8 = –177.5 (2)°. The hydrogen atoms of the propenone unit are *trans* configured and each is involved in an intramolecular short contact that forms an *S*(5) motif (Fig. 1, Table 1). The bond lengths and angles are consistent with those in related structures (Vu Quoc *et al.*, 2019; Yesilyurt *et al.*, 2018; Sreenatha *et al.*, 2018). The S atoms of the terminal 5-chlorothiophen-2-yl (S11/C10/C12–C14) and 3-methylthiophen-2-yl (S5/C4/C6–C8) rings are *anti* and the rings are inclined slightly to each other [dihedral angle = 6.92 (13)°].

3. Supramolecular features

The extended structure exhibits several hydrogen-bonding contacts (Table 1). The hydrogen bonds involve a carbonyl O atom serving as a double-acceptor with H atoms from the chlorothiophenyl unit, and a methyl group from the methylthiophenyl unit of a neighbouring molecule. Additional C–H···S contacts are also present (Table 1). Further interactions are detected, namely Cl···Cl [C12–C11···Cl1ⁱ of 3.3907 (8) Å and 142.92 (8)°; symmetry code: (i) $-x, 2 - y, 2 - z$], C–Cl··· π [C12–C115···Cgⁱⁱ = 3.6536 (14) Å]; symmetry code:

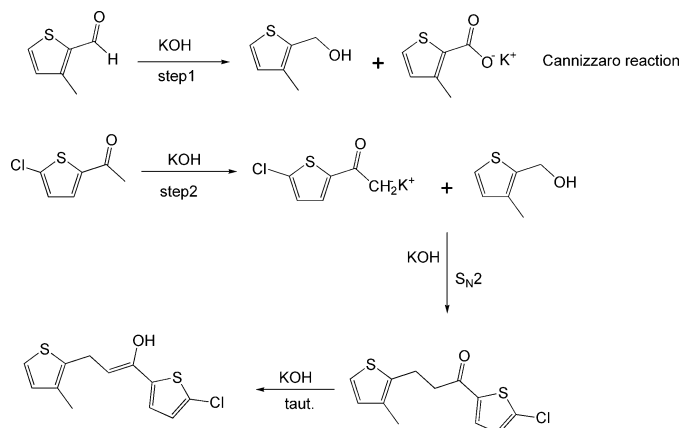


Figure 2
Possible mechanism for the formation of the minor enol component.

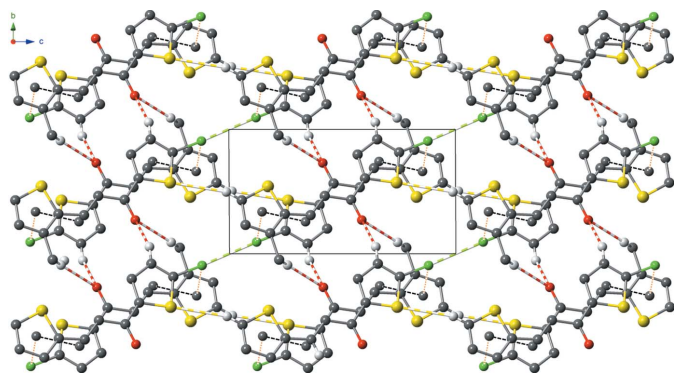


Figure 3
Overall packing of the major component with all intermolecular interactions (dotted and dashed lines) shown.

(ii) $1 - x, 1 - y, 1 - z$; Cg1 is the centroid of the S5/C4/C6–C8 ring] as well as π – π contacts [Cg1...Cg2ⁱⁱⁱ of 4.0139 (15) Å; symmetry code: (iii) $-x, 1 - y, 1 - z$; Cg2 is the centroid of the S11/C10/C12–C14 ring], which connect neighbouring molecules, consolidating a rather compact three-dimensional supramolecular network (Fig. 3).

4. Database survey

Similar structures to the title compound (major component) with the same chalcone skeleton and one or two thiophenyl rings include the following, which are identified by their CSD (Groom *et al.*, 2016) reference codes. In all compounds, the molecular skeletons are approximately planar, and have an *E* configuration about the C=C bond.

