

2,3-Bis[(4-methylphenyl)sulfanyl]- 4*H*-1-benzothiopyran-4-one 1,1-dioxide forms a framework built from C—H···O, C—H··· π (arene) and π – π interactions

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Molecules of the title compound, C₂₃H₁₈O₃S₃, are linked into sheets by a combination of one C—H···O hydrogen bond and two C—H··· π (arene) hydrogen bonds, and these sheets are weakly linked into a three-dimensional structure by means of a single aromatic π – π stacking interaction.

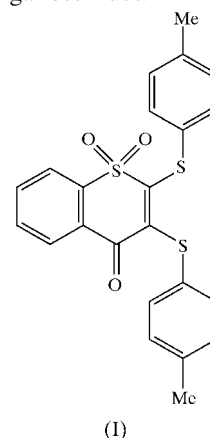
Comment

1,4-Naphthoquinone derivatives have been extensively studied as dyes and pigments (Tilak, 1971). Although 4*H*-1-benzothiopyran-4-one 1,1-dioxide derivatives have not been so well studied, it is known that their absorption spectra exhibit hypsochromic effects compared with the 1,4-naphthoquinone analogues (Christie *et al.*, 1980; Watanabe *et al.*, 1989, 1990). The crystal structures of two halogenated derivatives have been investigated as part of a study of non-linear optical materials (Watanabe *et al.*, 1989, 1992). Accordingly, we have now investigated the title non-halogenated analogue, (I) (Fig. 1), whose structure exhibits a rich variety of weak direction-specific intermolecular interactions.

The S—C distances in (I) (Table 1) show an unusual pattern. For the sulfone atom S1, formally S^{VI}, the S—C distance involving aryl C atoms is less than those involving alkene C atoms, whereas for the sulfide atoms S2 and S3, formally S^{II}, the bonds to alkene C atoms are the shorter. Within the heterocyclic ring, there is clear bond fixation with a short C8—C9 bond, while the π -bonding in each of the arene rings is fully delocalized.

The O—S—O bond angle in the sulfone fragment of (I) is significantly larger than the tetrahedral angle, while the opposed C—S—C angle at S1 is correspondingly much smaller

than the tetrahedral value. The bond angles at S2 and S3 are typical of those in organosulfides.



For the heterocyclic ring of (I), the ring-puckering parameters (Cremer & Pople, 1975) for the atom sequence S1/C1/C6—C9 are $\theta = 85.5(5)^\circ$ and $\varphi = 18.6(5)^\circ$, indicative of a conformation best described as twist-boat (Evans & Boeyens, 1989). The values of the torsion angles C9—C8—S2—C21 and C8—C9—S3—C31 are indicative of entirely different orientations for the two pendant groups (see also Fig. 1).

The molecules of (I) are linked into a three-dimensional framework by a variety of weak but direction-specific intermolecular forces, and the formation of this framework is readily analysed by means of the substructure approach (Gregson *et al.*, 2000). A single C—H···O hydrogen bond (Table 2) links the molecules into chains. These chains are linked into sheets by the combined action of two C—H··· π (arene) hydrogen bonds and the sheets are linked together by a single aromatic π – π stacking interaction.

Atom C32 in the molecule at (x, y, z) acts as hydrogen-bond donor to sulfone atom O11 in the molecule at $(x, \frac{1}{2} - y, z - \frac{1}{2})$, so producing a zigzag C(7) chain (Bernstein *et al.*, 1995)

