Acta Cryst C
STRUCTURAL
CHEMISTRY

ISSN 2053-2296

Synthesis and characterization of coumarin-derived sulfur analogues using Lawesson's reagent

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Received 11 November 2024
Accepted 2 February 2025

Edited by A. Lemmerer, University of the Witwatersrand, South Africa

Keywords: coumarin; thionation; UV–Vis absorption; crystal structure; Hirshfeld surface; energy framework; topology; Lawesson's reagent; Knoevenagel; chemosensor.

CCDC references: 2421185; 2421184; 2421183; 2354585; 2354584; 2354583

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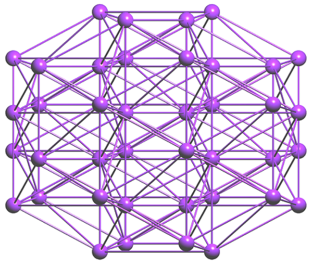
The synthesis and characterization of six novel coumarin derivatives containing O and S atoms are described here, namely, ethyl 2-oxo-2*H*-chromene-3-carboxylate, $C_{12}H_{10}O_4$ (**S1a**), ethyl 2-sulfanylidene-2*H*-chromene-3-carboxylate, $C_{12}H_{10}O_3S$ (**S2a**), ethyl 2-sulfanylidene-2*H*-chromene-3-carbothioate, $C_{12}H_{10}O_2S_2$ (**S3a**), ethyl 8-methoxy-2-oxo-2*H*-chromene-3-carboxylate, $C_{13}H_{12}O_5$ (**S1b**), ethyl 8-methoxy-2-sulfanylidene-2*H*-chromene-3-carboxylate, $C_{13}H_{12}O_4S$ (**S2b**), and ethyl 8-methoxy-2-sulfanylidene-2*H*-chromene-3-carbothioate, $C_{13}H_{12}O_3S_2$ (**S3b**). Compounds **S1a/b** were synthesized in good yields following the Knoevenagel condensation method. The thiocarbonyl analogues of these compounds, **S2a/b** and **S3a/b**, were obtained using Lawesson's reagent as a thionating compound. The structures of **S2a/b** and **S3a/b** were confirmed using FT–IR, ^{1}H and ^{13}C NMR, and UV–Vis spectroscopy, and single-crystal X-ray diffraction. Hirshfeld surface and energy framework analyses show that stacked π–π ring interactions occur for all the structures obtained here, and various hydrogen-bond interactions link the stacks to form three-dimensional energy frameworks.

1. Introduction

Coumarin derivatives are heterocyclic compounds that occur naturally and were first isolated from tonka beans in 1820 by Vogel (Matos *et al.*, 2015). Various reactions can be used to synthesize coumarin-based compounds. These reactions include the Perkin, Claisen, Pechmann, Heck lactonization, Baylis–Hillman, Michael, Wittig, Knoevenagel, Reformatsky and Kostanecki reactions. Coumarin derivatives are essential due to their various uses, such as photosensitizers, fluorescent materials, optical brighteners, laser dyes and pharmaceuticals (Liu *et al.*, 2012; Bakhtiari *et al.*, 2014; Zhang *et al.*, 2016; Abdallah *et al.*, 2020). In addition, these compounds possess desirable characteristics which include good spectral properties, the ability to undergo multiple substitution reactions offering versatility in chemical modification and the ability to carry out electrophilic substitution reactions to obtain various coumarin derivatives (Bojtár *et al.*, 2019; Olson *et al.*, 2013; Hansen *et al.*, 2015). Lawesson's reagent (Fig. 1) is a sulfur-rich thionating reagent that can be used in the conversion of carbonyl oxygen to form the corresponding thiocarbonyl analogues (Kayukova *et al.*, 2015; Jesberger *et al.*, 2003; Khatoon & Abdulmalek, 2021).

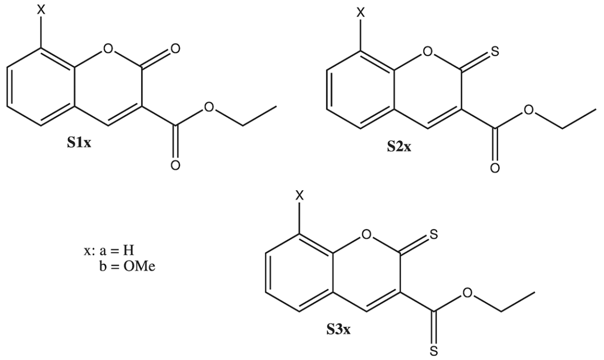
The compounds ethyl 2-oxo-2*H*-chromene-3-carboxylate (**S1a**), ethyl 2-sulfanylidene-2*H*-chromene-3-carboxylate (**S2a**), ethyl 2-sulfanylidene-2*H*-chromene-3-carbothioate (**S3a**), ethyl 8-methoxy-2-oxo-2*H*-chromene-3-carboxylate (**S1b**), ethyl 8-methoxy-2-sulfanylidene-2*H*-chromene-3-carboxylate (**S2b**) and ethyl 8-methoxy-2-sulfanylidene-2*H*-chromene-3-carbothioate (**S3b**) (Scheme 1) were prepared and characterized.



2. Experimental

2.1. Materials and procedures

The chemicals that were used in the synthesis and analysis of compounds **S1–S3** were purchased from Sigma Merck and were used without purification. The synthesis reactions were monitored using thin-layer chromatography (TLC) and nuclear magnetic resonance (NMR) and IR spectroscopy. The TLC plates that were used to monitor the reactions were aluminium sheets coated with silica gel 60 F254 and were viewed under UV light to confirm the formation of various products. The relevant NMR samples were prepared using $CDCl_3$ with tetramethylsilane (TMS) as an internal reference. The NMR chemical shifts are recorded in parts per million (ppm) and the coupling constants are recorded in Hz.



Scheme 1

2.2. Synthesis of coumarin derivatives S1 (Patil *et al.*, 2011)

Compounds **S1a** and **S1b** were prepared by refluxing a mixture containing equimolar quantities of diethyl malonate (0.01 *M*) and a salicylaldehyde derivative (0.01 *M*) in ethanol (25 ml) in the presence of 1 ml of piperidine and 5 drops of glacial acetic acid for 3 h. The mixture was placed on ice and the resulting precipitate was filtered off, washed with ice-cold ethanol and dried to yield **S1a** as a white solid and **S1b** as a yellow solid.

Analytical data for **S1a**: yield 95%. ^{1}H NMR ($CDCl_3$): δ 1.33–1.37 (*t*, 3H), 3.91 (*s*, 3H), 4.32–4.37 (*q*, 2H), 7.12–7.22 (*m*, 3H), 8.43 (*s*, 1H). ^{13}C NMR ($CDCl_3$): δ 14.18, 56.27, 61.84, 115.86, 118.29, 118.35, 120.60, 124.74, 144.70, 146.94, 148.74, 156.12, 162.92. IR $\nu_{\max}$ (cm^{-1}): 3040–2854 (C—H), 1735 (C=O), 1701 (C=O).

Analytical data for **S1b**: yield 47%. ^{1}H NMR: ($CDCl_3$): δ 1.42–1.45 (*t*, 3H), 4.41–4.47 (*q*, 2H), 7.34–7.39 (*m*, 2H), 7.63–7.69 (*m*, 2H), 8.54 (*s*, 1H). ^{13}C NMR ($CDCl_3$): δ 14.24, 62.00, 116.82, 117.92, 118.42, 124.84, 129.49, 134.32, 148.57, 155.21, 156.71, 163.10. IR $\nu_{\max}$ (cm^{-1}): 3065–2914 (C—H), 1761 (C=O). M.p. 93–95 °C.

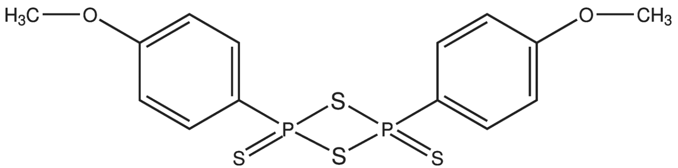
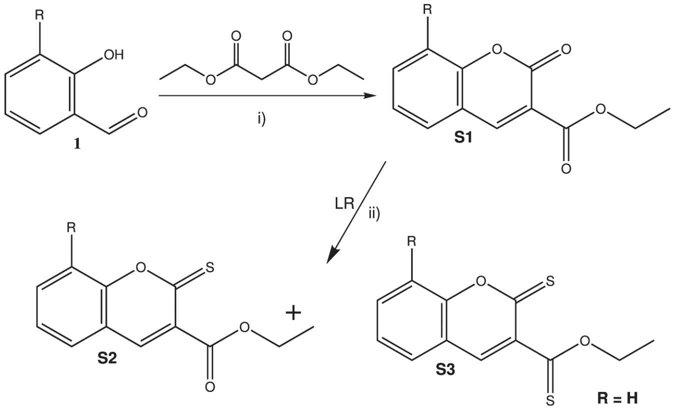


Figure 1
The molecular structure of Lawesson's reagent.

2.3. Preparation of S2 and S3

A mixture of coumarin derivative **S1a** or **S1b** and Lawesson's reagent (LR) was added in a 1:2 molar ratio to dry toluene (25 ml). The reaction mixture was refluxed under an N_2 atmosphere for 8 h (Scheme 2). The resulting solution was added to water and extracted three times using ethyl acetate. The extracts were washed with brine followed by water and dried using anhydrous Na_2SO_4. The ethyl acetate was removed under reduced pressure and the products were purified using preparative TLC (DCM–PET ether solvent).



Scheme 2

Analytical data for **S2a**, ^{1}H NMR ($CDCl_3$): δ 1.41–1.45 (*t*, 3H), 4.01 (*s*, 3H), 4.41–4.44 (*q*, 2H), 7.14–7.19 (*m*, 2H), 7.29–7.31 (*m*, 1H), 7.85 (*s*, 1H). ^{13}C NMR ($CDCl_3$): δ 14.06, 56.32, 62.24, 115.13, 119.78, 120.13, 125.69, 132.54, 135.72, 146.61, 146.98, 164.94, 191.38. IR $\nu_{\max}$ (cm^{-1}): 3022–2852 (C—H), 1728 (C=O).

Analytical data for **S2b**, ^{1}H NMR ($CDCl_3$): δ 1.42–1.45 (*t*, 3H), 4.41–4.47 (*q*, 2H), 7.36–7.39 (*t*, 1H), 7.48–7.61 (d-d, 2H), 7.66–7.70 (*t*, 1H), 7.88 (*s*, 1H). ^{13}C NMR ($CDCl_3$): δ 14.06, 62.28, 116.58, 119.44, 125.73, 128.76, 132.31, 133.78, 135.62, 157.01, 164.89, 192.16. IR $\nu_{\max}$ (cm^{-1}): 3055–2930 (C—H), 1718 (C=O). M.p. 80–84 °C.

Analytical data for **S3a**, ^{1}H NMR ($CDCl_3$): δ 1.51–1.54 (*t*, 3H), 4.01 (*s*, 3H), 4.71–4.76 (*q*, 2H), 7.13–7.16 (*m*, 2H), 7.28–7.29 (*m*, 1H), 7.74 (*s*, 1H). ^{13}C NMR ($CDCl_3$): δ 13.33, 25.32, 69.54, 114.53, 119.67, 120.69, 125.59, 133.97, 141.33, 146.61, 146.74, 191.63, 211.05. IR $\nu_{\max}$ (cm^{-1}): 3015–2845 (C—H).

Analytical data for **S3b**, ^{1}H NMR ($CDCl_3$): δ 1.51–1.55 (*t*, 3H), 4.71–4.77 (*q*, 2H), 7.34–7.38 (*t*, 1H), 7.48–7.60 (*dd*, 2H), 7.62–7.66 (*t*, 1H), 7.77 (*s*, 1H). ^{13}C NMR ($CDCl_3$) δ_C: 13.33, 69.56, 116.48, 119.97, 119.97, 125.64, 128.56, 133.06, 133.87, 141.11, 156.11, 192.40, 210.96. IR $\nu_{\max}$ (cm^{-1}): 3050–2840 (C—H). M.p. 77–82 °C.

2.4. Crystallization, refinement and analyses of the structures

Growing crystals for diffraction studies was achieved by slow vaporation from hexane. Crystal data, data collection and

Table 1
Experimental details.

Experiments were carried out with Mo $K\alpha$ radiation. H-atom parameters were constrained. **S3b** was refined as an inversion twin [0.28 (16)].

	S1a	**S2a**	**S3a**
Crystal data			
Chemical formula	$C_{12}H_{10}O_4$	$C_{12}H_{10}O_3S$	$C_{12}H_{10}O_2S_2$
M_r	218.20	234.26	250.32
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $C2/c$
Temperature (K)	296	200	200
a, b, c (Å)	7.9043 (7), 15.7768 (13), 8.7381 (7)	11.9040 (9), 7.1792 (5), 13.6794 (10)	12.5314 (5), 6.7175 (3), 27.7746 (10)
α, β, γ (°)	90, 108.115 (4), 90	90, 111.708 (3), 90	90, 92.7398 (14), 90
V (Å^3)	1035.67 (15)	1086.15 (14)	2335.38 (16)
Z	4	4	8
μ (mm^{-1})	0.11	0.29	0.44
Crystal size (mm)	1.00 × 0.75 × 0.44	0.87 × 0.66 × 0.58	0.30 × 0.16 × 0.11
Data collection			
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD	Bruker D8 QUEST
Absorption correction	Numerical (*SADABS*; Bruker, 2012)	Numerical (*SADABS*; Bruker, 2012)	Numerical (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.950, 1.000	0.941, 1.000	0.891, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19039, 2575, 2036	18714, 2710, 2368	27927, 2894, 2326
R_{int}	0.018	0.017	0.048
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.667	0.668	0.667
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.050, 0.141, 1.05	0.035, 0.105, 1.04	0.040, 0.100, 1.10
No. of reflections	2575	2710	2894
No. of parameters	146	146	146
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.35, −0.17	0.36, −0.26	0.30, −0.29

	S1b	**S2b**	**S3b**
Crystal data			
Chemical formula	$C_{13}H_{12}O_5$	$C_{13}H_{12}O_4S$	$C_{13}H_{12}O_3S_2$
M_r	248.23	264.29	280.35
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Orthorhombic, $P2_12_12_1$
Temperature (K)	200	199	200
a, b, c (Å)	6.8708 (3), 10.6766 (5), 15.7872 (8)	6.8534 (4), 11.2183 (7), 15.8581 (10)	6.9815 (3), 11.7185 (4), 15.9642 (5)
α, β, γ (°)	90, 100.253 (2), 90	90, 98.620 (2), 90	90, 90, 90
V (Å^3)	1139.60 (9)	1205.45 (13)	1306.07 (8)
Z	4	4	4
μ (mm^{-1})	0.11	0.27	0.40
Crystal size (mm)	1.17 × 0.83 × 0.51	0.67 × 0.62 × 0.50	0.48 × 0.15 × 0.15
Data collection			
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD	Bruker D8 QUEST
Absorption correction	Numerical (*SADABS*; Bruker, 2012)	Numerical (*SADABS*; Bruker, 2012)	Numerical (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.949, 1.000	0.938, 1.000	0.508, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	20764, 2822, 2493	20324, 2981, 2607	39191, 3236, 2716
R_{int}	0.023	0.021	0.091
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.667	0.667	0.666
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.035, 0.099, 1.07	0.035, 0.104, 1.04	0.055, 0.141, 1.24
No. of reflections	2822	2981	3236
No. of parameters	166	165	166
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.32, −0.21	0.40, −0.32	0.66, −0.43

Computer programs: *APEX2* (Bruker, 2012), *SAINT* (Bruker, 2012), *SHELXT2018* (Sheldrick, 2015*a*), *SHELXL2019* (Sheldrick, 2015*b*), *ShelXle* (Hübschle *et al.*, 2011), *ORTEP-3 for Windows* (Farrugia, 2012), *PLATON* (Spek, 2020) and *Mercury* (Macrae *et al.*, 2020).