The structures containing one thiophenyl rings include: 1-(5-chloro-2-thienyl)-3-(2,3,4-trimethoxyphenyl)prop-2-en-1-one (refcode LOVHAH; Chidan Kumar *et al.*, 2015), where the molecular structure features intramolecular C–H...O interactions. The molecules in 1-(4-bromophenyl)-3-(3-methyl-2-thienyl)prop-2-en-1-one (XICNON; Fun *et al.*, 2007), feature short intramolecular C–H...O/S contacts, which form S(5) rings. In the crystal structure, the molecules are linked into layers by weak C–H...O hydrogen bonds, and short Br...O contacts are also observed. In 1-(2-hydroxyphenyl)-3-(5-methylthiophen-2-yl)prop-2-en-1-one (AGEFUQ; Sreenatha *et al.*, 2018), the structure exhibits O–H...O and C–H...O/S intramolecular interactions.

The structures of bis-thiophenyl chalcones include 2,6-(*E,E*)-bis[(thiophene-2-yl)methylene]cyclohexanone (BOQYAK; Yakalı *et al.*, 2019) in which the terminal thiophene rings adopt a *syn* orientation. In the structure, the molecules display weak C–H...S and C–H...O intramolecular and only C–H...O intermolecular hydrogen bonds. In addition, π – π interactions are found between the thiophene rings. In 1,5-bis(3-methyl-2-thienyl)penta-1,4-dien-3-one (RUZCIZ; Contreras *et al.*, 2009), the molecule consists of terminal methylthiophenyl rings with the two S atoms being in a *syn* arrangement and *trans* to the carbonyl oxygen atom. The molecule is almost planar, with a slight twist along the bridging

Table 2
Experimental details.

Crystal data	
Chemical formula	0.93C ₁₂ H ₉ ClOS ₂ ·0.07C ₁₂ H ₁₁ ClOS ₂
<i>M_r</i>	268.90
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.3709 (4), 7.5063 (4), 12.4247 (6)
α , β , γ (°)	84.126 (4), 76.694 (4), 62.372 (4)
<i>V</i> (Å ³)	592.69 (6)
<i>Z</i>	2
Radiation type	Cu <i>K</i> α
μ (mm ^{−1})	5.93
Crystal size (mm)	0.25 × 0.21 × 0.14
Data collection	
Diffractometer	Stoe Stadivari
Absorption correction	Multi-scan (<i>LANA</i> ; Stoe, 2016)
<i>T_{min}</i> , <i>T_{max}</i>	0.079, 0.352
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	10865, 2398, 2221
<i>R_{int}</i>	0.024
(<i>sin</i> θ / λ) _{max} (Å ^{−1})	0.628
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.032, 0.088, 1.06
No. of reflections	2398
No. of parameters	291
No. of restraints	754
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ^{−3})	0.27, −0.28

Computer programs: *X-AREA* (Stoe & Cie, 2016), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b) and *DIAMOND* (Putz & Brandenburg, 2014).

unit, leading to a small rotation between the terminal thiophenyl rings. The molecules are connected *via* various types of intermolecular interactions, namely C–H...O, C–H... π and π – π , leading to a three-dimensional supramolecular network. The molecule of (2*E*,6*E*)-2,6-bis[(5-methylthiophen-2-yl)methylene]cyclohexanone (XILXUM; Liang *et al.*, 2007) displays two slightly twisted *syn* terminal methylthiophenyl rings in an *anti*-arrangement with respect to the carbonyl oxygen atom. In 1,5-bis(thiophen-3-yl)penta-1,4-dien-3-one (AYUPIU; Shalini *et al.*, 2011), the dihedral angle between the thiophenyl rings is 15.45 (10)°. The molecule features both C–H...O and C–H... π interactions. Both thiophene rings in 3-hydroxy-1-(thiophen-2-yl)-3-(thiophen-3-yl)prop-2-en-1-one (IBIRUJ; Oyarce *et al.*, 2017) are disordered with the major-disorder components inclined to each other by 12.1 (3)°. In the crystal, the molecules are connected through C–H...O interactions. In the crystal of 1,3-bis(3-thienyl)prop-2-en-1-one (UNAJIE; Baggio *et al.*, 2016), the thiophene rings are inclined to each other by a dihedral angle of 8.88 (10)°. The structure exhibits π – π interactions together with C–H...O interactions and short S...S contacts also occur.