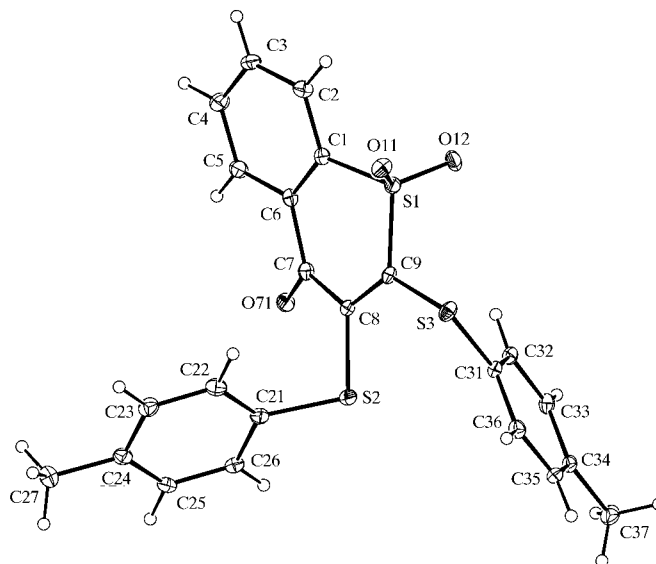


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

running parallel to the [001] direction and generated by the c -glide plane at $y = \frac{1}{4}$ (Fig. 2). The formation of this chain is modestly reinforced by a short dipolar contact between the negatively charged sulfone atom O11 in the molecule at (x, y, z) and the positively charged carbonyl atom C7 in the molecule at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$. The $O11 \cdots C7^{IV}$ distance is 2.938 (3) Å and the $S1-O11 \cdots C7^{IV}$ angle is 138.6 (2)° [symmetry code: (iv) $x, \frac{1}{2} - y, \frac{1}{2} + z$].

Atoms C5 and C35 in the molecule at (x, y, z) act as hydrogen-bond donors to, respectively, the C31–C36 ring in the molecule at $(x - 1, y, z)$ and the C21–C26 ring in the molecule at $(1 + x, y, z)$. In this manner, a chain of rings is generated by translation along the [100] direction (Fig. 3). The combination of the [100] and [001] chains produces an (010)

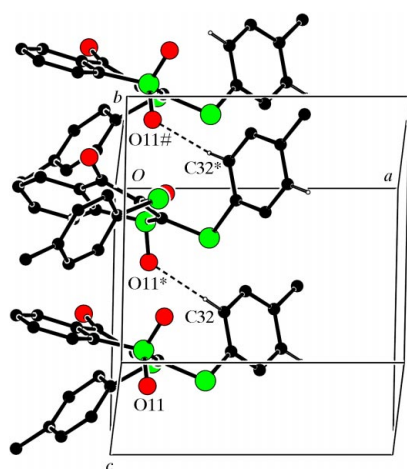


Figure 2

Part of the crystal structure of (I), showing the formation of a $C(7)$ chain along [001]. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x, \frac{1}{2} - y, z - \frac{1}{2})$ and $(x, y, z - 1)$, respectively.

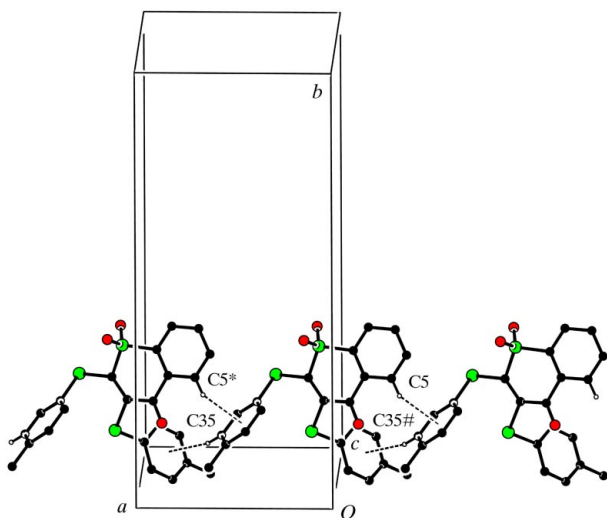


Figure 3

Part of the crystal structure of (I), showing the formation of a chain of rings along [100]. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(1 + x, y, z)$ and $(x - 1, y, z)$, respectively.