structure refinement details are summarized in Table 1. All H atoms were placed in calculated positions and refined using a riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$. The H atoms of the methyl groups were allowed to rotate with a fixed angle around the C—C bonds to best fit the experimental electron density, with $U_{iso}(H) = 1.5U_{eq}(C)$. Structure **S3b** was refined as an inversion twin. Fig. 2 shows the molecular structures obtained (Farrugia, 2012). *CrystalExplorer* (Spackman *et al.*, 2021) was utilized to investigate the intermolecular interactions using the Hirshfeld surfaces, fingerprint

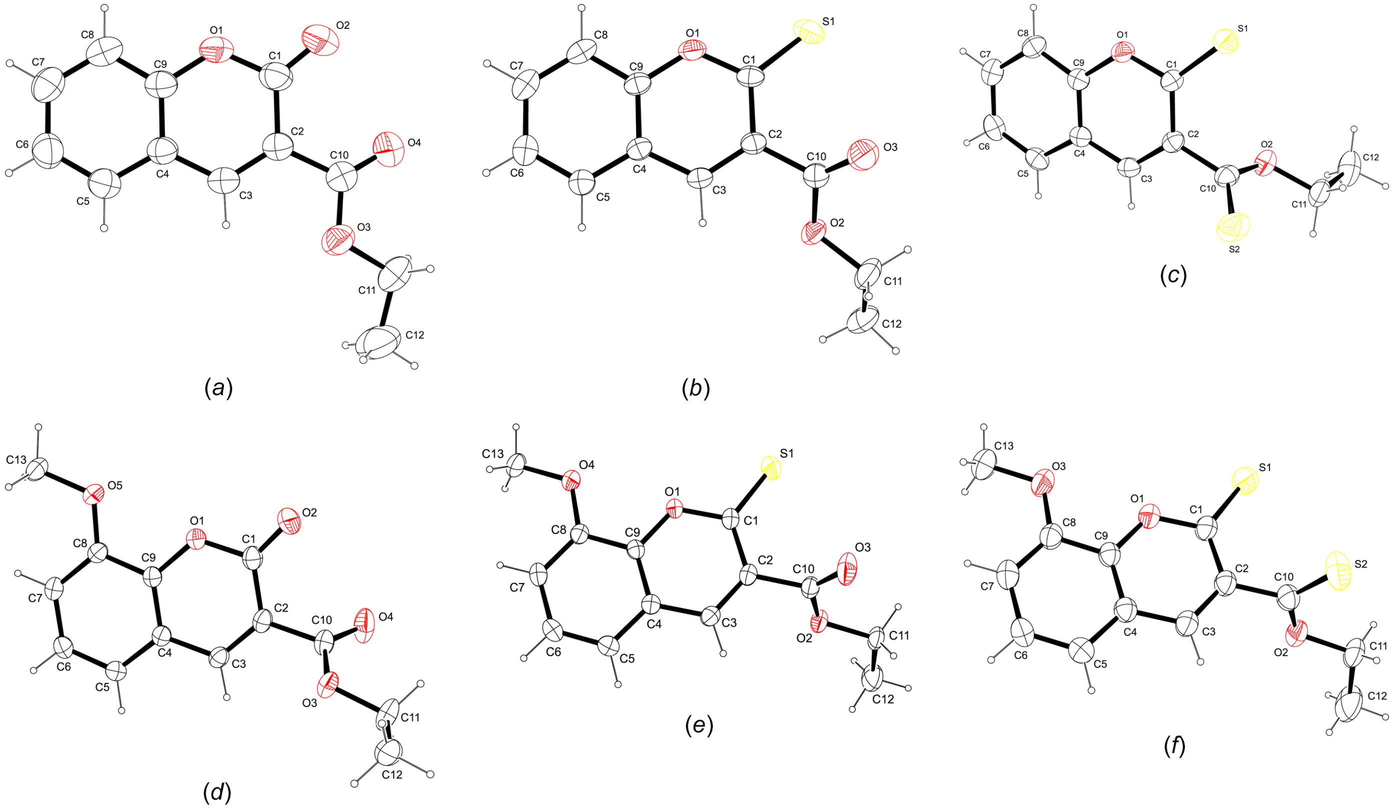


Figure 2
The molecular structures of (*a*) **S1a**, (*b*) **S2a**, (*c*) **S3a**, (*d*) **S1b**, (*e*) **S2b** and (*f*) **S3b**, showing the atom-labelling schemes. Displacement ellipsoids are drawn at the 50% probability level.

plots, energy frameworks and lattice energies (Tan *et al.*, 2019; Mackenzie *et al.*, 2017). The basis set B3LYP/631-G(d,p) was used for all calculations. The topologies of the electrostatic and van der Waals interactions were determined with *TopCryst* (Shevchenko & Blatov, 2021).

3. Results and discussion

3.1. Synthesis of coumarin derivatives S1–S3

The synthesis of coumarin ester derivatives **S1a/b** was achieved using the Knoevenagel condensation method, as outlined in Scheme 2. The reaction between coumarin ester derivatives and an excess of Lawesson's reagent was conducted in toluene under nitrogen gas to obtain thiocarbonyl analogues **S2** (major product) and **S3** (minor product) in good yields. The structures of these analogues were confirmed by FT–IR, ^{1}H NMR and ^{13}C NMR spectroscopic and X-ray crystallographic data.

3.2. UV–Vis absorption analysis of coumarin derivatives S1–S3

The absorption spectra of the coumarin derivatives **S1a/b**, **S2a/b** and **S3a/b** were obtained in acetonitrile and displayed absorbance properties in the region of 238–460 nm (Figs. 3 and

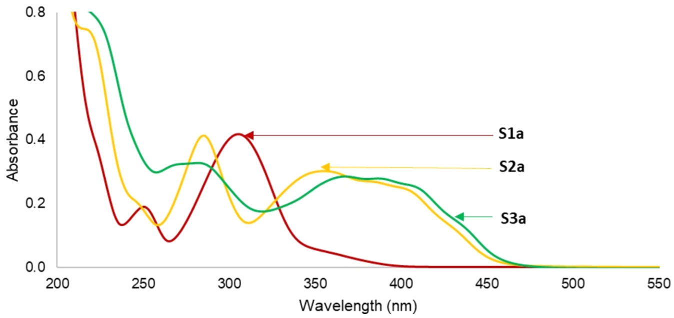


Figure 3
UV–Vis spectra of compounds **S1a**, **S2a** and **S3a** in acetonitrile medium.

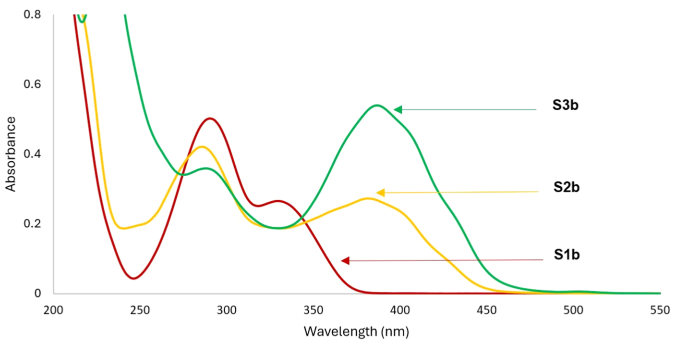


Figure 4
UV–Vis spectra of compounds **S1b**, **S2b** and **S3b** in acetonitrile medium.

Table 2
Hydrogen-bond geometry (Å,°) for **S1a**.

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···O3	0.93	2.38	2.7074 (18)	101
C6—H6···O2^{i}	0.93	2.72	3.352 (2)	126
C7—H7···O4^{i}	0.93	2.72	3.647 (2)	175
C8—H8···O2^{ii}	0.93	2.68	3.5281 (19)	153
C11—H11B···O4^{iii}	0.97	2.55	3.335 (2)	138

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

Table 3
Hydrogen-bond geometry (Å,°) for **S2a**.

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···S1^{i}	0.95	2.72	3.6489 (12)	166
C5—H5···O1^{i}	0.95	2.89	3.8188 (16)	167
C8—H8···O3^{ii}	0.95	2.54	3.4876 (19)	175
C12—H12A···S1^{iv}	0.98	3.07	4.0287 (16)	168
C12—H12B···O3^{iii}	0.98	2.69	3.567 (2)	150
C12—H12B···S1^{ii}	0.98	3.26	4.137 (6)	151
C12—H12C···S1^{i}	0.98	3.22	4.0821 (18)	148

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

4). The absorption spectra of **S1a** and **S1b** are characterized by intense absorption peaks near 270–350 nm, which could be attributed to π–π* transitions from the conjugated coumarin ring, whereas the less intense bands around 238–260 nm for **S1a** and at 272–341 nm for **S1b** were attributed to n–π from the carbonyl groups on the coumarin ring. The presence of the strong electron-donating group at position 8 in compound **S1b** seems to increase the electron density of the coumarin ring; thus, the π–π* transition of the molecule reflected in the observed less intense band at lower wavelength (242–255 nm).

On the other hand, the thiocarbonyl analogues **S2a/b** and **S3a/b** showed two strong absorption bands around 260–340 and 345–450 nm. The presence of the S atoms in compounds **S2** and **S3** resulted to a new band at 345–450 nm which is attributed to n–π* transitions from the S atoms.

3.3. Crystal structures

The title compounds crystallized in monoclinic space groups, except for **S3b**, which crystallized in an orthorhombic space group. All the bond lengths and angles are in the expected ranges. A search of the Cambridge Structural Database (CSD, Version 5.45, update of June 2024; Groom *et al.*, 2016) yielded only four crystal structures of **S1a** and **S1b** (García-Báez *et al.*, 2003; Mahendra *et al.*, 2003; Shang *et al.*, 2015; Takahashi *et al.*, 2006) identical to the structures reported here.

The structure of **S1a** is essentially planar, with the O2 and C10 atoms 0.279 (2) and 0.170 (2) Å in opposite directions out of the mean coumarin plane and the mean plane through C10/O3/O4 rotated by 10.7 (2)° from the coumarin plane. There is one intramolecular interaction, *i.e.* C3—H3···O3 (Table 2). The energy framework calculations show that the strongest interactions are due to centrosymmetric π-ring offset-stacked chains down the a axis and with total energy contributions of −55.91 and −48.0 kJ mol^{-1} (dispersion contributions are −61.3 and −64.8 kJ mol^{-1}, respectively). The distance between the mean coumarin planes alternates between 3.18 and 3.46 Å. The −55.9 kJ mol^{-1} interactions also include the C11—H11A···π-ring interaction with the C3–C9 ring, which is visible on the fingerprint plot as a broad wing, but obscured by the H···H contact surface [Fig. 5(*a*)]. Each π-stack is linked to six other stacks with interactions of total energies of −31.0 or −21.8 kJ mol^{-1}. The electrostatic interactions occur in all dimensions, while the dispersion interactions are in planes parallel to the *ac* plane. As a result, the total energy framework [Fig. 6(*a*)] extends in all dimensions, with the underlying net determined as **16T3** by *TopCryst*. Centrosymmetric pairs of C8—H8···O2^{ii} interactions link two molecules with an $R_2^2(12)$ graph-set motif (Bernstein *et al.*, 1995). This corresponds to the −31.0 kJ mol^{-1} interaction linking π-stacks. The C6—H6···O2^{i} and C7—H7···O4^{i} interactions [Fig. 7(*a*) and Table 2] link molecules with $C(8)$ and $C(9)$ descriptors, respectively, parallel to the b axis, with the molecules arranged in a zigzag chain fashion. This corresponds to the −21.8 kJ mol^{-1} interaction. The dominant intermolecular hydrogen-bond interaction, as shown by the $d_{\rm norm}$ Hirshfeld surface, is C11—H11B···O4^{iii}, which links molecules alternately in two planes parallel to the c axis, with a dihedral angle of 60.6° between the planes. This interaction can be described with a $C(5)$ descriptor and is visible on the fingerprint plot as a broad spike [Fig. 6(*a*)]. The energy framework interaction is only −7.5 kJ mol^{-1} in this orientation and is mainly dispersion in nature.

For **S2a**, the S1 and C10 atoms are 0.203 (1) and 0.210 (2) Å, respectively, in opposite directions out of the mean coumarin ring, and with the mean plane of the C10/O3/O2 carboxylate group rotated by 38.7 (1)° from the plane of the coumarin ring. The molecules are arranged in zigzag planes parallel to the *ac* plane and centrosymmetric offset π-ring chains stack parallel to the b axis, with alternating distances of 3.41 and 3.09 Å between the mean coumarin planes. The energy frameworks show the strongest interactions down the b axis, with alternating total energies of −48.9 and −35.1 kJ mol^{-1}. The total energy framework [Fig. 6(*b*)] extends in all dimensions, with the main interactions in the *bc* plane. The underlying net was determined as **bcu-x** or **sqc38by** by *TopCryst*. Adjacent stacks are linked with interactions of −31.0 kJ mol^{-1} total energy, with −20.4 and −21.2 kJ mol^{-1} electrostatic and dispersion contributions, respectively. This arises from the C8—H8···O3^{ii} chain interactions [Fig. 7(*b*)], with a $C(8)$ descriptor, seen as a sharp peak on the fingerprint plot [Fig. 5(*b*)]. Also, the Hirshfeld shape index indicates a prominent C1=S1···π ring interaction with the C4–C9 ring, with a herringbone packing orientation. The shortest S···centroid distance is 3.7011 (8) Å. Prominent on the Hirshfeld $d_{\rm norm}$ surface is the C3—H3···S1^{i} chain interaction down the c axis, with a $C(5)$ descriptor and a sharp peak on the fingerprint plot [Fig. 5(*b*)]. This corresponds to the −20.0 kJ mol^{-1} energy framework interaction, with electrostatic and dispersion contributions of −16.7 and −17.6 kJ mol^{-1}, respectively. The shape index surface also shows weaker C5—H5···O1^{i} and C12—H12C···S1^{i} contributions (Table 3).

Table 4
Hydrogen-bond geometry (Å,°) for **S3a**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···S1^{i}	0.95	3.03	3.8486 (18)	146
C8—H8···O1^{ii}	0.95	2.91	3.600 (2)	131
C12—H12*A*···S1^{iii}	0.98	3.15	3.981 (2)	144
C12—H12*C*···S2^{iv}	0.98	3.22	4.119 (3)	154
C12—H12*B*···S2^{v}	0.98	3.33	4.245 (3)	156

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

Table 5
Hydrogen-bond geometry (Å,°) for **S1b**.