5. Synthesis and crystallization

The synthesis was carried out using a reported method (Al-Maqtari *et al.*, 2015). Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation, at room temperature, of a solution in ethanol.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms were included in calculated positions ($C-H = 0.95-0.98 \text{ \AA}$) and refined using a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C\text{-methyl})$. Methyl groups were allowed to rotate about the bond to their next atom to fit the electron density.

The crystal structure was refined as a superposition of two molecular structures with formulae $C_{12}H_9ClO_2$ (93% occupancy component) and $C_{12}H_{11}ClO_2$ (7% occupancy component), respectively. Restraints were necessary during the refinement of geometric and anisotropic displacement parameters.

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Unexpected formation of a co-crystal containing the chalcone (*E*)-1-(5-chlorothiophen-2-yl)-3-(3-methylthiophen-2-yl)prop-2-en-1-one and the keto–enol tautomer (*Z*)-1-(5-chlorothiophen-2-yl)-3-(3-methylthiophen-2-yl)prop-1-en-1-ol

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Computing details

Data collection: *X-AREA* (Stoe & Cie, 2016); cell refinement: *X-AREA* (Stoe & Cie, 2016); data reduction: *X-AREA* (Stoe & Cie, 2016); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Putz & Brandenburg, 2014); software used to prepare material for publication: *X-AREA* (Stoe & Cie, 2016).

(*E*)-1-(5-Chlorothiophen-2-yl)-3-(3-methylthiophen-2-yl)prop-2-en-1-one–(*Z*)-1-(5-chlorothiophen-2-yl)-3-(3-methylthiophen-2-yl)prop-1-en-1-ol (0.93/0/07)

Crystal data

0.93C₁₂H₉ClOS₂·0.07C₁₂H₁₁ClOS₂

M_r = 268.90

Triclinic, *P*1̄

a = 7.3709 (4) Å

b = 7.5063 (4) Å

c = 12.4247 (6) Å

α = 84.126 (4)°

β = 76.694 (4)°

γ = 62.372 (4)°

V = 592.69 (6) Å³

Z = 2

F(000) = 276

D_x = 1.507 Mg m⁻³

Cu *K*α radiation, λ = 1.54186 Å

Cell parameters from 17498 reflections

θ = 3.7–76.0°

μ = 5.93 mm⁻¹

T = 100 K

Plate, yellow

0.25 × 0.21 × 0.14 mm

Data collection

Stoe Stadivari
diffractometer

Radiation source: GeniX 3D HF Cu

Detector resolution: 5.81 pixels mm⁻¹

rotation method, ω scans

Absorption correction: multi-scan
(*LANA*; Stoe, 2016)

T_{min} = 0.079, *T_{max}* = 0.352

10865 measured reflections

2398 independent reflections

2221 reflections with *I* > 2σ(*I*)

R_{int} = 0.024

θ_{max} = 75.5°, θ_{min} = 6.7°

h = -5→9

k = -8→9

l = -13→15

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.032

wR(*F*²) = 0.088

S = 1.06

2398 reflections

291 parameters
 754 restraints
 Primary atom site location: dual
 Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 0.4005P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.27 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$

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.