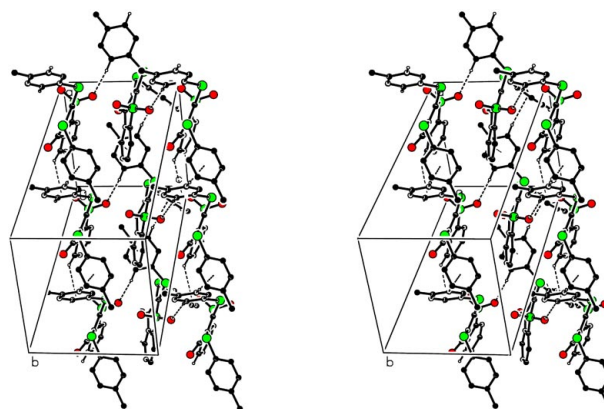


Figure 4

A stereoview of part of the crystal structure of (I), showing the formation of an (010) sheet by the combination of the [100] and [001] chains. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

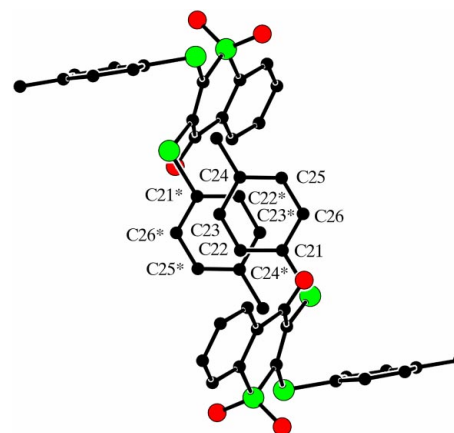


Figure 5

Part of the crystal structure of (I), showing the π - π stacking interaction which links adjacent (010) sheets. For the sake of clarity, H atoms have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(-x, -y, 2 - z)$.

sheet lying in the domain $-0.06 < y < 0.56$ and generated by the c -glide plane at $y = \frac{1}{4}$ (Fig. 4). A similar sheet, generated by the c -glide plane at $y = \frac{3}{4}$ and related to the first by inversion, lies in the domain $0.44 < y < 1.06$.

Adjacent (010) sheets are weakly linked by a π - π stacking interaction. The C21–C26 rings in the molecules at (x, y, z) and $(-x, -y, 2 - z)$ lie in (010) sheets generated by glide planes at $y = \frac{1}{4}$ and $-\frac{1}{4}$, respectively. These two rings are parallel, with an interplanar spacing of 3.548 (2) Å. The ring-centroid separation is 3.876 (2) Å, corresponding to a centroid offset of 1.561 (2) Å (Fig. 5). Propagation by the space group of this interaction is sufficient to link all of the (010) sheets into a single framework structure.

Experimental

A sample of compound (I) was prepared following the procedure of Christie *et al.* (1980). The crystals used in the present structure determination were grown by slow evaporation of a solution in ethanol [m.p. 432–434 K; literature m.p. 433–433.5 K (Christie *et al.*, 1980)].

Crystal data

$C_{23}H_{18}O_3S_3$	$D_x = 1.458 \text{ Mg m}^{-3}$
$M_r = 438.58$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 4564 reflections
$a = 9.6349 (3) \text{ \AA}$	$\theta = 3.2\text{--}27.5^\circ$
$b = 22.5791 (7) \text{ \AA}$	$\mu = 0.39 \text{ mm}^{-1}$
$c = 9.1895 (4) \text{ \AA}$	$T = 120 (2) \text{ K}$
$\beta = 91.253 (2)^\circ$	Block, orange
$V = 1998.67 (12) \text{ \AA}^3$	$0.30 \times 0.20 \times 0.10 \text{ mm}$
$Z = 4$	