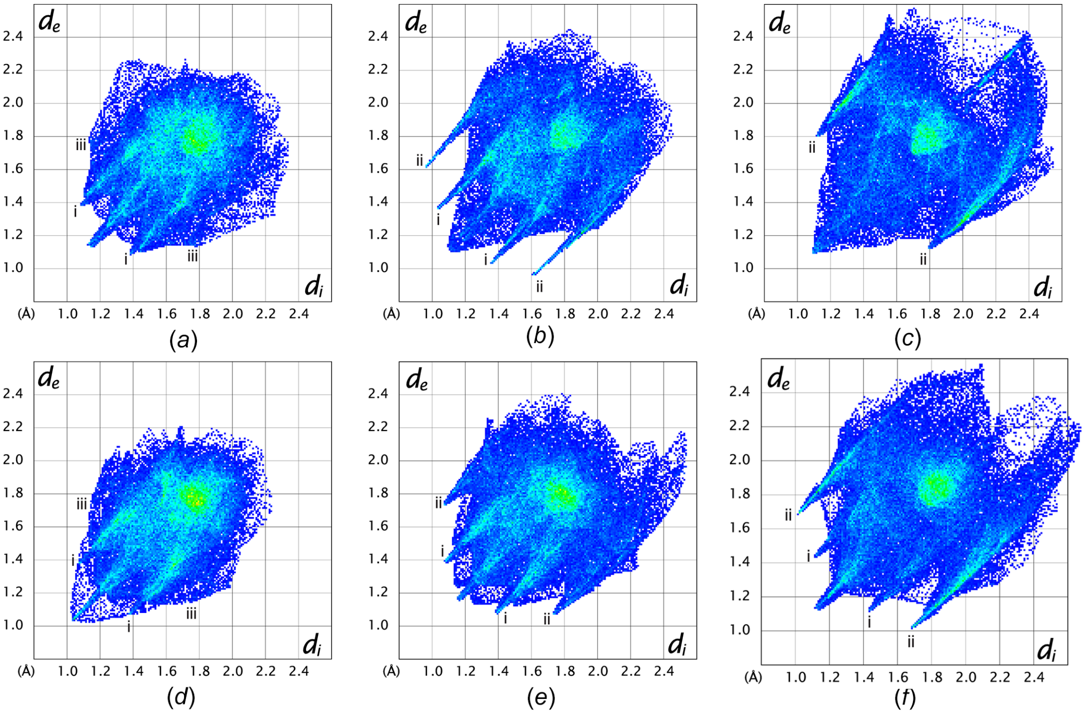
D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O4^{i}	0.95	2.58	3.4065 (14)	146

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

The C12—H12*A*···S1^{iv} hydrogen bond is also prominent on the shape index linking adjacent chains that correspond to the −19.9 kJ mol^{-1} interaction on the energy framework. Also contributing is the weak C12—H12*B*···O3^{iii} interaction with a *C*(6) descriptor.

In **S3a**, compared to **S1a** and **S2a**, the ethoxycarbonyl group is rotated most from the mean coumarin plane, by 75.41 (5)°. Atoms S1 and C10 are only 0.026 (2) and 0.030 (2) Å out of this plane. The d_{norm} surface for **S3a** is featureless [Fig. 7(*c*)]; however, the shape index indicates a number of possible interactions. On either side of the coumarin ring there are stacked centrosymmetrical π-ring interactions with alternating coumarin planes separated by 3.35 and 3.40 Å. The stacking occurs in the [110] and [1$\bar{1}$0] directions in planes parallel to the *ab* plane. The total energy alternates between −45.7 and −47.8 kJ mol^{-1} down the stack. Stacks in the *ab* plane are linked, with interactions having total energies of −14.7 and −23.0 kJ mol^{-1}, and the stack planes are joined with interactions of −13.4 kJ mol^{-1}. The total energy framework [Fig. 6(*c*)] extends in all dimensions and the underlying topology determined by *TopCryst* is **tcf-x**. The shortest interaction is C3—H3···S1^{i} [Fig. 7(*c*)], with a length of 3.03 Å. This links molecules down the *b* axis, with a *C*(5) descriptor, results in the only noticeable spike on the fingerprint plot [Fig. 5(*c*)] and corresponds to the −14.7 kJ mol^{-1} interaction. On each edge of the coumarin group there are two interactions, both of total energy −23.0 kJ mol^{-1}, which include centrosymmetric pairs of C8—H8···O1^{ii}, and C—H···π ring interactions including C8—H8, C3—H3 and C5—H5. The ethyl group is held in place by a number of C—H···π···S interactions, namely, C12—H12*A*···S1^{iii}, C12—H12*C*···S2^{iv} and C12—H12*B*···S2^{v}, with lengths varying from 3.15 to 3.33 Å (Table 4). The C12—H12*A*···S1^{iii} interaction contributes to the −13.4 kJ mol^{-1} interaction linking planes of stacks together and is mainly dispersion in nature. The fingerprint plot for **S3a** has broad wings for the O···H/H···O interactions which are obscured by the H···H contact surface.

The ethoxycarbonyl group of **S1b** is rotated to a larger extent [58.27 (4)°] from the coumarin plane compared to **S1a**, while the methoxy group is only rotated by 7.17 (8)°. In **S1b**, the O2, C10 and O5 atoms are all less that 0.06 Å out of the mean coumarin plane. The centrosymmetric staggered π-ring stacking is prominent down the *a* axis, with alternating layers



(*a*) (*b*) (*c*) (*d*) (*e*) (*f*)

Figure 5
Hirshfeld fingerprint plots of (*a*) **S1a**, (*b*) **S2a**, (*c*) **S3a**, (*d*) **S1b**, (*e*) **S2b** and (*f*) **S3b**. Spike indicators: (i) O···H/H···O; (ii) S···H/H···S; (iii) C···H/H···C.

of 3.28 and 3.43 Å between the mean coumarin planes; this is also evident on the $d_{\rm norm}$ surface. The dispersion energy (-74.2 kJ mol^{-1}) is dominant, with total energies of -63.9 and -54.9 kJ mol^{-1}. Adjacent π-ring stacks are linked on four sides, with interactions having total energies of -31.2 and -33.6 kJ mol^{-1}, and two other π-ring stacks with interactions of -11.6 kJ mol^{-1}. A three-dimensional framework [Fig. 6(*d*)] occurs with a **16-c** net topology. The $d_{\rm norm}$ surface shows one strong intramolecular interaction C5—H5$\cdots$O4$^{\rm i}$ [Fig. 7(*d*) and Table 5] linking atoms in a chain down the *b* axis, with a *C*(7) descriptor and corresponding to the -31.2 kJ mol^{-1} interaction. This interaction is also indicated as a spike on the fingerprint plot [Fig. 5(*d*)], but is obscured by the H$\cdots$H contact surface. The shape index surface also shows evidence of C11—H11*B*$\cdots$H11*B*—C11 π-interactions between the methylene C atom of the ethyl group corresponding to the -11.6 kJ mol^{-1} interaction, which has mainly a dispersion contribution. The -33.6 kJ mol^{-1} interaction, with both electrostatic and dispersion contributions, arises from a number of C—H$\cdots$O π-interactions involving the methoxy and ethoxy groups with atoms O1, O2, O3 and O5. The fingerprint plot has broad wings for the C$\cdots$H/H$\cdots$C contact (obscured by the H$\cdots$H surface) that correspond to C13—H13*B*$\cdots$C10 π-interactions between molecules in the π-stack.

In the **S2b** structure, the C10 and S1 atoms lie more than 0.1 Å from the mean coumarin plane, and the plane of the ethoxycarbonyl group is rotated by 65.67 (5)°. The methoxy group is rotated by 6.53 (10)° with respect to the coumarin plane. Offset π-ring interactions are also prominent, with pairs of centrosymmetric interactions stacking molecules down the *a* axis in alternating planes 3.31 and 3.37 Å apart. The energy framework calculations show strong dispersion effects of -84.2 and -75.6 kJ mol^{-1} alternating down the π-stacked rings (total energy -60.9 and -67.1 kJ mol^{-1}, respectively). The π-ring stacks are connected to four adjacent stacks, with interactions having total energies of -30.4 or -32.7 kJ mol^{-1}, resulting in a three-dimensional energy framework [Fig. 6(*e*)], with the underlying topology determined by *TopCryst* as a **16-c** net. Adjacent methoxy and ethoxycarbonyl groups are

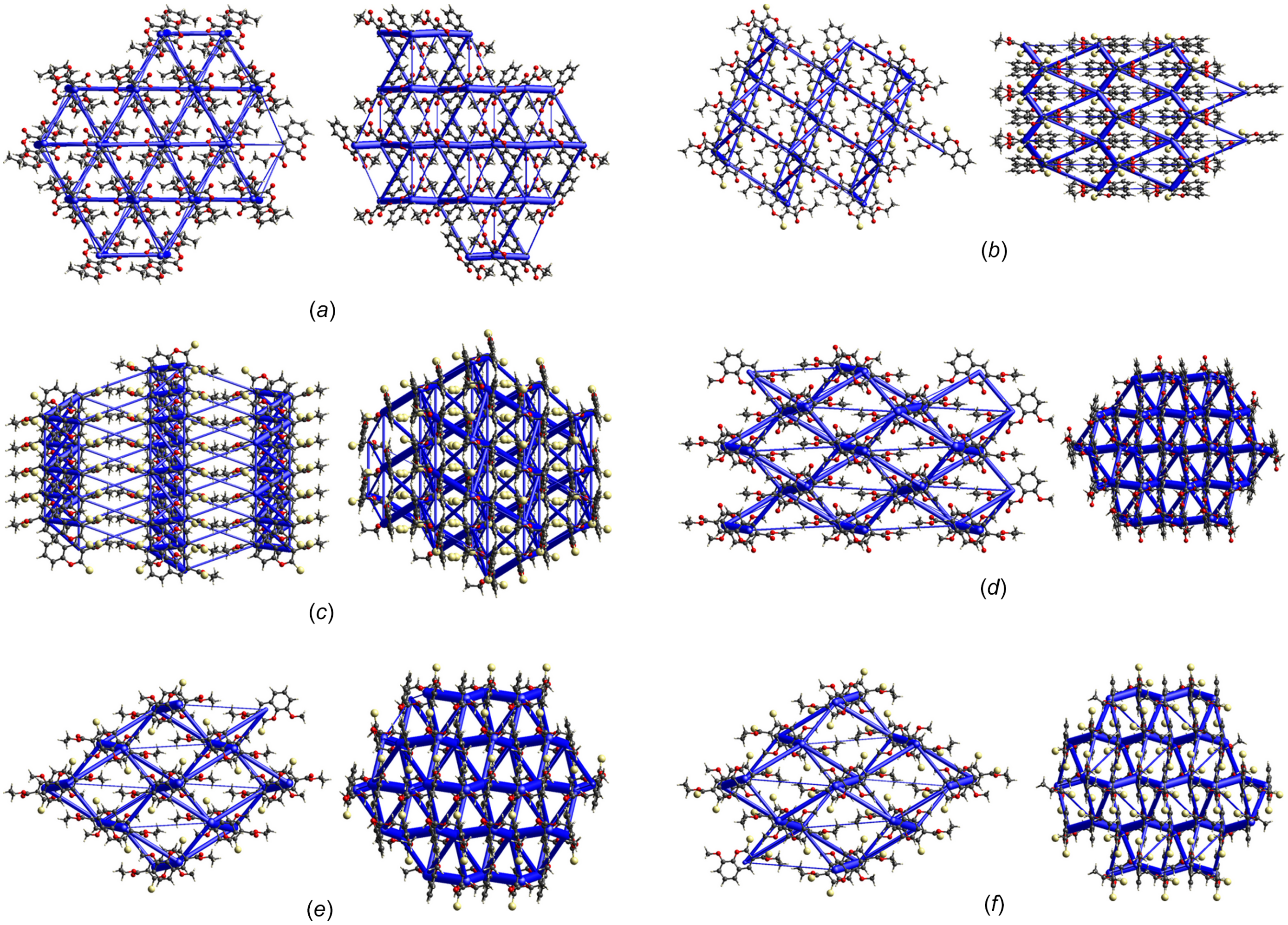


Figure 6
Energy frameworks within a 10 Å sphere and with a tube size of 100 and a cut-off at 5 kJ mol^{-1}. (*a*) **S1a** viewed down the *a* and *c* axes; (*b*) **S2a** viewed down the *b* and *c* axes; (*c*) **S3a** viewed down the *a* and *c* axes; (*d*) **S1b** viewed down the *a* and *c* axes; (*e*) **S2b** viewed down the *a* and *c* axes; (*f*) **S3b** viewed down the *a* and *c* axes.

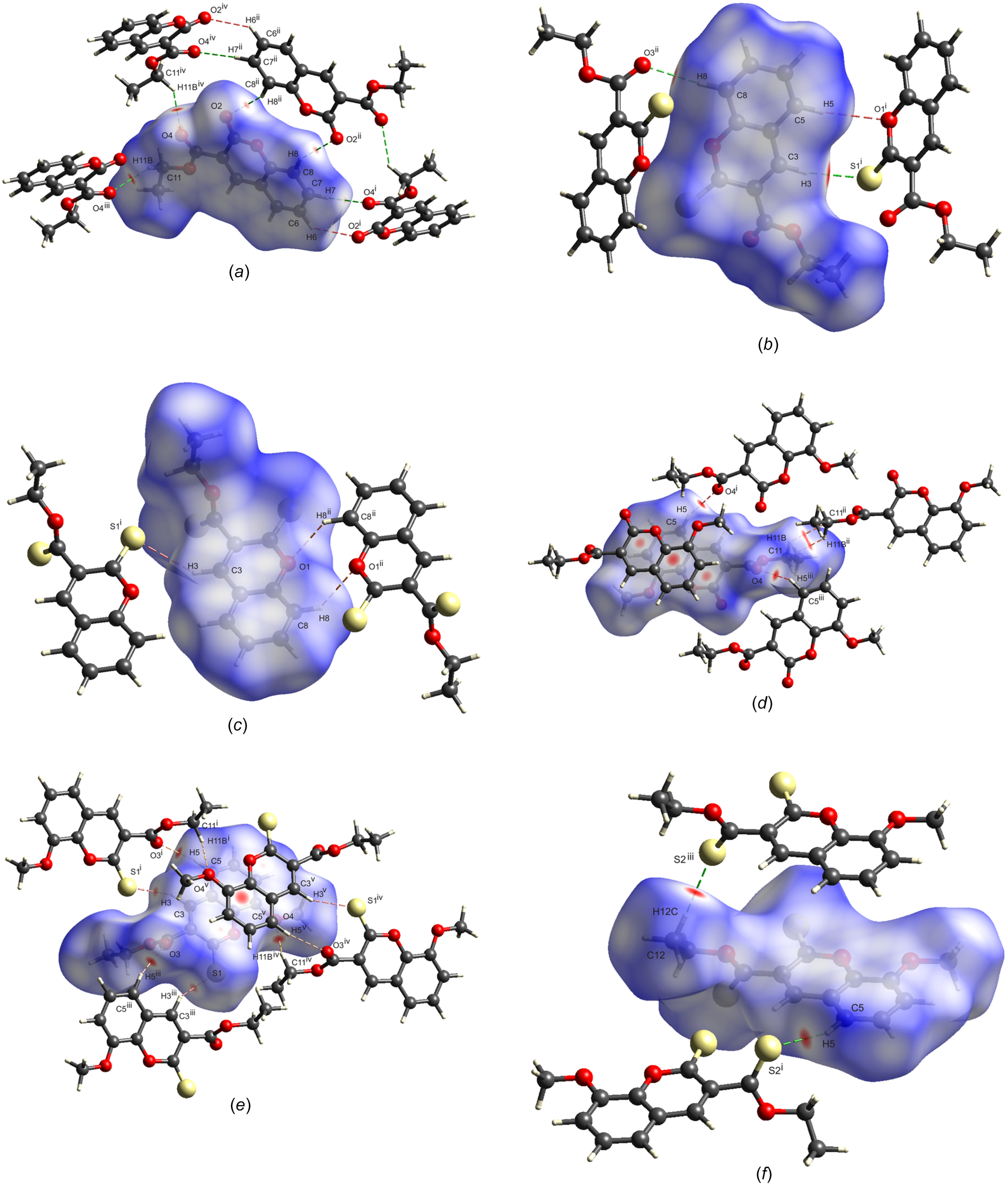


Figure 7

Hirshfeld $d_{\rm norm}$ surface and selected intermolecular hydrogen-bond interactions. For clarity, not all interactions are shown. [Symmetry codes for **S1a**: (i) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x, -y+1, -z$; (iii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (iv) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; for **S2a**: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; for **S3a**: (i) $x, y-1, z$; (ii) $-x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; for **S1b**: (i) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+1, -y+1, -z$; (iii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; for **S2b**: (i) $-x+\frac{3}{2}, y-\frac{1}{2}$; (iii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (v) $-x+2, -y+1, -z+1$; for **S3b**: (i) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x-1, y, z$.

Table 6
Hydrogen-bond geometry (Å,°) for **S2b**.