Refinement. The crystal structure is an overlay of two molecular structure with ratio 93:7.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	0.3137 (4)	0.2710 (3)	0.5851 (2)	0.0314 (5)	0.93
C1	0.2726 (3)	0.4337 (3)	0.53882 (16)	0.0247 (4)	0.93
C2	0.2535 (3)	0.4652 (3)	0.42238 (15)	0.0259 (4)	0.93
H2	0.213137	0.595628	0.391242	0.031*	0.93
C3	0.2928 (3)	0.3105 (3)	0.35969 (16)	0.0259 (4)	0.93
H3	0.334120	0.182539	0.394094	0.031*	0.93
C4	0.2784 (3)	0.3201 (3)	0.24557 (16)	0.0256 (4)	0.93
S5	0.21123 (9)	0.54296 (8)	0.17199 (4)	0.03242 (16)	0.93
C6	0.2248 (4)	0.4291 (4)	0.05595 (18)	0.0348 (5)	0.93
H6	0.198313	0.496677	-0.011889	0.042*	0.93
C7	0.2777 (4)	0.2310 (3)	0.07204 (18)	0.0314 (4)	0.93
H7	0.291283	0.145132	0.016418	0.038*	0.93
C8	0.3110 (3)	0.1643 (3)	0.18065 (17)	0.0262 (4)	0.93
C9	0.3748 (4)	-0.0483 (3)	0.21906 (19)	0.0312 (5)	0.93
H9A	0.422423	-0.136716	0.154993	0.047*	0.93
H9B	0.254852	-0.057161	0.268618	0.047*	0.93
H9C	0.488738	-0.090123	0.258667	0.047*	0.93
C10	0.2397 (3)	0.6067 (3)	0.60062 (16)	0.0233 (4)	0.93
S11	0.24466 (9)	0.57165 (8)	0.74011 (4)	0.02410 (15)	0.93
C12	0.1984 (3)	0.8151 (3)	0.75171 (17)	0.0251 (4)	0.93
C13	0.1837 (3)	0.9193 (3)	0.65490 (19)	0.0276 (4)	0.93
H13	0.161182	1.054853	0.646974	0.033*	0.93
C14	0.2066 (4)	0.7980 (3)	0.56787 (18)	0.0268 (4)	0.93
H14	0.199724	0.844259	0.494119	0.032*	0.93
C11	0.17230 (10)	0.90570 (8)	0.87916 (4)	0.03112 (15)	0.93
O1A	0.354 (6)	0.286 (4)	0.602 (3)	0.035 (6)	0.07
H1A	0.343705	0.215573	0.557340	0.053*	0.07
C1A	0.257 (5)	0.496 (4)	0.569 (2)	0.028 (3)	0.07
C2A	0.126 (4)	0.535 (4)	0.497 (2)	0.029 (3)	0.07
H2A	0.031913	0.671106	0.487244	0.035*	0.07
C3A	0.121 (5)	0.385 (4)	0.435 (2)	0.034 (3)	0.07

H3A	-0.022191	0.397317	0.458163	0.041*	0.07
H3B	0.216209	0.252274	0.460874	0.041*	0.07
C4A	0.175 (5)	0.377 (3)	0.3079 (17)	0.032 (3)	0.07
S5A	0.1043 (15)	0.6046 (12)	0.2374 (7)	0.0485 (18)	0.07
C6A	0.200 (5)	0.482 (3)	0.1107 (16)	0.034 (3)	0.07
H6A	0.209319	0.547565	0.041533	0.041*	0.07
C7A	0.260 (5)	0.281 (3)	0.1218 (18)	0.035 (3)	0.07
H7A	0.296091	0.192728	0.062046	0.042*	0.07
C8A	0.261 (5)	0.219 (3)	0.2331 (19)	0.032 (3)	0.07
C9A	0.331 (5)	0.001 (3)	0.272 (3)	0.036 (5)	0.07
H9AA	0.370744	-0.086268	0.208833	0.053*	0.07
H9AB	0.214815	-0.008058	0.325911	0.053*	0.07
H9AC	0.450522	-0.041072	0.307367	0.053*	0.07
C10A	0.262 (5)	0.615 (4)	0.6395 (18)	0.029 (2)	0.07
S11A	0.3211 (17)	0.5574 (13)	0.7707 (9)	0.0450 (19)	0.07
C12A	0.238 (5)	0.810 (3)	0.7933 (17)	0.031 (3)	0.07
C13A	0.213 (5)	0.918 (4)	0.6986 (19)	0.032 (3)	0.07
H13A	0.186143	1.054308	0.694311	0.039*	0.07
C14A	0.228 (5)	0.812 (4)	0.6075 (19)	0.029 (3)	0.07
H14A	0.217023	0.865457	0.535253	0.034*	0.07
Cl1A	0.255 (2)	0.8778 (18)	0.9186 (11)	0.067 (3)	0.07