Data collection

Nonius KappaCCD area-detector diffractometer	4564 independent reflections
φ scans, and ω scans with κ offsets	3002 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SORTAV; Blessing, 1995, 1997)	$R_{\text{int}} = 0.051$
$T_{\text{min}} = 0.891$, $T_{\text{max}} = 0.962$	$\theta_{\text{max}} = 27.5^\circ$
8989 measured reflections	$h = -12 \rightarrow 12$
	$k = -27 \rightarrow 29$
	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.044$	$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2]$
$wR(F^2) = 0.107$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{\text{max}} = 0.001$
4564 reflections	$\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
264 parameters	$\Delta\rho_{\text{min}} = -0.52 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

S1—C1	1.753 (2)	S1—O11	1.4363 (17)
S1—C9	1.770 (2)	S1—O12	1.4311 (16)
C8—S2	1.756 (2)	C6—C7	1.488 (3)
S2—C21	1.778 (2)	C7—C8	1.513 (3)
C9—S3	1.757 (2)	C8—C9	1.349 (3)
S3—C31	1.784 (2)	C7—O71	1.213 (3)
O11—S1—O12	117.38 (10)	C8—S2—C21	101.52 (10)
C1—S1—C9	104.88 (10)	C9—S3—C31	103.53 (11)
S1—C1—C6—C7	8.8 (3)	O71—C7—C8—C9	159.0 (2)
C1—C6—C7—C8	13.2 (3)	O71—C7—C6—C1	-167.9 (2)
C6—C7—C8—C9	-22.1 (3)	C9—C8—S2—C21	133.62 (19)
C7—C8—C9—S1	7.4 (3)	C8—S2—C21—C22	-49.7 (2)
C8—C9—S1—C1	11.8 (2)	C8—C9—S3—C31	49.6 (2)
C9—S1—C1—C6	-19.7 (2)	C9—S3—C31—C32	35.3 (2)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

C_{g1} is the centroid of the C31—C36 ring and C_{g2} is the centroid of the C21—C26 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C32—H32 \cdots O11 ⁱ	0.95	2.32	3.197 (3)	154
C5—H5 \cdots Cg1 ⁱⁱ	0.95	2.55	3.308 (2)	137
C35—H35 \cdots Cg2 ⁱⁱⁱ	0.95	2.73	3.658 (2)	164

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

The space group $P2_1/c$ was uniquely assigned from the systematic absences. All H atoms were located from difference maps and then treated as riding atoms, with C—H distances of 0.95 (aromatic) or 0.98 \AA (methyl), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic H and $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

The X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work. JLW thanks CNPq and FAPERJ for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1715). Services for accessing these data are described at the back of the journal.

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Computing details

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: -P 2ybc	Cell parameters from 4564 reflections
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Graphite monochromator	3002 reflections with $I > 2\sigma(I)$
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Absorption correction: multi-scan (<i>SORTAV</i> ; Blessing, 1995, 1997)	$\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 3.2^\circ$
$T_{\text{min}} = 0.891$, $T_{\text{max}} = 0.962$	$h = -12 \rightarrow 12$
	$k = -27 \rightarrow 29$
	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.044$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.107$	H-atom parameters constrained
$S = 1.00$	
4564 reflections	
264 parameters	
0 restraints	

$$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.32 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.52 \text{ e } \text{\AA}^{-3}$$