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···S1$^{\rm i}$	0.95	2.91	3.7460 (12)	147
C5—H5···O3$^{\rm i}$	0.95	2.59	3.4774 (17)	156
C11—H11B···O4$^{\rm ii}$	0.99	2.53	3.2803 (17)	132

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

Table 7
Hydrogen-bond geometry (Å,°) for **S3b**.

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···S2$^{\rm i}$	0.95	2.86	3.764 (4)	160
C11—H11A···O3$^{\rm ii}$	0.99	2.64	3.460 (6)	140
C11—H11B···S2	0.99	2.67	3.005 (5)	100
C12—H12C···S2$^{\rm iii}$	0.98	2.83	3.805 (7)	178
C13—H13C···S1$^{\rm iv}$	0.98	2.94	3.656 (5)	131

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

linked by a C11—H11B···O4$^{\rm ii}$ interaction [Fig. 7(*e*)], linking molecules in the [101] direction with a $C(10)$ motif and corresponding to the −32.7 kJ mol^{-1} interaction, which has −21.5 and −24.36 kJ mol^{-1} electrostatic and dispersion contributions, respectively. The shape index indicates possible π-interaction of the ethoxy group with atom S1, and of the methoxy group with atoms S1 and O2. The $d_{\rm norm}$ surface [Fig. 7(*e*)] shows a prominent intermolecular C5—H5···O3$^{\rm i}$ interaction that, together with the C3—H3···S1$^{\rm i}$ interaction, links two molecules in a ring $R_2^2(10)$ motif (Table 6). Both these interactions cause noticeable spikes on the fingerprint plot [Fig. 5(*e*)]. Furthermore, these two interactions form a chain of interactions with $C(7)$ and $C(5)$ descriptors, respectively, that link molecules down the b axis. These interactions correspond to the −30.4 kJ mol^{-1} interaction, with −21.9 and −25.0 kJ mol^{-1} electrostatic and dispersion contributions, respectively.

Table 8
Calculated lattice energies (kJ mol^{-1}).

S1a	−262	**S1b**	−326
S2a	−256	**S2b**	−318
S3a	−235	**S3b**	−295

For **S3b**, the S1 and C10 atoms both lie more than 0.09 Å in opposite directions out of the mean coumarin plane. The ethoxycarbonyl and methoxy groups are rotated by 73.56 (11) and 1.84 (5)°, respectively, from the mean coumarin plane. There is one intramolecular C11—H11B···S2 interaction of length 2.67 Å. Unlike the previous structures, where the stacked coumarin groups are centrosymmetric and their mean planes parallel, the coumarin groups in **S3c** have twofold screw-axis symmetry and an angle of 4.30° between the successive mean coumarin planes. The coumarin rings are stacked down the a axis, with centroid-to-centroid distances of 3.60 Å. The total energy of the interaction is −58.9 kJ mol^{-1}, with dispersion and electrostatic contributions of −69.0 and −20.4 kJ mol^{-1}, respectively. There is a prominent C12—H12C···S2$^{\rm iii}$ interaction [Fig. 7(*f*)], with a $C(6)$ motif, that links alternate molecules in the π-ring stack along the a axis, contributing to the electrostatic contribution and indicated by sharp spikes on the fingerprint plot [Fig. 5(*f*)]. Electrostatic and dispersion contributions with total energies of −12.2, −24.2 and −32.5 kJ mol^{-1} link four adjacent π-stacks, creating a three-dimensional framework [Fig. 6(*f*)] with an **18-c** net topology. The C5—H5···S2$^{\rm i}$ interaction links molecules down the b axis with a $C(7)$ graph-set descriptor. This corresponds to the −24.2 kJ mol^{-1} interaction, with −19.2 and −25.38 kJ mol^{-1} electrostatic and dispersion contributions, respectively. The −32.5 kJ mol^{-1} framework interaction has electrostatic and dispersion contributions of −22.5 and −20.3 kJ mol^{-1}, respectively. The shape index

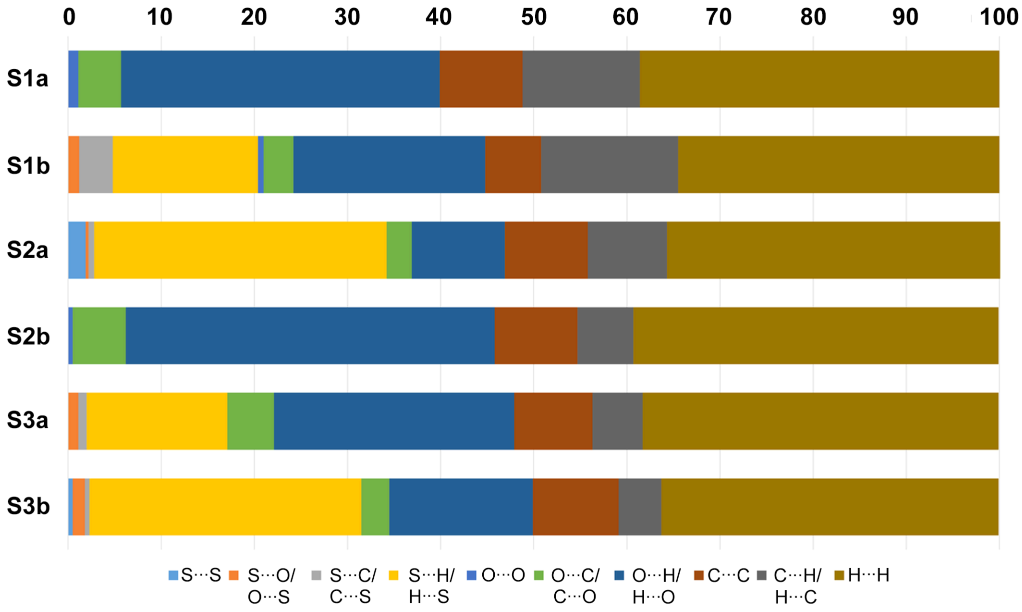


Figure 8
Relative percentage contributions of close contacts to the Hirshfeld surfaces.

indicates that this arises from C11—H11*A*$\cdots$O3^{ii}, C12—H12*B*$\cdots$S1^{ii} and C13—H13*C*$\cdots$S1^{iv} interactions that link molecules down the *c* axis (Table 7). The C11—H11*A*$\cdots$O3 interaction has a noticeable spike on the fingerprint plot [Fig. 5(*f*)]. The remaining interaction of -12.1 kJ mol^{-1} arises from interactions between atom S2 and the methoxy group.

Fig. 8 compares the relative percentage contributions of close contacts to the Hirshfeld surfaces for all the structures. As can be seen, the contributions of the O$\cdots$H/H$\cdots$O and S$\cdots$H/H$\cdots$S contacts together form a significant part of the intermolecular interactions. Also indicated is the presence of O$\cdots$C/C$\cdots$O, C$\cdots$C and C$\cdots$H/H$\cdots$C interactions in all the structures. Table 8 lists the lattice energies calculated with *CrystalExplorer*, taking into account all molecules within a 20 Å radius. The energy framework diagrams (Fig. 6) show that all the structures have a three-dimensional framework. *TopCryst* and *Topospro* (Shevchenko & Blatov, 2021; Shevchenko *et al.*, 2022) can be used to determine the underlying topology network of all the intramolecular interactions and provide a convenient way to describe the interaction network. The network of the electrostatic and van der Waals interactions determined with *TopCryst* are shown in Fig. 9. All the networks determined for the structures are three-dimensional and correspond with the energy frameworks determined by *CrystalExplorer*.

4. Conclusion

A number of novel coumarin derivatives were successfully synthesized and characterized. The intermolecular interactions were investigated extensively using the energy framework feature of *CrystalExplorer*. This proved particularly useful for locating π-type interactions to better understand the total energy network, more so than what can be

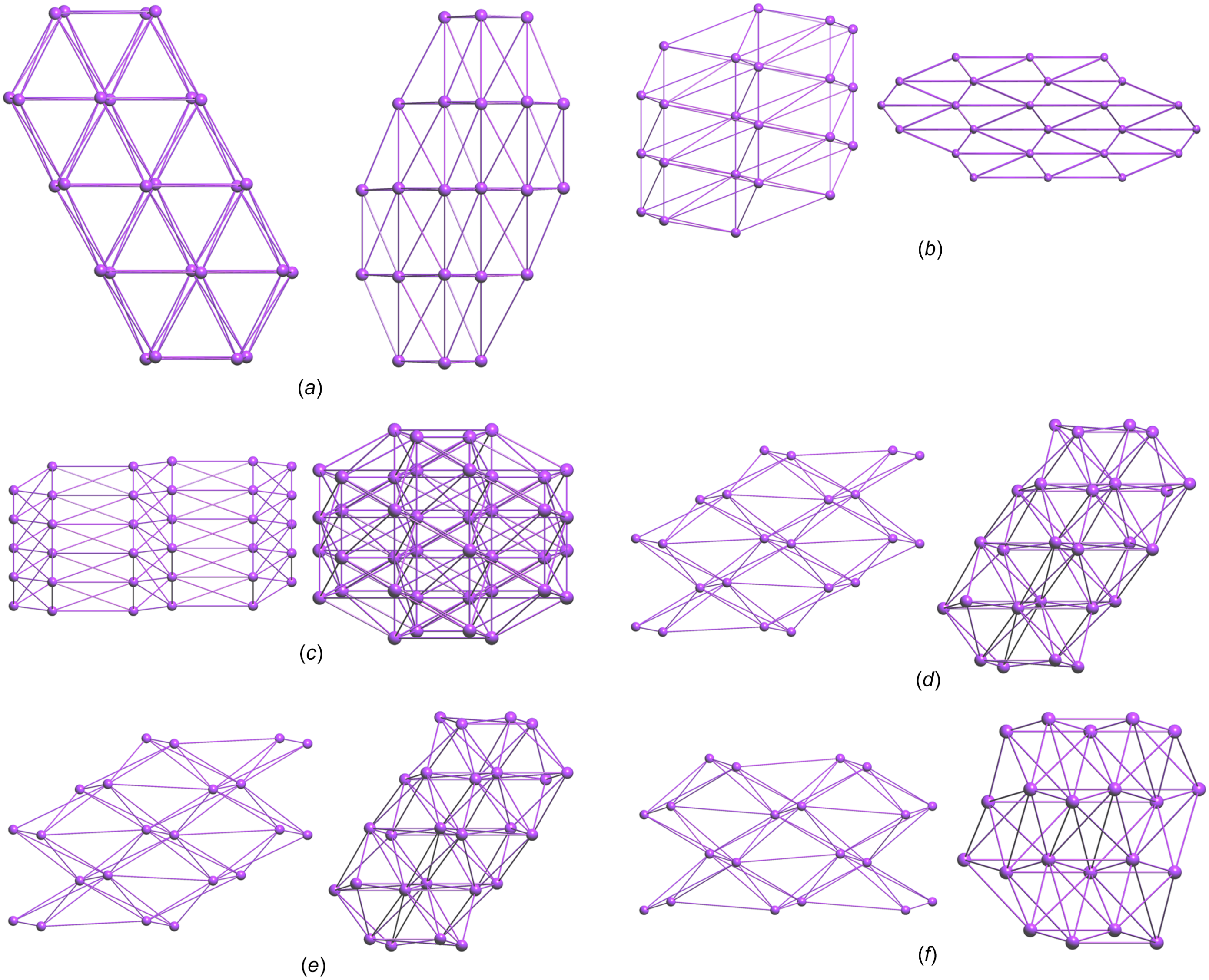


Figure 9
Topology networks determined with *TopCryst*. (*a*) **S1a** viewed down the *a* and *c* axes; (*b*) **S2a** viewed down the *b* and *c* axes; (*c*) **S3a** viewed down the *a* and *c* axes; (*d*) **S1b** viewed down the *a* and *c* axes; (*e*) **S2b** viewed down the *a* and *c* axes; (*f*) **S3b** viewed down the *a* and *c* axes.

obtained by just looking at conventional intermolecular hydrogen-bond interactions. Furthermore, the topology of the different energy frameworks can be conveniently compared using *TopCryst*. The coumarin derivatives synthesized here all show extensive π-interactions in their structures. This, together with preliminary absorption spectrometry, indicate that the compounds are well suited for further investigations as chemosensors.

Acknowledgements

NMU is thanked for funding and facilities.

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supporting information

Acta Cryst. (2025). C**81**, 170-180 [https://doi.org/10.1107/S2053229625000956]

Synthesis and characterization of coumarin-derived sulfur analogues using Lawesson's reagent

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Computing details

Ethyl 2-oxo-2*H*-chromene-3-carboxylate (S1a)

Crystal data

$C_{12}H_{10}O_4$
$M_r = 218.20$
Monoclinic, $P2_1/c$
$a = 7.9043$ (7) Å
$b = 15.7768$ (13) Å
$c = 8.7381$ (7) Å
$\beta = 108.115$ (4)°
$V = 1035.67$ (15) Å^3
$Z = 4$
$F(000) = 456$
$D_x = 1.399$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9584 reflections
$\theta = 2.5–28.3°$
$\mu = 0.11$ mm^{-1}
$T = 296$ K
Block, colourless
1.00 × 0.75 × 0.44 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: numerical (SADABS; Bruker, 2012)
$T_{min} = 0.950$, $T_{max} = 1.000$
19039 measured reflections
2575 independent reflections
2036 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 28.3°$, $\theta_{min} = 2.6°$
$h = -9 \rightarrow 10$
$k = -21 \rightarrow 21$
$l = -11 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.141$
$S = 1.05$
2575 reflections
146 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0618P)^2 + 0.3474P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ 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.