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0477 (13)	0.0282 (8)	0.0229 (10)	-0.0213 (8)	-0.0077 (7)	0.0027 (6)
C1	0.0291 (10)	0.0248 (10)	0.0217 (10)	-0.0149 (8)	-0.0016 (8)	-0.0017 (7)
C2	0.0297 (9)	0.0260 (9)	0.0215 (9)	-0.0130 (8)	-0.0042 (7)	0.0013 (7)
C3	0.0287 (10)	0.0281 (9)	0.0216 (9)	-0.0146 (8)	-0.0034 (7)	0.0017 (7)
C4	0.0308 (10)	0.0251 (9)	0.0214 (9)	-0.0141 (8)	-0.0040 (8)	0.0013 (7)
S5	0.0476 (3)	0.0276 (3)	0.0260 (3)	-0.0194 (2)	-0.0118 (2)	0.0051 (2)
C6	0.0465 (12)	0.0405 (12)	0.0214 (9)	-0.0218 (10)	-0.0108 (9)	0.0027 (9)
C7	0.0373 (11)	0.0359 (11)	0.0224 (9)	-0.0177 (9)	-0.0050 (8)	-0.0031 (8)
C8	0.0273 (10)	0.0290 (10)	0.0221 (9)	-0.0132 (8)	-0.0025 (8)	-0.0028 (8)
C9	0.0366 (12)	0.0267 (10)	0.0285 (11)	-0.0132 (9)	-0.0047 (9)	-0.0028 (9)
C10	0.0282 (10)	0.0259 (9)	0.0156 (9)	-0.0130 (7)	-0.0027 (8)	0.0001 (8)
S11	0.0318 (3)	0.0229 (2)	0.0182 (2)	-0.0139 (2)	-0.0033 (2)	0.00121 (18)
C12	0.0315 (10)	0.0249 (9)	0.0207 (9)	-0.0146 (8)	-0.0030 (8)	-0.0036 (8)
C13	0.0327 (11)	0.0245 (9)	0.0252 (10)	-0.0136 (8)	-0.0049 (9)	0.0016 (8)
C14	0.0329 (10)	0.0280 (10)	0.0201 (9)	-0.0154 (8)	-0.0048 (8)	0.0035 (8)
Cl1	0.0378 (3)	0.0319 (3)	0.0246 (3)	-0.0173 (2)	-0.0021 (2)	-0.00631 (19)
O1A	0.045 (11)	0.024 (6)	0.034 (10)	-0.013 (7)	-0.008 (8)	-0.002 (7)
C1A	0.033 (4)	0.027 (4)	0.022 (4)	-0.013 (4)	-0.002 (4)	0.002 (4)
C2A	0.034 (4)	0.028 (4)	0.022 (4)	-0.015 (4)	-0.002 (4)	0.005 (4)
C3A	0.038 (5)	0.030 (5)	0.027 (4)	-0.011 (4)	-0.002 (4)	0.000 (4)
C4A	0.039 (4)	0.028 (4)	0.026 (4)	-0.014 (4)	-0.001 (4)	0.002 (4)
S5A	0.057 (4)	0.035 (3)	0.036 (3)	-0.014 (3)	0.006 (3)	0.005 (3)
C6A	0.047 (4)	0.032 (4)	0.022 (4)	-0.016 (4)	-0.009 (4)	-0.002 (4)

C7A	0.041 (4)	0.035 (4)	0.026 (4)	-0.015 (4)	-0.006 (4)	-0.001 (4)
C8A	0.035 (4)	0.032 (4)	0.025 (4)	-0.012 (4)	-0.005 (4)	0.000 (3)
C9A	0.031 (9)	0.035 (7)	0.039 (10)	-0.014 (7)	-0.007 (9)	-0.002 (7)
C10A	0.034 (4)	0.027 (3)	0.023 (4)	-0.013 (3)	-0.004 (3)	0.000 (3)
S11A	0.045 (4)	0.040 (3)	0.044 (4)	-0.018 (3)	-0.005 (3)	0.008 (3)
C12A	0.036 (4)	0.031 (4)	0.027 (4)	-0.018 (4)	-0.004 (4)	0.001 (4)
C13A	0.038 (5)	0.029 (4)	0.024 (4)	-0.012 (4)	-0.004 (4)	0.001 (4)
C14A	0.035 (4)	0.028 (4)	0.020 (4)	-0.014 (4)	-0.003 (4)	0.002 (4)
C11A	0.059 (6)	0.068 (6)	0.070 (7)	-0.030 (5)	-0.004 (5)	-0.001 (5)

Geometric parameters (Å, °)