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.10208 (6)	0.27529 (2)	0.70282 (7)	0.01843 (16)
S2	0.13922 (6)	0.08214 (2)	0.68332 (7)	0.02260 (17)
S3	0.32554 (6)	0.19732 (3)	0.79040 (7)	0.02217 (16)
O11	0.11720 (15)	0.30057 (7)	0.84572 (18)	0.0233 (4)
O12	0.17223 (16)	0.30414 (7)	0.58686 (19)	0.0267 (4)
O71	-0.10696 (15)	0.12330 (6)	0.51304 (18)	0.0218 (4)
C1	-0.0756 (2)	0.27169 (9)	0.6587 (3)	0.0171 (5)
C2	-0.1518 (2)	0.32310 (10)	0.6758 (3)	0.0236 (6)
C3	-0.2905 (2)	0.32394 (10)	0.6330 (3)	0.0257 (6)
C4	-0.3504 (2)	0.27408 (10)	0.5710 (3)	0.0281 (6)
C5	-0.2743 (2)	0.22280 (10)	0.5535 (3)	0.0231 (6)
C6	-0.1351 (2)	0.22067 (10)	0.5987 (3)	0.0182 (5)
C7	-0.0597 (2)	0.16342 (10)	0.5866 (3)	0.0183 (5)
C8	0.0763 (2)	0.15497 (9)	0.6694 (3)	0.0167 (5)
C9	0.1564 (2)	0.20056 (10)	0.7156 (3)	0.0172 (5)
C21	-0.0051 (2)	0.04489 (10)	0.7584 (3)	0.0198 (5)
C22	-0.0710 (2)	0.06696 (10)	0.8804 (3)	0.0246 (6)
C23	-0.1755 (3)	0.03432 (10)	0.9435 (3)	0.0255 (6)
C24	-0.2159 (2)	-0.02075 (10)	0.8883 (3)	0.0219 (5)
C25	-0.1481 (2)	-0.04205 (10)	0.7681 (3)	0.0207 (5)
C26	-0.0441 (2)	-0.00996 (9)	0.7019 (3)	0.0199 (5)
C27	-0.3309 (2)	-0.05497 (11)	0.9582 (3)	0.0283 (6)
C31	0.4161 (2)	0.15200 (10)	0.6649 (3)	0.0176 (5)
C32	0.3887 (2)	0.15339 (10)	0.5171 (3)	0.0204 (5)
C33	0.4637 (2)	0.11650 (10)	0.4260 (3)	0.0205 (5)
C34	0.5672 (2)	0.07933 (9)	0.4805 (3)	0.0206 (5)
C35	0.5950 (2)	0.07985 (10)	0.6290 (3)	0.0218 (6)
C36	0.5194 (2)	0.11533 (10)	0.7220 (3)	0.0206 (5)
C37	0.6488 (2)	0.04015 (10)	0.3807 (3)	0.0277 (6)
H2	-0.1093	0.3575	0.7165	0.028*
H3	-0.3443	0.3587	0.6462	0.031*
H4	-0.4450	0.2751	0.5400	0.034*
H5	-0.3168	0.1889	0.5106	0.028*
H22	-0.0444	0.1042	0.9202	0.030*
H23	-0.2207	0.0498	1.0261	0.031*
H25	-0.1734	-0.0797	0.7297	0.025*
H26	0.0002	-0.0253	0.6187	0.024*
H27A	-0.4202	-0.0432	0.9142	0.042*
H27B	-0.3308	-0.0465	1.0628	0.042*
H27C	-0.3163	-0.0975	0.9431	0.042*
H32	0.3195	0.1792	0.4778	0.025*