Refinement. Carbon-bound H atoms were placed in calculated positions and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2 U_{eq}(C).
The H atoms of the methyl groups were allowed to rotate with a fixed angle around the C—C bonds to best fit the experimental electron density (HFIX 137 in the SHELXL program (Sheldrick, 2015b)), with U_{iso}(H) set to 1.5U_{eq}(C).
A reflection with large difference between its observed and calculated intensities was omitted. This is due to obstruction by the beam stop.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.10842 (15)	0.48136 (7)	0.22105 (12)	0.0511 (3)
O2	0.2851 (2)	0.37275 (9)	0.23199 (15)	0.0754 (4)
O3	0.50441 (15)	0.40453 (7)	0.73198 (13)	0.0502 (3)
O4	0.4520 (2)	0.30744 (8)	0.53748 (16)	0.0705 (4)
C1	0.2398 (2)	0.42700 (9)	0.30712 (18)	0.0481 (4)
C2	0.30961 (18)	0.44272 (9)	0.48090 (16)	0.0391 (3)
C3	0.26476 (18)	0.51395 (9)	0.54409 (16)	0.0405 (3)
H3	0.315334	0.524519	0.653570	0.049*
C4	0.14146 (19)	0.57366 (9)	0.44718 (16)	0.0398 (3)
C5	0.0936 (2)	0.64961 (10)	0.50492 (19)	0.0513 (4)
H5	0.146159	0.664765	0.612101	0.062*
C6	−0.0306 (2)	0.70194 (11)	0.4043 (2)	0.0546 (4)
H6	−0.061234	0.752617	0.443226	0.066*
C7	−0.1106 (2)	0.67955 (11)	0.2448 (2)	0.0521 (4)
H7	−0.195610	0.715130	0.177780	0.063*
C8	−0.0658 (2)	0.60542 (11)	0.18455 (18)	0.0502 (4)
H8	−0.120164	0.590389	0.077569	0.060*
C9	0.06156 (19)	0.55350 (9)	0.28588 (16)	0.0413 (3)
C10	0.43036 (19)	0.37694 (9)	0.58187 (17)	0.0422 (3)
C11	0.6066 (2)	0.34219 (11)	0.8463 (2)	0.0557 (4)
H11A	0.714478	0.327653	0.821662	0.067*
H11B	0.537059	0.290991	0.841208	0.067*
C12	0.6513 (4)	0.38057 (16)	1.0093 (2)	0.0846 (7)
H12A	0.717687	0.431803	1.012208	0.127*
H12B	0.721409	0.341395	1.087627	0.127*
H12C	0.543534	0.393302	1.033485	0.127*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0624 (7)	0.0513 (6)	0.0330 (5)	−0.0007 (5)	0.0051 (4)	−0.0070 (4)
O2	0.1098 (11)	0.0635 (8)	0.0468 (7)	0.0178 (8)	0.0156 (7)	−0.0126 (6)
O3	0.0551 (6)	0.0465 (6)	0.0419 (5)	0.0010 (5)	0.0046 (5)	0.0059 (4)
O4	0.0885 (10)	0.0569 (7)	0.0596 (7)	0.0243 (7)	0.0134 (7)	−0.0046 (6)

C1	0.0614 (9)	0.0415 (7)	0.0388 (7)	−0.0052 (6)	0.0118 (6)	−0.0052 (6)
C2	0.0403 (7)	0.0402 (7)	0.0364 (6)	−0.0047 (5)	0.0113 (5)	−0.0001 (5)
C3	0.0427 (7)	0.0446 (7)	0.0324 (6)	−0.0045 (6)	0.0090 (5)	−0.0022 (5)
C4	0.0446 (7)	0.0399 (7)	0.0344 (6)	−0.0044 (5)	0.0115 (5)	0.0002 (5)
C5	0.0627 (10)	0.0476 (8)	0.0419 (8)	0.0011 (7)	0.0137 (7)	−0.0034 (6)
C6	0.0649 (10)	0.0458 (8)	0.0569 (9)	0.0059 (7)	0.0244 (8)	0.0038 (7)
C7	0.0489 (9)	0.0560 (9)	0.0524 (9)	0.0033 (7)	0.0172 (7)	0.0140 (7)
C8	0.0486 (8)	0.0605 (9)	0.0375 (7)	−0.0054 (7)	0.0075 (6)	0.0056 (6)
C9	0.0454 (8)	0.0426 (7)	0.0353 (7)	−0.0077 (6)	0.0120 (5)	−0.0007 (5)
C10	0.0408 (7)	0.0444 (7)	0.0423 (7)	−0.0027 (6)	0.0142 (6)	0.0018 (6)
C11	0.0509 (9)	0.0588 (10)	0.0517 (9)	0.0050 (7)	0.0080 (7)	0.0174 (7)
C12	0.1002 (17)	0.0838 (15)	0.0499 (10)	−0.0008 (12)	−0.0055 (10)	0.0109 (10)

Geometric parameters (Å, º)

O1—C9	1.3726 (18)	C5—H5	0.9300
O1—C1	1.3762 (19)	C6—C7	1.385 (2)
O2—C1	1.199 (2)	C6—H6	0.9300
O3—C10	1.3323 (18)	C7—C8	1.374 (2)
O3—C11	1.4546 (18)	C7—H7	0.9300
O4—C10	1.1930 (19)	C8—C9	1.384 (2)
C1—C2	1.4665 (19)	C8—H8	0.9300
C2—C3	1.347 (2)	C11—C12	1.486 (3)
C2—C10	1.498 (2)	C11—H11A	0.9700
C3—C4	1.4286 (19)	C11—H11B	0.9700
C3—H3	0.9300	C12—H12A	0.9600
C4—C9	1.3903 (19)	C12—H12B	0.9600
C4—C5	1.397 (2)	C12—H12C	0.9600
C5—C6	1.372 (2)		
C9—O1—C1	123.08 (11)	C6—C7—H7	119.6
C10—O3—C11	115.81 (13)	C7—C8—C9	118.80 (14)
O2—C1—O1	116.66 (13)	C7—C8—H8	120.6
O2—C1—C2	127.39 (15)	C9—C8—H8	120.6
O1—C1—C2	115.95 (13)	O1—C9—C8	117.57 (12)
C3—C2—C1	120.21 (13)	O1—C9—C4	120.81 (13)
C3—C2—C10	122.49 (12)	C8—C9—C4	121.61 (14)
C1—C2—C10	117.29 (13)	O4—C10—O3	123.84 (14)
C2—C3—C4	121.66 (12)	O4—C10—C2	125.09 (14)
C2—C3—H3	119.2	O3—C10—C2	110.98 (12)
C4—C3—H3	119.2	O3—C11—C12	107.38 (16)
C9—C4—C5	118.27 (14)	O3—C11—H11A	110.2
C9—C4—C3	117.47 (13)	C12—C11—H11A	110.2
C5—C4—C3	124.25 (13)	O3—C11—H11B	110.2
C6—C5—C4	120.31 (14)	C12—C11—H11B	110.2
C6—C5—H5	119.8	H11A—C11—H11B	108.5
C4—C5—H5	119.8	C11—C12—H12A	109.5
C5—C6—C7	120.22 (15)	C11—C12—H12B	109.5

C5—C6—H6	119.9	H12A—C12—H12B	109.5
C7—C6—H6	119.9	C11—C12—H12C	109.5
C8—C7—C6	120.76 (15)	H12A—C12—H12C	109.5
C8—C7—H7	119.6	H12B—C12—H12C	109.5

C9—O1—C1—O2	−170.12 (15)	C1—O1—C9—C8	176.51 (13)
C9—O1—C1—C2	9.4 (2)	C1—O1—C9—C4	−2.7 (2)
O2—C1—C2—C3	169.72 (18)	C7—C8—C9—O1	−177.68 (14)
O1—C1—C2—C3	−9.7 (2)	C7—C8—C9—C4	1.6 (2)
O2—C1—C2—C10	−10.3 (3)	C5—C4—C9—O1	177.48 (14)
O1—C1—C2—C10	170.26 (12)	C3—C4—C9—O1	−3.9 (2)
C1—C2—C3—C4	3.6 (2)	C5—C4—C9—C8	−1.7 (2)
C10—C2—C3—C4	−176.39 (12)	C3—C4—C9—C8	176.86 (13)
C2—C3—C4—C9	3.3 (2)	C11—O3—C10—O4	−4.2 (2)
C2—C3—C4—C5	−178.17 (14)	C11—O3—C10—C2	172.48 (12)
C9—C4—C5—C6	0.7 (2)	C3—C2—C10—O4	167.43 (16)
C3—C4—C5—C6	−177.81 (15)	C1—C2—C10—O4	−12.5 (2)
C4—C5—C6—C7	0.5 (3)	C3—C2—C10—O3	−9.2 (2)
C5—C6—C7—C8	−0.7 (3)	C1—C2—C10—O3	170.81 (12)
C6—C7—C8—C9	−0.3 (2)	C10—O3—C11—C12	−170.62 (16)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O3	0.93	2.38	2.7074 (18)	101
C6—H6···O2^{i}	0.93	2.72	3.352 (2)	126
C7—H7···O4^{i}	0.93	2.72	3.647 (2)	175
C8—H8···O2^{ii}	0.93	2.68	3.5281 (19)	153
C11—H11*B*···O4^{iii}	0.97	2.55	3.335 (2)	138

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

Ethyl 2-sulfanylidene-2*H*-chromene-3-carboxylate (S2a)

Crystal data

$C_{12}H_{10}O_3S$
M_r = 234.26
Monoclinic, $P2_1/c$
a = 11.9040 (9) Å
b = 7.1792 (5) Å
c = 13.6794 (10) Å
β = 111.708 (3)°
V = 1086.15 (14) Å^3
Z = 4

F(000) = 488
D_x = 1.433 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 9977 reflections
θ = 2.8–28.3°
μ = 0.28 mm^{-1}
T = 200 K
Block, orange
0.87 × 0.66 × 0.58 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}

φ and *ω* scans
Absorption correction: numerical (SADABS; Bruker, 2012)
T_{min} = 0.941, T_{max} = 1.000
18714 measured reflections

2710 independent reflections
2368 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.017$
$\theta_{\text{max}} = 28.3°$, $\theta_{\text{min}} = 3.1°$

$h = -15 \rightarrow 15$
$k = -9 \rightarrow 9$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.105$
$S = 1.04$
2710 reflections
146 parameters
0 restraints
Primary atom site location: dual

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0565P)^2 + 0.3885P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} = 0.001$
$\Delta\rho_{\text{max}} = 0.36$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.26$ 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.

Refinement. Carbon-bound H atoms were placed in calculated positions and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2 U_{eq}(C).
The H atoms of the methyl groups were allowed to rotate with a fixed angle around the C—C bonds to best fit the experimental electron density (HFIX 137 in the SHELXL program (Sheldrick, 2015b)), with U_{iso}(H) set to $1.5U_{\text{eq}}$(C).

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

	x	y	z	U_{iso}*/U_{eq}
S1	0.68456 (3)	0.43084 (6)	0.84814 (3)	0.04121 (13)
O1	0.48774 (8)	0.39467 (14)	0.68841 (7)	0.0318 (2)
O2	0.83417 (8)	0.21273 (15)	0.62860 (8)	0.0365 (2)
O3	0.83740 (11)	0.1203 (2)	0.78624 (9)	0.0553 (3)
C1	0.60892 (11)	0.35577 (17)	0.72921 (10)	0.0281 (3)
C2	0.65837 (11)	0.26139 (17)	0.66052 (10)	0.0265 (2)
C3	0.58888 (11)	0.22923 (17)	0.55840 (10)	0.0260 (2)
H3	0.624245	0.174648	0.513348	0.031*
C4	0.46333 (11)	0.27595 (16)	0.51726 (10)	0.0256 (2)
C5	0.38646 (12)	0.24153 (18)	0.41294 (11)	0.0308 (3)
H5	0.417869	0.188928	0.364605	0.037*
C6	0.26519 (12)	0.2843 (2)	0.38078 (12)	0.0364 (3)
H6	0.212784	0.260143	0.310366	0.044*
C7	0.21943 (12)	0.3631 (2)	0.45177 (13)	0.0383 (3)
H7	0.135610	0.390826	0.428998	0.046*
C8	0.29350 (12)	0.4014 (2)	0.55439 (12)	0.0351 (3)
H8	0.262173	0.457387	0.601913	0.042*
C9	0.41497 (11)	0.35579 (17)	0.58591 (10)	0.0275 (3)
C10	0.78606 (12)	0.19249 (19)	0.70162 (10)	0.0312 (3)
C11	0.95289 (12)	0.1308 (3)	0.65020 (13)	0.0454 (4)
H11A	0.945526	−0.005515	0.638459	0.054*

H11B	1.006123	0.153982	0.724223	0.054*
C12	1.00447 (14)	0.2189 (2)	0.57749 (14)	0.0466 (4)
H12A	1.080684	0.157390	0.584930	0.070*
H12B	1.019497	0.351332	0.594885	0.070*
H12C	0.947173	0.206148	0.504812	0.070*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0483 (2)	0.0499 (2)	0.02965 (19)	−0.00848 (16)	0.01939 (16)	−0.00791 (14)
O1	0.0326 (5)	0.0368 (5)	0.0325 (5)	−0.0007 (4)	0.0197 (4)	−0.0041 (4)
O2	0.0249 (4)	0.0532 (6)	0.0350 (5)	0.0072 (4)	0.0153 (4)	0.0087 (4)
O3	0.0511 (7)	0.0791 (9)	0.0405 (6)	0.0246 (6)	0.0225 (5)	0.0245 (6)
C1	0.0335 (6)	0.0277 (6)	0.0292 (6)	−0.0035 (5)	0.0187 (5)	0.0007 (5)
C2	0.0282 (6)	0.0277 (6)	0.0277 (6)	−0.0010 (4)	0.0150 (5)	0.0019 (4)
C3	0.0277 (6)	0.0269 (6)	0.0283 (6)	−0.0002 (4)	0.0159 (5)	−0.0008 (4)
C4	0.0267 (6)	0.0225 (5)	0.0310 (6)	−0.0014 (4)	0.0147 (5)	0.0012 (4)
C5	0.0319 (6)	0.0294 (6)	0.0323 (6)	−0.0014 (5)	0.0133 (5)	−0.0002 (5)
C6	0.0312 (6)	0.0362 (7)	0.0383 (7)	−0.0014 (5)	0.0086 (5)	0.0041 (6)
C7	0.0278 (6)	0.0368 (7)	0.0515 (8)	0.0025 (5)	0.0161 (6)	0.0086 (6)
C8	0.0325 (6)	0.0336 (7)	0.0477 (8)	0.0028 (5)	0.0246 (6)	0.0036 (6)
C9	0.0300 (6)	0.0243 (6)	0.0334 (6)	−0.0021 (4)	0.0177 (5)	0.0009 (5)
C10	0.0301 (6)	0.0355 (7)	0.0296 (6)	0.0006 (5)	0.0128 (5)	0.0011 (5)
C11	0.0255 (6)	0.0597 (10)	0.0529 (9)	0.0104 (6)	0.0168 (6)	0.0099 (7)
C12	0.0331 (7)	0.0524 (9)	0.0632 (10)	0.0002 (6)	0.0282 (7)	−0.0041 (8)

Geometric parameters (Å, º)

S1—C1	1.6322 (13)	C5—H5	0.9500
O1—C1	1.3692 (16)	C6—C7	1.397 (2)
O1—C9	1.3768 (16)	C6—H6	0.9500
O2—C10	1.3304 (15)	C7—C8	1.381 (2)
O2—C11	1.4566 (16)	C7—H7	0.9500
O3—C10	1.2078 (17)	C8—C9	1.3867 (17)
C1—C2	1.4483 (16)	C8—H8	0.9500
C2—C3	1.3543 (17)	C11—C12	1.490 (2)
C2—C10	1.4963 (17)	C11—H11A	0.9900
C3—C4	1.4286 (16)	C11—H11B	0.9900
C3—H3	0.9500	C12—H12A	0.9800
C4—C9	1.3935 (16)	C12—H12B	0.9800
C4—C5	1.4031 (18)	C12—H12C	0.9800
C5—C6	1.3792 (19)		
C1—O1—C9	123.02 (10)	C6—C7—H7	119.3
C10—O2—C11	117.29 (11)	C7—C8—C9	117.98 (13)
O1—C1—C2	116.79 (11)	C7—C8—H8	121.0
O1—C1—S1	116.65 (9)	C9—C8—H8	121.0
C2—C1—S1	126.47 (10)	O1—C9—C8	117.37 (11)

C3—C2—C1	120.61 (11)	O1—C9—C4	120.56 (11)
C3—C2—C10	118.63 (11)	C8—C9—C4	122.06 (12)
C1—C2—C10	120.74 (11)	O3—C10—O2	124.10 (12)
C2—C3—C4	121.14 (11)	O3—C10—C2	125.84 (12)
C2—C3—H3	119.4	O2—C10—C2	109.97 (11)
C4—C3—H3	119.4	O2—C11—C12	107.54 (13)
C9—C4—C5	118.77 (11)	O2—C11—H11A	110.2
C9—C4—C3	117.64 (11)	C12—C11—H11A	110.2
C5—C4—C3	123.57 (11)	O2—C11—H11B	110.2
C6—C5—C4	119.81 (12)	C12—C11—H11B	110.2
C6—C5—H5	120.1	H11A—C11—H11B	108.5
C4—C5—H5	120.1	C11—C12—H12A	109.5
C5—C6—C7	119.98 (13)	C11—C12—H12B	109.5
C5—C6—H6	120.0	H12A—C12—H12B	109.5
C7—C6—H6	120.0	C11—C12—H12C	109.5
C8—C7—C6	121.39 (13)	H12A—C12—H12C	109.5
C8—C7—H7	119.3	H12B—C12—H12C	109.5