O1—C1	1.227 (3)	O1A—H1A	0.8400
C1—C10	1.470 (3)	C1A—C10A	1.328 (10)
C1—C2	1.470 (3)	C1A—C2A	1.38 (4)
C2—C3	1.344 (3)	C2A—C3A	1.44 (4)
C2—H2	0.9500	C2A—H2A	0.9500
C3—C4	1.438 (3)	C3A—C4A	1.54 (3)
C3—H3	0.9500	C3A—H3A	0.9900
C4—C8	1.385 (3)	C3A—H3B	0.9900
C4—S5	1.734 (2)	C4A—C8A	1.386 (18)
S5—C6	1.711 (2)	C4A—S5A	1.744 (16)
C6—C7	1.356 (3)	S5A—C6A	1.734 (18)
C6—H6	0.9500	C6A—C7A	1.367 (18)
C7—C8	1.425 (3)	C6A—H6A	0.9500
C7—H7	0.9500	C7A—C8A	1.414 (18)
C8—C9	1.499 (3)	C7A—H7A	0.9500
C9—H9A	0.9800	C8A—C9A	1.531 (17)
C9—H9B	0.9800	C9A—H9AA	0.9800
C9—H9C	0.9800	C9A—H9AB	0.9800
C10—C14	1.374 (3)	C9A—H9AC	0.9800
C10—S11	1.732 (2)	C10A—C14A	1.412 (18)
S11—C12	1.712 (2)	C10A—S11A	1.743 (18)
C12—C13	1.364 (3)	S11A—C12A	1.735 (17)
C12—C11	1.722 (2)	C12A—C13A	1.356 (18)
C13—C14	1.415 (3)	C12A—C11A	1.732 (17)
C13—H13	0.9500	C13A—C14A	1.399 (19)
C14—H14	0.9500	C13A—H13A	0.9500
O1A—C1A	1.453 (10)	C14A—H14A	0.9500
O1—C1—C10	119.75 (19)	C10A—C1A—O1A	112 (2)
O1—C1—C2	122.7 (2)	C2A—C1A—O1A	113 (2)
C10—C1—C2	117.52 (17)	C1A—C2A—C3A	126 (3)
C3—C2—C1	120.42 (18)	C1A—C2A—H2A	117.2
C3—C2—H2	119.8	C3A—C2A—H2A	117.2
C1—C2—H2	119.8	C2A—C3A—C4A	123 (2)
C2—C3—C4	126.27 (19)	C2A—C3A—H3A	106.7
C2—C3—H3	116.9	C4A—C3A—H3A	106.7

C4—C3—H3	116.9	C2A—C3A—H3B	106.7
C8—C4—C3	127.20 (18)	C4A—C3A—H3B	106.7
C8—C4—S5	111.23 (14)	H3A—C3A—H3B	106.6
C3—C4—S5	121.56 (15)	C8A—C4A—C3A	132.5 (18)
C6—S5—C4	91.72 (10)	C8A—C4A—S5A	110.0 (13)
C7—C6—S5	112.16 (16)	C3A—C4A—S5A	117.4 (16)
C7—C6—H6	123.9	C6A—S5A—C4A	91.4 (10)
S5—C6—H6	123.9	C7A—C6A—S5A	112.2 (15)
C6—C7—C8	113.4 (2)	C7A—C6A—H6A	123.9
C6—C7—H7	123.3	S5A—C6A—H6A	123.9
C8—C7—H7	123.3	C6A—C7A—C8A	111.7 (18)
C4—C8—C7	111.53 (18)	C6A—C7A—H7A	124.2
C4—C8—C9	124.48 (19)	C8A—C7A—H7A	124.2
C7—C8—C9	123.99 (19)	C4A—C8A—C7A	113.9 (16)
C8—C9—H9A	109.5	C4A—C8A—C9A	121.3 (19)
C8—C9—H9B	109.5	C7A—C8A—C9A	125 (2)
H9A—C9—H9B	109.5	C8A—C9A—H9AA	109.5
C8—C9—H9C	109.5	C8A—C9A—H9AB	109.5
H9A—C9—H9C	109.5	H9AA—C9A—H9AB	109.5
H9B—C9—H9C	109.5	C8A—C9A—H9AC	109.5
C14—C10—C1	131.62 (19)	H9AA—C9A—H9AC	109.5
C14—C10—S11	111.50 (16)	H9AB—C9A—H9AC	109.5
C1—C10—S11	116.88 (14)	C1A—C10A—C14A	120 (2)
C12—S11—C10	90.29 (10)	C1A—C10A—S11A	128.3 (19)
C13—C12—S11	114.16 (16)	C14A—C10A—S11A	111.9 (14)
C13—C12—C11	126.56 (16)	C12A—S11A—C10A	89.6 (10)
S11—C12—C11	119.28 (12)	C13A—C12A—C11A	129.0 (16)
C12—C13—C14	110.72 (18)	C13A—C12A—S11A	111.6 (14)
C12—C13—H13	124.6	C11A—C12A—S11A	117.7 (12)
C14—C13—H13	124.6	C12A—C13A—C14A	115.1 (17)
C10—C14—C13	113.32 (18)	C12A—C13A—H13A	122.4
C10—C14—H14	123.3	C14A—C13A—H13A	122.4
C13—C14—H14	123.3	C13A—C14A—C10A	109.6 (17)
C1A—O1A—H1A	109.5	C13A—C14A—H14A	125.2
C10A—C1A—C2A	131 (3)	C10A—C14A—H14A	125.2
O1—C1—C2—C3	-3.8 (3)	C10A—C1A—C2A—C3A	-171 (3)
C10—C1—C2—C3	176.41 (19)	O1A—C1A—C2A—C3A	-16 (5)
C1—C2—C3—C4	179.37 (19)	C1A—C2A—C3A—C4A	-117 (3)
C2—C3—C4—C8	-177.5 (2)	C2A—C3A—C4A—C8A	150 (3)
C2—C3—C4—S5	1.6 (3)	C2A—C3A—C4A—S5A	-35 (4)
C8—C4—S5—C6	0.42 (17)	C8A—C4A—S5A—C6A	-2 (3)
C3—C4—S5—C6	-178.88 (18)	C3A—C4A—S5A—C6A	-178 (3)
C4—S5—C6—C7	0.04 (19)	C4A—S5A—C6A—C7A	7 (3)
S5—C6—C7—C8	-0.5 (3)	S5A—C6A—C7A—C8A	-10 (4)
C3—C4—C8—C7	178.5 (2)	C3A—C4A—C8A—C7A	172 (3)
S5—C4—C8—C7	-0.7 (2)	S5A—C4A—C8A—C7A	-3 (4)
C3—C4—C8—C9	-1.9 (3)	C3A—C4A—C8A—C9A	-2 (6)