H33	0.4436	0.1168	0.3243	0.025*
H35	0.6672	0.0555	0.6679	0.026*
H36	0.5382	0.1145	0.8239	0.025*
H37A	0.5900	0.0286	0.2970	0.042*
H37B	0.6792	0.0046	0.4336	0.042*
H37C	0.7301	0.0618	0.3466	0.042*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0175 (3)	0.0173 (3)	0.0205 (4)	−0.0009 (2)	0.0010 (2)	−0.0026 (2)
S2	0.0189 (3)	0.0167 (3)	0.0323 (4)	0.0018 (2)	0.0023 (3)	−0.0008 (3)
S3	0.0159 (3)	0.0273 (3)	0.0233 (4)	0.0013 (2)	−0.0016 (2)	−0.0079 (3)
O11	0.0212 (8)	0.0240 (9)	0.0245 (10)	0.0006 (7)	−0.0043 (7)	−0.0101 (7)
O12	0.0263 (9)	0.0234 (9)	0.0308 (11)	−0.0068 (7)	0.0088 (8)	0.0022 (8)
O71	0.0213 (8)	0.0199 (9)	0.0243 (10)	−0.0032 (7)	−0.0010 (7)	−0.0043 (7)
C1	0.0178 (11)	0.0189 (12)	0.0147 (13)	−0.0008 (10)	0.0006 (10)	0.0002 (9)
C2	0.0268 (13)	0.0185 (12)	0.0256 (15)	0.0005 (10)	−0.0006 (11)	−0.0004 (11)
C3	0.0231 (13)	0.0192 (12)	0.0349 (17)	0.0058 (10)	−0.0012 (12)	0.0027 (11)
C4	0.0186 (12)	0.0264 (13)	0.0390 (17)	0.0028 (11)	−0.0049 (11)	0.0043 (12)
C5	0.0231 (12)	0.0195 (12)	0.0267 (15)	−0.0010 (10)	−0.0019 (11)	0.0024 (10)
C6	0.0180 (11)	0.0197 (12)	0.0170 (13)	−0.0023 (9)	0.0021 (10)	0.0003 (10)
C7	0.0175 (11)	0.0207 (12)	0.0168 (13)	−0.0021 (10)	0.0007 (10)	−0.0010 (10)
C8	0.0151 (11)	0.0169 (11)	0.0183 (13)	0.0008 (9)	0.0040 (10)	−0.0006 (10)
C9	0.0148 (11)	0.0209 (12)	0.0162 (13)	0.0015 (10)	0.0037 (10)	−0.0024 (10)
C21	0.0207 (12)	0.0185 (12)	0.0201 (14)	0.0023 (9)	−0.0020 (10)	0.0018 (10)
C22	0.0299 (13)	0.0192 (12)	0.0247 (15)	0.0013 (11)	−0.0007 (11)	−0.0030 (11)
C23	0.0284 (13)	0.0273 (13)	0.0211 (15)	0.0050 (11)	0.0040 (11)	−0.0016 (11)
C24	0.0237 (12)	0.0221 (12)	0.0197 (14)	0.0033 (10)	−0.0016 (11)	0.0054 (10)
C25	0.0239 (12)	0.0145 (12)	0.0236 (15)	0.0003 (9)	−0.0039 (11)	0.0009 (10)
C26	0.0221 (12)	0.0194 (12)	0.0182 (13)	0.0051 (10)	−0.0012 (10)	−0.0004 (10)
C27	0.0290 (13)	0.0284 (14)	0.0275 (16)	−0.0041 (11)	0.0035 (12)	0.0032 (11)
C31	0.0127 (10)	0.0189 (12)	0.0213 (14)	0.0007 (9)	0.0022 (10)	0.0001 (10)
C32	0.0131 (11)	0.0230 (12)	0.0250 (15)	0.0002 (10)	−0.0009 (10)	0.0018 (11)
C33	0.0170 (11)	0.0257 (12)	0.0187 (14)	−0.0040 (10)	0.0006 (10)	−0.0027 (10)
C34	0.0150 (11)	0.0175 (12)	0.0293 (16)	−0.0028 (9)	0.0041 (11)	−0.0032 (10)
C35	0.0148 (11)	0.0187 (12)	0.0320 (16)	0.0028 (10)	0.0013 (11)	0.0038 (11)
C36	0.0198 (12)	0.0241 (13)	0.0178 (14)	−0.0016 (10)	−0.0009 (10)	0.0042 (10)
C37	0.0237 (13)	0.0233 (13)	0.0364 (17)	−0.0006 (10)	0.0059 (12)	−0.0095 (12)

Geometric parameters (Å, °)

C1—C2	1.384 (3)	C22—H22	0.95
C1—C6	1.395 (3)	C23—C24	1.395 (3)
S1—C1	1.753 (2)	C23—H23	0.95
S1—C9	1.770 (2)	C24—C25	1.382 (3)
C8—S2	1.756 (2)	C24—C27	1.506 (3)
S2—C21	1.778 (2)	C25—C26	1.388 (3)