C9—O1—C1—C2	−3.00 (17)	C1—O1—C9—C8	179.75 (11)
C9—O1—C1—S1	173.67 (9)	C1—O1—C9—C4	−1.07 (18)
O1—C1—C2—C3	5.61 (18)	C7—C8—C9—O1	−179.95 (12)
S1—C1—C2—C3	−170.68 (10)	C7—C8—C9—C4	0.9 (2)
O1—C1—C2—C10	−172.58 (11)	C5—C4—C9—O1	−178.91 (11)
S1—C1—C2—C10	11.13 (18)	C3—C4—C9—O1	2.65 (17)
C1—C2—C3—C4	−4.18 (19)	C5—C4—C9—C8	0.24 (19)
C10—C2—C3—C4	174.05 (11)	C3—C4—C9—C8	−178.21 (12)
C2—C3—C4—C9	0.02 (18)	C11—O2—C10—O3	4.4 (2)
C2—C3—C4—C5	−178.35 (11)	C11—O2—C10—C2	−172.26 (12)
C9—C4—C5—C6	−0.95 (19)	C3—C2—C10—O3	−138.68 (16)
C3—C4—C5—C6	177.39 (12)	C1—C2—C10—O3	39.5 (2)
C4—C5—C6—C7	0.5 (2)	C3—C2—C10—O2	37.89 (16)
C5—C6—C7—C8	0.6 (2)	C1—C2—C10—O2	−143.88 (12)
C6—C7—C8—C9	−1.3 (2)	C10—O2—C11—C12	−162.40 (13)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···S1^{i}	0.95	2.72	3.6489 (12)	166
C5—H5···O1^{i}	0.95	2.89	3.8188 (16)	167
C8—H8···O3^{ii}	0.95	2.54	3.4876 (19)	175
C12—H12*B*···O3^{iii}	0.98	2.69	3.567 (2)	150
C12—H12*C*···S1^{i}	0.98	3.22	4.0821 (18)	148

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

Ethyl 2-sulfanylidene-2*H*-chromene-3-carbothioate (S3a)

Crystal data

$C_{12}H_{10}O_2S_2$	$F(000) = 1040$
$M_r = 250.32$	$D_x = 1.424$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 12.5314$ (5) Å	Cell parameters from 9948 reflections
$b = 6.7175$ (3) Å	$\theta = 2.9$–28.2°
$c = 27.7746$ (10) Å	$\mu = 0.44$ mm^{-1}
$\beta = 92.7398$ (14)°	$T = 200$ K
$V = 2335.38$ (16) Å^3	Rod, orange
$Z = 8$	0.30 × 0.16 × 0.11 mm

Data collection

Bruker D8 QUEST diffractometer	27927 measured reflections
Radiation source: sealed x-ray tube	2894 independent reflections
Graphite monochromator	2326 reflections with $I > 2\sigma(I)$
Detector resolution: 7.3910 pixels mm^{-1}	$R_{int} = 0.048$
φ and ω scans	$\theta_{max} = 28.3°$, $\theta_{min} = 2.9°$
Absorption correction: numerical (SADABS; Krause *et al.*, 2015)	$h = -16 \rightarrow 16$
$T_{min} = 0.891$, $T_{max} = 1.000$	$k = -8 \rightarrow 8$
	$l = -33 \rightarrow 36$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.040$	H-atom parameters constrained
$wR(F^2) = 0.100$	$w = 1/[\sigma^2(F_o^2) + (0.0316P)^2 + 3.2817P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = 0.001$
2894 reflections	$\Delta\rho_{max} = 0.30$ e Å^{-3}
146 parameters	$\Delta\rho_{min} = -0.29$ e Å^{-3}
0 restraints	
Primary atom site location: dual	

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. Carbon-bound H atoms were placed in calculated positions and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2 U_{eq}(C).
The H atoms of the methyl groups were allowed to rotate with a fixed angle around the C—C bonds to best fit the experimental electron density (HFIX 137 in the SHELXL program (Sheldrick, 2015b)), with U_{iso}(H) set to 1.5U_{eq}(C).
A number of reflections with large differences between their observed and calculated intensities were omitted. This is due to obstruction by the beam stop.

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

	x	y	z	U_{iso}*/U_{eq}
S1	0.33053 (5)	0.71005 (7)	0.36927 (2)	0.04185 (15)
S2	0.47874 (5)	0.19497 (10)	0.32452 (2)	0.05020 (18)
O1	0.35045 (10)	0.59732 (17)	0.45755 (4)	0.0295 (3)

O2	0.27152 (11)	0.2486 (2)	0.33205 (4)	0.0355 (3)
C1	0.35078 (14)	0.5383 (3)	0.41040 (6)	0.0278 (4)
C2	0.37054 (13)	0.3305 (3)	0.40137 (6)	0.0265 (4)
C3	0.38614 (13)	0.1999 (3)	0.43782 (6)	0.0275 (4)
H3	0.398708	0.063641	0.430891	0.033*
C4	0.38402 (13)	0.2640 (2)	0.48677 (6)	0.0257 (3)
C5	0.39758 (14)	0.1369 (3)	0.52671 (7)	0.0320 (4)
H5	0.408704	−0.001439	0.521883	0.038*
C6	0.39487 (14)	0.2112 (3)	0.57283 (7)	0.0347 (4)
H6	0.405039	0.124661	0.599711	0.042*
C7	0.37716 (14)	0.4136 (3)	0.57998 (7)	0.0347 (4)
H7	0.375724	0.464228	0.611875	0.042*
C8	0.36169 (14)	0.5416 (3)	0.54140 (6)	0.0315 (4)
H8	0.348392	0.679137	0.546402	0.038*
C9	0.36600 (13)	0.4651 (3)	0.49526 (6)	0.0262 (3)
C10	0.37067 (15)	0.2590 (3)	0.35052 (7)	0.0310 (4)
C11	0.25325 (19)	0.1735 (3)	0.28332 (7)	0.0444 (5)
H11A	0.278869	0.034569	0.281081	0.053*
H11B	0.291611	0.256207	0.260237	0.053*
C12	0.1350 (2)	0.1834 (4)	0.27231 (8)	0.0565 (6)
H12A	0.118947	0.137715	0.239239	0.085*
H12B	0.110442	0.320961	0.275675	0.085*
H12C	0.098262	0.097810	0.294827	0.085*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0659 (4)	0.0276 (2)	0.0319 (3)	0.0031 (2)	0.0009 (2)	0.00342 (19)
S2	0.0475 (3)	0.0589 (4)	0.0456 (3)	0.0074 (3)	0.0162 (2)	−0.0089 (3)
O1	0.0372 (7)	0.0229 (6)	0.0284 (6)	−0.0007 (5)	0.0028 (5)	−0.0014 (5)
O2	0.0391 (7)	0.0395 (7)	0.0278 (6)	−0.0046 (6)	−0.0013 (5)	−0.0060 (5)
C1	0.0301 (9)	0.0257 (8)	0.0278 (8)	−0.0016 (7)	0.0024 (7)	−0.0029 (7)
C2	0.0239 (8)	0.0272 (8)	0.0285 (8)	−0.0028 (6)	0.0016 (6)	−0.0039 (7)
C3	0.0239 (8)	0.0231 (8)	0.0355 (9)	0.0001 (6)	0.0011 (7)	−0.0034 (7)
C4	0.0187 (7)	0.0258 (8)	0.0327 (9)	−0.0017 (6)	0.0015 (6)	−0.0003 (7)
C5	0.0255 (8)	0.0309 (9)	0.0397 (10)	0.0015 (7)	0.0011 (7)	0.0053 (8)
C6	0.0274 (9)	0.0442 (11)	0.0325 (9)	−0.0003 (8)	0.0015 (7)	0.0097 (8)
C7	0.0305 (9)	0.0439 (11)	0.0299 (9)	−0.0067 (8)	0.0026 (7)	−0.0015 (8)
C8	0.0313 (9)	0.0294 (9)	0.0341 (9)	−0.0055 (7)	0.0041 (7)	−0.0047 (7)
C9	0.0222 (8)	0.0256 (8)	0.0308 (9)	−0.0035 (6)	0.0018 (6)	0.0008 (7)
C10	0.0384 (10)	0.0233 (8)	0.0315 (9)	−0.0031 (7)	0.0043 (7)	−0.0016 (7)
C11	0.0662 (14)	0.0416 (12)	0.0248 (9)	−0.0024 (10)	−0.0039 (9)	−0.0057 (8)
C12	0.0621 (15)	0.0708 (17)	0.0352 (11)	−0.0166 (13)	−0.0112 (10)	−0.0020 (11)

Geometric parameters (Å, º)

S1—C1	1.6346 (18)	C5—H5	0.9500
S2—C10	1.6229 (19)	C6—C7	1.393 (3)

O1—C1	1.368 (2)	C6—H6	0.9500
O1—C9	1.380 (2)	C7—C8	1.380 (3)
O2—C10	1.323 (2)	C7—H7	0.9500
O2—C11	1.452 (2)	C8—C9	1.384 (2)
C1—C2	1.442 (2)	C8—H8	0.9500
C2—C3	1.347 (2)	C11—C12	1.501 (3)
C2—C10	1.492 (2)	C11—H11A	0.9900
C3—C4	1.427 (2)	C11—H11B	0.9900
C3—H3	0.9500	C12—H12A	0.9800
C4—C9	1.392 (2)	C12—H12B	0.9800
C4—C5	1.404 (2)	C12—H12C	0.9800
C5—C6	1.377 (3)		

C1—O1—C9	122.23 (13)	C6—C7—H7	119.5
C10—O2—C11	118.87 (16)	C7—C8—C9	118.49 (17)
O1—C1—C2	117.08 (15)	C7—C8—H8	120.8
O1—C1—S1	117.19 (13)	C9—C8—H8	120.8
C2—C1—S1	125.73 (13)	O1—C9—C8	116.96 (15)
C3—C2—C1	121.31 (16)	O1—C9—C4	120.94 (15)
C3—C2—C10	119.70 (16)	C8—C9—C4	122.09 (16)
C1—C2—C10	118.97 (15)	O2—C10—C2	109.90 (15)
C2—C3—C4	120.72 (16)	O2—C10—S2	126.98 (14)
C2—C3—H3	119.6	C2—C10—S2	123.05 (14)
C4—C3—H3	119.6	O2—C11—C12	106.55 (18)
C9—C4—C5	118.09 (16)	O2—C11—H11A	110.4
C9—C4—C3	117.71 (16)	C12—C11—H11A	110.4
C5—C4—C3	124.20 (16)	O2—C11—H11B	110.4
C6—C5—C4	120.49 (18)	C12—C11—H11B	110.4
C6—C5—H5	119.8	H11A—C11—H11B	108.6
C4—C5—H5	119.8	C11—C12—H12A	109.5
C5—C6—C7	119.84 (18)	C11—C12—H12B	109.5
C5—C6—H6	120.1	H12A—C12—H12B	109.5
C7—C6—H6	120.1	C11—C12—H12C	109.5
C8—C7—C6	120.98 (17)	H12A—C12—H12C	109.5
C8—C7—H7	119.5	H12B—C12—H12C	109.5

C9—O1—C1—C2	−1.3 (2)	C1—O1—C9—C8	−178.67 (15)
C9—O1—C1—S1	179.57 (12)	C1—O1—C9—C4	0.7 (2)
O1—C1—C2—C3	1.1 (2)	C7—C8—C9—O1	−179.84 (15)
S1—C1—C2—C3	−179.87 (14)	C7—C8—C9—C4	0.8 (3)
O1—C1—C2—C10	179.45 (14)	C5—C4—C9—O1	−179.03 (14)
S1—C1—C2—C10	−1.5 (2)	C3—C4—C9—O1	0.2 (2)
C1—C2—C3—C4	−0.3 (3)	C5—C4—C9—C8	0.3 (2)
C10—C2—C3—C4	−178.61 (15)	C3—C4—C9—C8	179.51 (15)
C2—C3—C4—C9	−0.4 (2)	C11—O2—C10—C2	−177.29 (15)
C2—C3—C4—C5	178.78 (16)	C11—O2—C10—S2	−0.2 (2)
C9—C4—C5—C6	−1.1 (2)	C3—C2—C10—O2	103.35 (19)
C3—C4—C5—C6	179.71 (16)	C1—C2—C10—O2	−75.04 (19)

C4—C5—C6—C7	0.8 (3)	C3—C2—C10—S2	−73.9 (2)
C5—C6—C7—C8	0.3 (3)	C1—C2—C10—S2	107.75 (18)
C6—C7—C8—C9	−1.1 (3)	C10—O2—C11—C12	−178.91 (18)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···S1^{i}	0.95	3.03	3.8486 (18)	146
C8—H8···O1^{ii}	0.95	2.91	3.600 (2)	131
C12—H12*A*···S1^{iii}	0.98	3.15	3.981 (2)	144
C12—H12*C*···S2^{iv}	0.98	3.22	4.119 (3)	154
C12—H12*B*···S2^{v}	0.98	3.33	4.245 (3)	156

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

Ethyl 8-methoxy-2-oxo-2*H*-1-benzopyran-3-carboxylate (S1b)

Crystal data

$C_{13}H_{12}O_5$
M_r = 248.23
Monoclinic, $P2_1/n$
a = 6.8708 (3) Å
b = 10.6766 (5) Å
c = 15.7872 (8) Å
β = 100.253 (2)°
V = 1139.60 (9) Å^3
Z = 4
F(000) = 520
D_x = 1.447 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 9891 reflections
θ = 2.6–28.3°
µ = 0.11 mm^{-1}
T = 200 K
Rods, colourless
1.17 × 0.83 × 0.51 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}
φ and *ω* scans
Absorption correction: numerical (SADABS; Bruker, 2012)
T_{min} = 0.949, T_{max} = 1.000
20764 measured reflections
2822 independent reflections
2493 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 28.3°, θ_{min} = 2.6°
h = −9→9
k = −14→14
l = −21→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.099
S = 1.07
2822 reflections
166 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0477P)^2 + 0.329P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Extinction correction: SHELXL2019 (Sheldrick 2015b), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.079 (6)

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. Carbon-bound H atoms were placed in calculated positions and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2 U_{eq}(C).
The H atoms of the methyl groups were allowed to rotate with a fixed angle around the C—C bonds to best fit the experimental electron density (HFIX 137 in the SHELXL program (Sheldrick, 2015b)), with U_{iso}(H) set to 1.5U_{eq}(C).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.79762 (11)	0.34334 (7)	0.46569 (5)	0.02538 (19)
O2	0.79077 (14)	0.21576 (8)	0.35507 (6)	0.0396 (2)
O3	0.50507 (11)	0.44015 (8)	0.19049 (5)	0.0301 (2)
O4	0.81267 (13)	0.36747 (11)	0.19048 (6)	0.0462 (3)
O5	0.84494 (13)	0.36117 (7)	0.63348 (5)	0.0316 (2)
C1	0.77090 (15)	0.32183 (10)	0.37830 (7)	0.0260 (2)
C2	0.71575 (14)	0.42995 (10)	0.32256 (6)	0.0248 (2)
C3	0.68992 (14)	0.54435 (10)	0.35502 (6)	0.0237 (2)
H3	0.653204	0.612851	0.317136	0.028*
C4	0.71753 (14)	0.56343 (9)	0.44657 (6)	0.0217 (2)
C5	0.69055 (15)	0.67998 (10)	0.48436 (7)	0.0259 (2)
H5	0.654344	0.751578	0.449367	0.031*
C6	0.71718 (17)	0.68909 (10)	0.57258 (7)	0.0290 (2)
H6	0.699072	0.767685	0.598295	0.035*
C7	0.77047 (16)	0.58465 (10)	0.62509 (7)	0.0268 (2)
H7	0.789198	0.593193	0.685903	0.032*
C8	0.79613 (14)	0.46880 (10)	0.58905 (6)	0.0232 (2)
C9	0.77019 (14)	0.45954 (9)	0.49892 (6)	0.0210 (2)
C10	0.68750 (16)	0.40812 (10)	0.22747 (7)	0.0277 (2)
C11	0.45817 (19)	0.43114 (14)	0.09661 (7)	0.0388 (3)
H11A	0.507576	0.350933	0.077155	0.047*
H11B	0.521333	0.500698	0.070073	0.047*
C12	0.2378 (2)	0.43823 (13)	0.07087 (8)	0.0408 (3)
H12A	0.201660	0.432843	0.008068	0.061*
H12B	0.190598	0.517849	0.090568	0.061*
H12C	0.176997	0.368630	0.097143	0.061*
C13	0.85078 (18)	0.36488 (12)	0.72464 (7)	0.0339 (3)
H13A	0.723713	0.395328	0.736432	0.051*
H13B	0.956702	0.421322	0.751243	0.051*
H13C	0.875908	0.280532	0.748572	0.051*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0304 (4)	0.0234 (4)	0.0220 (4)	0.0014 (3)	0.0037 (3)	−0.0014 (3)
O2	0.0543 (6)	0.0292 (4)	0.0336 (5)	0.0017 (4)	0.0032 (4)	−0.0089 (3)