S5—C4—C8—C9	178.87 (17)	S5A—C4A—C8A—C9A	-178 (2)
C6—C7—C8—C4	0.8 (3)	C6A—C7A—C8A—C4A	9 (4)
C6—C7—C8—C9	-178.8 (2)	C6A—C7A—C8A—C9A	-177 (3)
O1—C1—C10—C14	175.0 (3)	C2A—C1A—C10A—C14A	-41 (6)
C2—C1—C10—C14	-5.2 (3)	O1A—C1A—C10A—C14A	163 (3)
O1—C1—C10—S11	-4.2 (3)	C2A—C1A—C10A—S11A	143 (3)
C2—C1—C10—S11	175.62 (15)	O1A—C1A—C10A—S11A	-13 (5)
C14—C10—S11—C12	0.86 (17)	C1A—C10A—S11A—C12A	-170 (4)
C1—C10—S11—C12	-179.83 (17)	C14A—C10A—S11A—C12A	13 (3)
C10—S11—C12—C13	-1.24 (18)	C10A—S11A—C12A—C13A	-12 (3)
C10—S11—C12—C11	178.05 (14)	C10A—S11A—C12A—C11A	-179 (2)
S11—C12—C13—C14	1.3 (3)	C11A—C12A—C13A—C14A	173 (3)
C11—C12—C13—C14	-177.96 (16)	S11A—C12A—C13A—C14A	9 (4)
C1—C10—C14—C13	-179.5 (2)	C12A—C13A—C14A—C10A	2 (4)
S11—C10—C14—C13	-0.3 (2)	C1A—C10A—C14A—C13A	172 (3)
C12—C13—C14—C10	-0.6 (3)	S11A—C10A—C14A—C13A	-11 (4)

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>
C3—H3 \cdots O1	0.95	2.48	2.818 (3)	101
C2—H2 \cdots S5	0.95	2.80	3.166 (2)	104
C13—H13 \cdots O1 ⁱ	0.95	2.35	3.184 (4)	146
C9—H9C \cdots O1 ⁱⁱ	0.98	2.58	3.488 (4)	154
C6—H6 \cdots S11 ⁱⁱⁱ	0.95	3.04	3.948 (2)	160

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