C9—S3	1.757 (2)	C25—H25	0.95
S3—C31	1.784 (2)	C26—H26	0.95
S1—O11	1.4363 (17)	C27—H27A	0.98
S1—O12	1.4311 (16)	C27—H27B	0.98
C6—C7	1.488 (3)	C27—H27C	0.98
C7—C8	1.513 (3)	C31—C32	1.379 (3)
C8—C9	1.349 (3)	C31—C36	1.388 (3)
C7—O71	1.213 (3)	C32—C33	1.394 (3)
C2—C3	1.385 (3)	C32—H32	0.95
C2—H2	0.95	C33—C34	1.389 (3)
C3—C4	1.382 (3)	C33—H33	0.95
C3—H3	0.95	C34—C35	1.384 (3)
C4—C5	1.381 (3)	C34—C37	1.508 (3)
C4—H4	0.95	C35—C36	1.390 (3)
C5—C6	1.396 (3)	C35—H35	0.95
C5—H5	0.95	C36—H36	0.95
C21—C26	1.391 (3)	C37—H37A	0.98
C21—C22	1.392 (3)	C37—H37B	0.98
C22—C23	1.385 (3)	C37—H37C	0.98
C2—C1—C6	121.6 (2)	C24—C23—H23	119.3
C2—C1—S1	116.90 (17)	C25—C24—C23	117.9 (2)
C6—C1—S1	121.35 (17)	C25—C24—C27	121.8 (2)
C1—C2—C3	119.3 (2)	C23—C24—C27	120.3 (2)
C1—C2—H2	120.3	C24—C25—C26	121.8 (2)
C3—C2—H2	120.3	C24—C25—H25	119.1
C4—C3—C2	119.8 (2)	C26—C25—H25	119.1
C4—C3—H3	120.1	C25—C26—C21	119.5 (2)
C2—C3—H3	120.1	C25—C26—H26	120.2
C5—C4—C3	120.9 (2)	C21—C26—H26	120.2
C5—C4—H4	119.6	C24—C27—H27A	109.5
C3—C4—H4	119.6	C24—C27—H27B	109.5
C4—C5—C6	120.2 (2)	H27A—C27—H27B	109.5
C4—C5—H5	119.9	C24—C27—H27C	109.5
C6—C5—H5	119.9	H27A—C27—H27C	109.5
C1—C6—C5	118.2 (2)	H27B—C27—H27C	109.5
C1—C6—C7	123.4 (2)	C9—S3—C31	103.53 (11)
C5—C6—C7	118.3 (2)	C32—C31—C36	120.4 (2)
O71—C7—C6	120.8 (2)	C32—C31—S3	122.52 (17)
O71—C7—C8	119.8 (2)	C36—C31—S3	117.03 (18)
C6—C7—C8	119.37 (19)	C31—C32—C33	119.1 (2)
C9—C8—C7	123.0 (2)	C31—C32—H32	120.4
C9—C8—S2	119.85 (18)	C33—C32—H32	120.4
C7—C8—S2	116.63 (16)	C34—C33—C32	121.5 (2)
C8—C9—S3	127.61 (18)	C34—C33—H33	119.3
C8—C9—S1	122.73 (18)	C32—C33—H33	119.3
S3—C9—S1	109.64 (12)	C35—C34—C33	118.2 (2)
O11—S1—O12	117.38 (10)	C35—C34—C37	120.8 (2)