O3	0.0310 (4)	0.0405 (4)	0.0179 (4)	−0.0014 (3)	0.0018 (3)	−0.0010 (3)
O4	0.0362 (5)	0.0734 (7)	0.0298 (5)	0.0051 (4)	0.0082 (4)	−0.0159 (4)
O5	0.0454 (5)	0.0287 (4)	0.0206 (4)	0.0055 (3)	0.0058 (3)	0.0038 (3)
C1	0.0253 (5)	0.0285 (5)	0.0236 (5)	−0.0022 (4)	0.0027 (4)	−0.0046 (4)
C2	0.0214 (5)	0.0333 (5)	0.0195 (5)	−0.0016 (4)	0.0027 (4)	−0.0023 (4)
C3	0.0209 (4)	0.0295 (5)	0.0202 (5)	0.0008 (4)	0.0025 (3)	0.0015 (4)
C4	0.0182 (4)	0.0259 (5)	0.0209 (5)	0.0000 (3)	0.0036 (3)	−0.0005 (3)
C5	0.0281 (5)	0.0241 (5)	0.0258 (5)	0.0031 (4)	0.0056 (4)	0.0017 (4)
C6	0.0351 (6)	0.0254 (5)	0.0278 (5)	0.0024 (4)	0.0087 (4)	−0.0043 (4)
C7	0.0299 (5)	0.0305 (5)	0.0204 (5)	−0.0003 (4)	0.0057 (4)	−0.0025 (4)
C8	0.0220 (4)	0.0264 (5)	0.0211 (5)	0.0004 (4)	0.0037 (4)	0.0022 (4)
C9	0.0185 (4)	0.0234 (5)	0.0213 (5)	−0.0005 (3)	0.0038 (3)	−0.0018 (3)
C10	0.0288 (5)	0.0323 (5)	0.0218 (5)	−0.0046 (4)	0.0041 (4)	−0.0048 (4)
C11	0.0422 (7)	0.0551 (8)	0.0173 (5)	−0.0094 (6)	0.0008 (4)	−0.0021 (5)
C12	0.0459 (7)	0.0387 (6)	0.0323 (6)	0.0044 (5)	−0.0082 (5)	−0.0042 (5)
C13	0.0402 (6)	0.0403 (6)	0.0214 (5)	0.0062 (5)	0.0062 (4)	0.0063 (4)

Geometric parameters (Å, º)

O1—C9	1.3729 (12)	C5—H5	0.9500
O1—C1	1.3784 (12)	C6—C7	1.3988 (15)
O2—C1	1.2055 (13)	C6—H6	0.9500
O3—C10	1.3298 (13)	C7—C8	1.3858 (14)
O3—C11	1.4627 (12)	C7—H7	0.9500
O4—C10	1.2033 (14)	C8—C9	1.4057 (13)
O5—C8	1.3569 (12)	C11—C12	1.4981 (18)
O5—C13	1.4330 (12)	C11—H11A	0.9900
C1—C2	1.4601 (15)	C11—H11B	0.9900
C2—C3	1.3483 (14)	C12—H12A	0.9800
C2—C10	1.4973 (13)	C12—H12B	0.9800
C3—C4	1.4384 (13)	C12—H12C	0.9800
C3—H3	0.9500	C13—H13A	0.9800
C4—C9	1.3920 (14)	C13—H13B	0.9800
C4—C5	1.4065 (14)	C13—H13C	0.9800
C5—C6	1.3754 (14)		

C9—O1—C1	122.01 (8)	C7—C8—C9	118.42 (9)
C10—O3—C11	116.64 (9)	O1—C9—C4	122.15 (9)
C8—O5—C13	117.12 (8)	O1—C9—C8	116.68 (8)
O2—C1—O1	117.31 (10)	C4—C9—C8	121.17 (9)
O2—C1—C2	126.21 (10)	O4—C10—O3	125.37 (10)
O1—C1—C2	116.46 (9)	O4—C10—C2	124.51 (10)
C3—C2—C1	121.66 (9)	O3—C10—C2	110.12 (9)
C3—C2—C10	121.31 (9)	O3—C11—C12	107.53 (10)
C1—C2—C10	117.03 (9)	O3—C11—H11A	110.2
C2—C3—C4	120.49 (9)	C12—C11—H11A	110.2
C2—C3—H3	119.8	O3—C11—H11B	110.2
C4—C3—H3	119.8	C12—C11—H11B	110.2

C9—C4—C5	119.55 (9)	H11A—C11—H11B	108.5
C9—C4—C3	117.23 (9)	C11—C12—H12A	109.5
C5—C4—C3	123.21 (9)	C11—C12—H12B	109.5
C6—C5—C4	119.22 (9)	H12A—C12—H12B	109.5
C6—C5—H5	120.4	C11—C12—H12C	109.5
C4—C5—H5	120.4	H12A—C12—H12C	109.5
C5—C6—C7	121.16 (10)	H12B—C12—H12C	109.5
C5—C6—H6	119.4	O5—C13—H13A	109.5
C7—C6—H6	119.4	O5—C13—H13B	109.5
C8—C7—C6	120.47 (9)	H13A—C13—H13B	109.5
C8—C7—H7	119.8	O5—C13—H13C	109.5
C6—C7—H7	119.8	H13A—C13—H13C	109.5
O5—C8—C7	125.54 (9)	H13B—C13—H13C	109.5
O5—C8—C9	116.03 (9)		

C9—O1—C1—O2	−177.15 (10)	C1—O1—C9—C4	−1.30 (14)
C9—O1—C1—C2	1.26 (13)	C1—O1—C9—C8	178.13 (8)
O2—C1—C2—C3	177.42 (11)	C5—C4—C9—O1	179.69 (8)
O1—C1—C2—C3	−0.83 (15)	C3—C4—C9—O1	0.79 (14)
O2—C1—C2—C10	−2.14 (16)	C5—C4—C9—C8	0.28 (15)
O1—C1—C2—C10	179.62 (8)	C3—C4—C9—C8	−178.62 (8)
C1—C2—C3—C4	0.40 (15)	O5—C8—C9—O1	−0.25 (13)
C10—C2—C3—C4	179.93 (9)	C7—C8—C9—O1	179.76 (9)
C2—C3—C4—C9	−0.35 (14)	O5—C8—C9—C4	179.19 (9)
C2—C3—C4—C5	−179.21 (10)	C7—C8—C9—C4	−0.80 (14)
C9—C4—C5—C6	0.13 (15)	C11—O3—C10—O4	−3.49 (17)
C3—C4—C5—C6	178.96 (9)	C11—O3—C10—C2	176.49 (9)
C4—C5—C6—C7	−0.01 (16)	C3—C2—C10—O4	121.76 (13)
C5—C6—C7—C8	−0.53 (17)	C1—C2—C10—O4	−58.69 (15)
C13—O5—C8—C7	6.71 (15)	C3—C2—C10—O3	−58.23 (13)
C13—O5—C8—C9	−173.27 (9)	C1—C2—C10—O3	121.32 (10)
C6—C7—C8—O5	−179.07 (10)	C10—O3—C11—C12	165.49 (10)
C6—C7—C8—C9	0.92 (15)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O4^{i}	0.95	2.58	3.4065 (14)	146

Symmetry code: (i) $-x+3/2, y+1/2, -z+1/2$.

Ethyl 8-methoxy-2-sulfanylidene-2*H*-chromene-3-carboxylate (S2b)

Crystal data

$C_{13}H_{12}O_4S$
$M_r = 264.29$
Monoclinic, $P2_1/n$
$a = 6.8534\ (4)$ Å
$b = 11.2183\ (7)$ Å
$c = 15.8581\ (10)$ Å
$\beta = 98.620\ (2)°$
$V = 1205.45\ (13)$ Å^3
$Z = 4$
$F(000) = 552$
$D_x = 1.456$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9873 reflections
$\theta = 2.6–28.2°$
$\mu = 0.27$ mm^{-1}
$T = 199$ K
Block, orange
0.67 × 0.62 × 0.50 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: numerical (SADABS; Bruker, 2012)
$T_{\min} = 0.938$, $T_{\max} = 1.000$
20324 measured reflections
2981 independent reflections
2607 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.021$
$\theta_{\max} = 28.3°$, $\theta_{\min} = 2.6°$
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.104$
$S = 1.04$
2981 reflections
165 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0572P)^2 + 0.4794P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ 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.

Refinement. Carbon-bound H atoms were placed in calculated positions and were included in the refinement in the riding model approximation, with $U_{\text{iso}}(\text{H})$ set to 1.2 $U_{\text{eq}}(\text{C})$.
The H atoms of the methyl groups were allowed to rotate with a fixed angle around the C—C bonds to best fit the experimental electron density (HFIX 137 in the SHELXL program (Sheldrick, 2015b)), with $U_{\text{iso}}(\text{H})$ set to $1.5U_{\text{eq}}(\text{C})$.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.81219 (6)	0.81003 (3)	0.35733 (2)	0.03729 (13)
O1	0.80196 (13)	0.64604 (8)	0.46888 (5)	0.02304 (19)
O2	0.52085 (13)	0.58357 (9)	0.19721 (5)	0.0275 (2)
O3	0.84037 (16)	0.62830 (12)	0.19238 (6)	0.0431 (3)
O4	0.82689 (15)	0.62262 (9)	0.63363 (6)	0.0312 (2)
C1	0.78184 (18)	0.67129 (11)	0.38399 (7)	0.0227 (2)
C2	0.73279 (17)	0.57362 (11)	0.32548 (7)	0.0228 (2)
C3	0.70415 (17)	0.46181 (11)	0.35402 (7)	0.0232 (2)
H3	0.673325	0.398698	0.314315	0.028*
C4	0.72010 (17)	0.43832 (11)	0.44368 (7)	0.0213 (2)
C5	0.68396 (19)	0.32579 (11)	0.47790 (8)	0.0258 (3)
H5	0.651227	0.259254	0.441457	0.031*

C6	0.69689 (19)	0.31399 (11)	0.56490 (9)	0.0277 (3)
H6	0.671803	0.238510	0.588238	0.033*
C7	0.74618 (19)	0.41066 (12)	0.61991 (8)	0.0263 (3)
H7	0.755650	0.399798	0.679800	0.032*
C8	0.78121 (17)	0.52209 (11)	0.58746 (7)	0.0227 (2)
C9	0.76794 (16)	0.53401 (10)	0.49865 (7)	0.0204 (2)
C10	0.70779 (19)	0.59960 (11)	0.23125 (8)	0.0253 (3)
C11	0.4701 (2)	0.60326 (12)	0.10494 (8)	0.0294 (3)
H11A	0.555050	0.554053	0.073447	0.035*
H11B	0.488335	0.688148	0.090920	0.035*
C12	0.2582 (3)	0.56793 (18)	0.08158 (10)	0.0469 (4)
H12A	0.215039	0.583907	0.020897	0.070*
H12B	0.177050	0.614028	0.115732	0.070*
H12C	0.243843	0.482724	0.092827	0.070*
C13	0.8240 (2)	0.61662 (14)	0.72369 (8)	0.0344 (3)
H13A	0.692175	0.592954	0.734223	0.052*
H13B	0.856919	0.694987	0.749237	0.052*
H13C	0.921080	0.557826	0.749199	0.052*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0570 (3)	0.02629 (19)	0.02802 (19)	−0.00167 (15)	0.00464 (16)	0.00597 (12)
O1	0.0290 (4)	0.0220 (4)	0.0179 (4)	−0.0019 (3)	0.0028 (3)	0.0025 (3)
O2	0.0302 (5)	0.0348 (5)	0.0171 (4)	0.0004 (4)	0.0017 (3)	0.0026 (3)
O3	0.0361 (6)	0.0699 (8)	0.0242 (5)	−0.0023 (5)	0.0079 (4)	0.0090 (5)
O4	0.0466 (6)	0.0287 (5)	0.0185 (4)	−0.0060 (4)	0.0051 (4)	−0.0012 (3)
C1	0.0228 (6)	0.0262 (6)	0.0191 (5)	0.0016 (4)	0.0032 (4)	0.0033 (4)
C2	0.0214 (5)	0.0293 (6)	0.0179 (5)	0.0009 (5)	0.0034 (4)	0.0012 (4)
C3	0.0217 (5)	0.0269 (6)	0.0208 (5)	−0.0013 (4)	0.0028 (4)	−0.0021 (4)
C4	0.0183 (5)	0.0241 (6)	0.0216 (5)	0.0005 (4)	0.0032 (4)	0.0008 (4)
C5	0.0257 (6)	0.0237 (6)	0.0284 (6)	−0.0015 (4)	0.0050 (5)	0.0001 (5)
C6	0.0290 (6)	0.0239 (6)	0.0309 (6)	0.0007 (5)	0.0068 (5)	0.0064 (5)
C7	0.0278 (6)	0.0299 (6)	0.0217 (6)	0.0009 (5)	0.0054 (5)	0.0061 (5)
C8	0.0221 (5)	0.0259 (6)	0.0199 (5)	−0.0001 (4)	0.0023 (4)	0.0005 (4)
C9	0.0185 (5)	0.0222 (5)	0.0207 (5)	0.0005 (4)	0.0033 (4)	0.0026 (4)
C10	0.0301 (6)	0.0266 (6)	0.0195 (5)	0.0017 (5)	0.0050 (5)	0.0010 (4)
C11	0.0388 (7)	0.0323 (6)	0.0160 (5)	0.0027 (5)	0.0012 (5)	0.0041 (5)
C12	0.0463 (9)	0.0625 (11)	0.0282 (7)	−0.0113 (8)	−0.0064 (6)	0.0089 (7)
C13	0.0421 (8)	0.0422 (8)	0.0190 (6)	−0.0058 (6)	0.0053 (5)	−0.0019 (5)

Geometric parameters (Å, º)

S1—C1	1.6343 (13)	C5—H5	0.9500
O1—C1	1.3623 (14)	C6—C7	1.4011 (19)
O1—C9	1.3747 (14)	C6—H6	0.9500
O2—C10	1.3258 (16)	C7—C8	1.3864 (17)
O2—C11	1.4692 (14)	C7—H7	0.9500

O3—C10	1.2154 (16)	C8—C9	1.4040 (16)
O4—C8	1.3555 (15)	C11—C12	1.497 (2)
O4—C13	1.4327 (15)	C11—H11A	0.9900
C1—C2	1.4425 (17)	C11—H11B	0.9900
C2—C3	1.3577 (18)	C12—H12A	0.9800
C2—C10	1.5068 (16)	C12—H12B	0.9800
C3—C4	1.4341 (16)	C12—H12C	0.9800
C3—H3	0.9500	C13—H13A	0.9800
C4—C9	1.3907 (16)	C13—H13B	0.9800
C4—C5	1.4105 (17)	C13—H13C	0.9800
C5—C6	1.3757 (18)		