O12—S1—C1	108.89 (11)	C33—C34—C37	121.0 (2)
O11—S1—C1	108.00 (10)	C34—C35—C36	121.2 (2)
O12—S1—C9	109.85 (10)	C34—C35—H35	119.4
O11—S1—C9	107.11 (11)	C36—C35—H35	119.4
C1—S1—C9	104.88 (10)	C31—C36—C35	119.5 (2)
C8—S2—C21	101.52 (10)	C31—C36—H36	120.3
C26—C21—C22	119.7 (2)	C35—C36—H36	120.3
C26—C21—S2	118.90 (17)	C34—C37—H37A	109.5
C22—C21—S2	121.16 (18)	C34—C37—H37B	109.5
C23—C22—C21	119.6 (2)	H37A—C37—H37B	109.5
C23—C22—H22	120.2	C34—C37—H37C	109.5
C21—C22—H22	120.2	H37A—C37—H37C	109.5
C22—C23—C24	121.4 (2)	H37B—C37—H37C	109.5
C22—C23—H23	119.3		
C6—C1—C2—C3	0.3 (3)	C6—C1—S1—O11	-133.73 (19)
S1—C1—C2—C3	175.50 (19)	C2—C1—S1—C9	165.02 (18)
C1—C2—C3—C4	-1.4 (4)	C8—C9—S1—O12	-105.1 (2)
C2—C3—C4—C5	1.2 (4)	S3—C9—S1—O12	73.40 (14)
C3—C4—C5—C6	0.1 (4)	C8—C9—S1—O11	126.4 (2)
C2—C1—C6—C5	1.0 (3)	S3—C9—S1—O11	-55.11 (13)
S1—C1—C6—C5	-174.01 (17)	S3—C9—S1—C1	-169.72 (11)
C2—C1—C6—C7	-176.1 (2)	C7—C8—S2—C21	-54.35 (18)
S1—C1—C6—C7	8.8 (3)	C8—S2—C21—C26	136.3 (2)
C1—C6—C7—C8	13.2 (3)	C26—C21—C22—C23	-0.6 (4)
C6—C7—C8—C9	-22.1 (3)	S2—C21—C22—C23	-174.58 (19)
C7—C8—C9—S1	7.4 (3)	C21—C22—C23—C24	0.6 (4)
C8—C9—S1—C1	11.8 (2)	C22—C23—C24—C25	0.0 (4)
C9—S1—C1—C6	-19.7 (2)	C22—C23—C24—C27	-179.4 (2)
O71—C7—C8—C9	159.0 (2)	C23—C24—C25—C26	-0.7 (4)
O71—C7—C6—C1	-167.9 (2)	C27—C24—C25—C26	178.7 (2)
C9—C8—S2—C21	133.62 (19)	C24—C25—C26—C21	0.8 (4)
C8—S2—C21—C22	-49.7 (2)	C22—C21—C26—C25	-0.1 (4)
C8—C9—S3—C31	49.6 (2)	S2—C21—C26—C25	174.04 (18)
C9—S3—C31—C32	35.3 (2)	S1—C9—S3—C31	-128.77 (12)
C4—C5—C6—C1	-1.2 (3)	C9—S3—C31—C36	-145.94 (17)
C4—C5—C6—C7	176.1 (2)	C36—C31—C32—C33	1.5 (3)
C5—C6—C7—O71	15.0 (3)	S3—C31—C32—C33	-179.84 (15)
C5—C6—C7—C8	-163.9 (2)	C31—C32—C33—C34	-1.3 (3)
O71—C7—C8—S2	-12.7 (3)	C32—C33—C34—C35	-0.3 (3)
C6—C7—C8—S2	166.13 (16)	C32—C33—C34—C37	-179.28 (19)
C7—C8—C9—S3	-170.73 (16)	C33—C34—C35—C36	1.7 (3)
S2—C8—C9—S3	0.8 (3)	C37—C34—C35—C36	-179.29 (19)
S2—C8—C9—S1	178.94 (12)	C32—C31—C36—C35	-0.1 (3)
C2—C1—S1—O12	-77.4 (2)	S3—C31—C36—C35	-178.85 (16)
C6—C1—S1—O12	97.8 (2)	C34—C35—C36—C31	-1.5 (3)
C2—C1—S1—O11	51.0 (2)		

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>
C32—H32 \cdots O11 ⁱ	0.95	2.32	3.197 (3)	154
C5—H5 \cdots Cg1 ⁱⁱ	0.95	2.55	3.308 (2)	137
C35—H35 \cdots Cg2 ⁱⁱⁱ	0.95	2.73	3.658 (2)	164

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