C1—O1—C9	122.15 (10)	C7—C8—C9	118.00 (11)
C10—O2—C11	117.07 (10)	O1—C9—C4	121.78 (10)
C8—O4—C13	117.57 (10)	O1—C9—C8	116.28 (10)
O1—C1—C2	117.20 (11)	C4—C9—C8	121.93 (11)
O1—C1—S1	117.11 (9)	O3—C10—O2	125.43 (12)
C2—C1—S1	125.69 (9)	O3—C10—C2	124.87 (12)
C3—C2—C1	121.25 (11)	O2—C10—C2	109.68 (10)
C3—C2—C10	120.57 (11)	O2—C11—C12	106.41 (11)
C1—C2—C10	118.16 (11)	O2—C11—H11A	110.4
C2—C3—C4	120.46 (11)	C12—C11—H11A	110.4
C2—C3—H3	119.8	O2—C11—H11B	110.4
C4—C3—H3	119.8	C12—C11—H11B	110.4
C9—C4—C5	119.23 (11)	H11A—C11—H11B	108.6
C9—C4—C3	117.09 (11)	C11—C12—H12A	109.5
C5—C4—C3	123.65 (11)	C11—C12—H12B	109.5
C6—C5—C4	118.90 (12)	H12A—C12—H12B	109.5
C6—C5—H5	120.5	C11—C12—H12C	109.5
C4—C5—H5	120.5	H12A—C12—H12C	109.5
C5—C6—C7	121.55 (11)	H12B—C12—H12C	109.5
C5—C6—H6	119.2	O4—C13—H13A	109.5
C7—C6—H6	119.2	O4—C13—H13B	109.5
C8—C7—C6	120.38 (11)	H13A—C13—H13B	109.5
C8—C7—H7	119.8	O4—C13—H13C	109.5
C6—C7—H7	119.8	H13A—C13—H13C	109.5
O4—C8—C7	126.05 (11)	H13B—C13—H13C	109.5
O4—C8—C9	115.95 (10)		

C9—O1—C1—C2	−3.16 (16)	C1—O1—C9—C4	3.16 (17)
C9—O1—C1—S1	175.96 (8)	C1—O1—C9—C8	−175.89 (10)
O1—C1—C2—C3	1.27 (17)	C5—C4—C9—O1	−179.07 (10)
S1—C1—C2—C3	−177.76 (10)	C3—C4—C9—O1	−1.08 (17)
O1—C1—C2—C10	179.41 (10)	C5—C4—C9—C8	−0.08 (18)
S1—C1—C2—C10	0.38 (17)	C3—C4—C9—C8	177.92 (10)
C1—C2—C3—C4	0.66 (18)	O4—C8—C9—O1	−0.24 (16)
C10—C2—C3—C4	−177.43 (10)	C7—C8—C9—O1	179.45 (10)
C2—C3—C4—C9	−0.77 (17)	O4—C8—C9—C4	−179.29 (11)

C2—C3—C4—C5	177.13 (12)	C7—C8—C9—C4	0.40 (18)
C9—C4—C5—C6	0.08 (18)	C11—O2—C10—O3	−0.6 (2)
C3—C4—C5—C6	−177.78 (11)	C11—O2—C10—C2	−179.06 (10)
C4—C5—C6—C7	−0.42 (19)	C3—C2—C10—O3	−113.31 (16)
C5—C6—C7—C8	0.8 (2)	C1—C2—C10—O3	68.54 (18)
C13—O4—C8—C7	−5.25 (19)	C3—C2—C10—O2	65.20 (15)
C13—O4—C8—C9	174.41 (11)	C1—C2—C10—O2	−112.95 (12)
C6—C7—C8—O4	178.93 (12)	C10—O2—C11—C12	174.50 (12)
C6—C7—C8—C9	−0.73 (18)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···S1^{i}	0.95	2.91	3.7460 (12)	147
C5—H5···O3^{i}	0.95	2.59	3.4774 (17)	156
C11—H11*B*···O4^{ii}	0.99	2.53	3.2803 (17)	132

Symmetry codes: (i) $-x+3/2, y-1/2, -z+1/2$; (ii) $x-1/2, -y+3/2, z-1/2$.

Ethyl 8-methoxy-2-sulfanylidene-2*H*-chromene-3-carbothioate (S3b)

Crystal data

$C_{13}H_{12}O_3S_2$
$M_r = 280.35$
Orthorhombic, $P2_12_12_1$
$a = 6.9815 (3)$ Å
$b = 11.7185 (4)$ Å
$c = 15.9642 (5)$ Å
$V = 1306.07 (8)$ Å^3
$Z = 4$
$F(000) = 584$
$D_x = 1.426$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9921 reflections
$\theta = 2.6–28.3°$
$\mu = 0.40$ mm^{-1}
$T = 200$ K
Block, orange
0.48 × 0.15 × 0.15 mm

Data collection

Bruker D8 QUEST diffractometer
Radiation source: sealed x-ray tube
Graphite monochromator
Detector resolution: 7.3910 pixels mm^{-1}
φ and ω scans
Absorption correction: numerical (SADABS; Krause *et al.*, 2015)
$T_{min} = 0.508, T_{max} = 1.000$
39191 measured reflections
3236 independent reflections
2716 reflections with $I > 2\sigma(I)$
$R_{int} = 0.091$
$\theta_{max} = 28.3°, \theta_{min} = 2.2°$
$h = -9 \rightarrow 9$
$k = -15 \rightarrow 15$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.141$
$S = 1.24$
3236 reflections
166 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.059P)^2 + 0.5127P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.66$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}
Absolute structure: Refined as an inversion twin.
Absolute structure parameter: 0.28 (16)

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. Carbon-bound H atoms were placed in calculated positions and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2 U_{eq}(C).
The H atoms of the methyl groups were allowed to rotate with a fixed angle around the C—C bonds to best fit the experimental electron density (HFIX 137 in the SHELXL program (Sheldrick, 2015b*Acta Cryst.* A**71**, 3–8.)), with U_{iso}(H) set to 1.5U_{eq}(C).
Refined as a 2-component inversion twin.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.4505 (2)	0.42794 (9)	0.64815 (7)	0.0549 (3)
S2	0.65791 (17)	0.60773 (12)	0.81399 (7)	0.0576 (4)
O1	0.4600 (4)	0.5818 (2)	0.53460 (14)	0.0366 (5)
O2	0.2942 (4)	0.6656 (2)	0.79980 (15)	0.0396 (6)
O3	0.4718 (5)	0.5983 (2)	0.37205 (15)	0.0477 (7)
C1	0.4566 (6)	0.5617 (3)	0.6188 (2)	0.0346 (7)
C2	0.4547 (5)	0.6598 (3)	0.6730 (2)	0.0332 (7)
C3	0.4485 (5)	0.7675 (3)	0.6411 (2)	0.0336 (7)
H3	0.442878	0.830990	0.678033	0.040*
C4	0.4504 (5)	0.7861 (3)	0.5523 (2)	0.0316 (7)
C5	0.4439 (6)	0.8948 (3)	0.5152 (2)	0.0394 (8)
H5	0.436584	0.961497	0.548912	0.047*
C6	0.4484 (6)	0.9031 (3)	0.4291 (2)	0.0420 (8)
H6	0.444656	0.976303	0.403595	0.050*
C7	0.4585 (6)	0.8055 (3)	0.3785 (2)	0.0386 (8)
H7	0.461900	0.813305	0.319335	0.046*
C8	0.4635 (5)	0.6985 (3)	0.4140 (2)	0.0345 (7)
C9	0.4585 (5)	0.6903 (3)	0.5017 (2)	0.0300 (7)
C10	0.4616 (6)	0.6432 (3)	0.7656 (2)	0.0361 (7)
C11	0.2741 (7)	0.6566 (4)	0.8913 (2)	0.0478 (10)
H11A	0.254324	0.576048	0.907750	0.057*
H11B	0.391389	0.685042	0.919242	0.057*
C12	0.1089 (9)	0.7255 (6)	0.9162 (3)	0.0795 (19)
H12A	0.130065	0.805098	0.899767	0.119*
H12B	0.092360	0.721120	0.977080	0.119*
H12C	−0.006428	0.696472	0.888450	0.119*
C13	0.4702 (8)	0.6049 (4)	0.2824 (2)	0.0530 (10)
H13A	0.472751	0.527718	0.258801	0.079*
H13B	0.582927	0.647326	0.263161	0.079*
H13C	0.353765	0.644242	0.263827	0.079*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0899 (9)	0.0342 (5)	0.0404 (5)	0.0014 (5)	0.0125 (6)	0.0063 (4)
S2	0.0494 (6)	0.0810 (9)	0.0425 (5)	0.0054 (6)	−0.0037 (5)	0.0205 (6)
O1	0.0486 (14)	0.0347 (12)	0.0265 (10)	0.0022 (12)	0.0039 (11)	0.0021 (9)
O2	0.0466 (15)	0.0476 (15)	0.0247 (11)	0.0026 (12)	0.0035 (10)	0.0002 (10)
O3	0.0749 (19)	0.0425 (14)	0.0258 (11)	0.0013 (15)	0.0017 (12)	−0.0030 (11)
C1	0.0406 (18)	0.0355 (17)	0.0276 (14)	−0.0001 (16)	0.0063 (15)	0.0025 (13)
C2	0.0323 (16)	0.0401 (17)	0.0272 (15)	0.0019 (16)	0.0030 (14)	0.0028 (13)
C3	0.0334 (17)	0.0399 (17)	0.0274 (15)	0.0010 (16)	0.0012 (14)	0.0005 (13)
C4	0.0297 (16)	0.0349 (16)	0.0301 (16)	0.0006 (15)	0.0009 (14)	0.0027 (13)
C5	0.048 (2)	0.0338 (17)	0.0365 (17)	0.0027 (18)	−0.0010 (16)	0.0012 (14)
C6	0.051 (2)	0.0395 (18)	0.0357 (17)	0.0040 (19)	−0.0003 (17)	0.0107 (15)
C7	0.0394 (18)	0.047 (2)	0.0293 (15)	0.0001 (18)	−0.0028 (16)	0.0071 (15)
C8	0.0353 (17)	0.0401 (17)	0.0281 (15)	0.0013 (16)	−0.0017 (15)	0.0006 (14)
C9	0.0296 (16)	0.0328 (15)	0.0276 (15)	−0.0009 (14)	0.0020 (14)	0.0036 (12)
C10	0.0426 (19)	0.0339 (16)	0.0319 (16)	−0.0020 (16)	0.0019 (15)	0.0052 (13)
C11	0.067 (3)	0.054 (2)	0.0215 (16)	0.000 (2)	0.0053 (17)	0.0026 (16)
C12	0.084 (4)	0.120 (5)	0.035 (2)	0.037 (4)	0.018 (2)	0.003 (3)
C13	0.071 (3)	0.060 (2)	0.0284 (16)	0.005 (2)	−0.0058 (19)	−0.0045 (17)

Geometric parameters (Å, º)

S1—C1	1.636 (4)	C5—H5	0.9500
S2—C10	1.627 (4)	C6—C7	1.402 (6)
O1—C1	1.365 (4)	C6—H6	0.9500
O1—C9	1.376 (4)	C7—C8	1.376 (5)
O2—C10	1.316 (5)	C7—H7	0.9500
O2—C11	1.471 (4)	C8—C9	1.403 (5)
O3—C8	1.353 (5)	C11—C12	1.463 (7)
O3—C13	1.434 (4)	C11—H11A	0.9900
C1—C2	1.439 (5)	C11—H11B	0.9900
C2—C3	1.362 (5)	C12—H12A	0.9800
C2—C10	1.492 (5)	C12—H12B	0.9800
C3—C4	1.434 (4)	C12—H12C	0.9800
C3—H3	0.9500	C13—H13A	0.9800
C4—C9	1.385 (5)	C13—H13B	0.9800
C4—C5	1.405 (5)	C13—H13C	0.9800
C5—C6	1.378 (5)		
C1—O1—C9	122.4 (3)	C7—C8—C9	118.2 (3)
C10—O2—C11	118.8 (3)	O1—C9—C4	121.8 (3)
C8—O3—C13	116.6 (3)	O1—C9—C8	116.4 (3)
O1—C1—C2	117.0 (3)	C4—C9—C8	121.8 (3)
O1—C1—S1	116.6 (3)	O2—C10—C2	110.8 (3)
C2—C1—S1	126.4 (3)	O2—C10—S2	127.0 (3)
C3—C2—C1	121.0 (3)	C2—C10—S2	122.0 (3)

C3—C2—C10	119.5 (3)	C12—C11—O2	107.8 (4)
C1—C2—C10	119.4 (3)	C12—C11—H11A	110.1
C2—C3—C4	120.7 (3)	O2—C11—H11A	110.1
C2—C3—H3	119.6	C12—C11—H11B	110.1
C4—C3—H3	119.6	O2—C11—H11B	110.1
C9—C4—C5	119.4 (3)	H11A—C11—H11B	108.5
C9—C4—C3	117.0 (3)	C11—C12—H12A	109.5
C5—C4—C3	123.7 (3)	C11—C12—H12B	109.5
C6—C5—C4	118.9 (3)	H12A—C12—H12B	109.5
C6—C5—H5	120.5	C11—C12—H12C	109.5
C4—C5—H5	120.5	H12A—C12—H12C	109.5
C5—C6—C7	121.2 (3)	H12B—C12—H12C	109.5
C5—C6—H6	119.4	O3—C13—H13A	109.5
C7—C6—H6	119.4	O3—C13—H13B	109.5
C8—C7—C6	120.5 (3)	H13A—C13—H13B	109.5
C8—C7—H7	119.8	O3—C13—H13C	109.5
C6—C7—H7	119.8	H13A—C13—H13C	109.5
O3—C8—C7	126.0 (3)	H13B—C13—H13C	109.5
O3—C8—C9	115.8 (3)		

C9—O1—C1—C2	−1.1 (5)	C1—O1—C9—C4	−1.0 (5)
C9—O1—C1—S1	177.7 (3)	C1—O1—C9—C8	179.6 (3)
O1—C1—C2—C3	2.7 (5)	C5—C4—C9—O1	−178.3 (3)
S1—C1—C2—C3	−176.0 (3)	C3—C4—C9—O1	1.5 (5)
O1—C1—C2—C10	−176.7 (3)	C5—C4—C9—C8	1.1 (5)
S1—C1—C2—C10	4.6 (5)	C3—C4—C9—C8	−179.2 (4)
C1—C2—C3—C4	−2.2 (6)	O3—C8—C9—O1	−0.8 (5)
C10—C2—C3—C4	177.2 (3)	C7—C8—C9—O1	178.8 (3)
C2—C3—C4—C9	0.1 (6)	O3—C8—C9—C4	179.8 (3)
C2—C3—C4—C5	179.9 (4)	C7—C8—C9—C4	−0.6 (6)
C9—C4—C5—C6	−0.9 (6)	C11—O2—C10—C2	−178.5 (3)
C3—C4—C5—C6	179.4 (4)	C11—O2—C10—S2	−1.2 (5)
C4—C5—C6—C7	0.3 (7)	C3—C2—C10—O2	73.3 (5)
C5—C6—C7—C8	0.2 (6)	C1—C2—C10—O2	−107.2 (4)
C13—O3—C8—C7	−1.7 (6)	C3—C2—C10—S2	−104.1 (4)
C13—O3—C8—C9	177.9 (4)	C1—C2—C10—S2	75.3 (4)
C6—C7—C8—O3	179.5 (4)	C10—O2—C11—C12	158.3 (4)
C6—C7—C8—C9	−0.1 (6)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···S2^{i}	0.95	2.86	3.764 (4)	160
C11—H11*A*···O3^{ii}	0.99	2.64	3.460 (6)	140
C11—H11*B*···S2	0.99	2.67	3.005 (5)	100

C12—H12*C*···S2^{iii}	0.98	2.83	3.805 (7)	178
C13—H13*C*···S1^{iv}	0.98	2.94	3.656 (5)	131

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