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5,17-Dibromo-26,28-bis[(methoxy-carbonyl)methoxy]-25,27-dipropoxy-2,8,14,20-tetrathiacalix[4]arene

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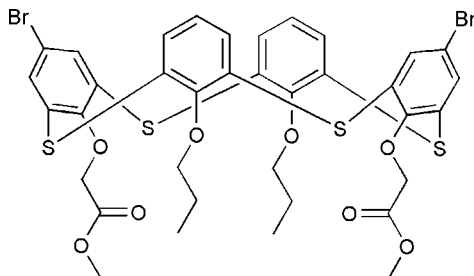
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 Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.042; wR factor = 0.091; data-to-parameter ratio = 15.4.

The title thiacalix[4]arene derivative, $\text{C}_{36}\text{H}_{34}\text{Br}_2\text{O}_8\text{S}_4$, adopts an unusual pinched cone conformation with the propoxy-substituted benzene rings inclined inward [forming a dihedral angle of $33.4(1)^\circ$] and with the brominated benzene rings bent outward, making a dihedral angle of $66.1(1)^\circ$. In the crystal, the molecules form chains along [001] via $\text{C}-\text{H}\cdots\text{S}$ hydrogen bonds and $\text{S}\cdots\text{S}$ contacts [$\text{S}\cdots\text{S} = 3.492(3)$ Å]. The chains are associated into bilayers through $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds, generating an $R_2^2(10)$ motif.

Related literature

For general background to the chemistry of thiacalix[4]arenes, see: Shokova & Kovalev (2003); Lhoták (2004); Morohashi *et al.* (2006); Kajiwara *et al.* (2007); Guo *et al.* (2007). For related structures, see: Lhoták *et al.* (2000, 2003); Himl *et al.* (2005); Xu *et al.* (2008); Chen *et al.* (2010); Liu *et al.* (2011). For hydrogen-bond motifs, see: Bernstein *et al.* (1995); Hu *et al.* (2009). For atomic van der Waals radii, see: Bondi (1964).



Experimental

Crystal data

 $\text{C}_{36}\text{H}_{34}\text{Br}_2\text{O}_8\text{S}_4$
 $M_r = 882.69$

 Monoclinic, $P2_1/c$
 $a = 16.024(3)$ Å

 $b = 14.808(3)$ Å
 $c = 15.872(3)$ Å
 $\beta = 100.065(3)^\circ$
 $V = 3708.3(12)$ Å³
 $Z = 4$

 Mo $K\alpha$ radiation
 $\mu = 2.46$ mm⁻¹
 $T = 173$ K
 $0.38 \times 0.18 \times 0.13$ mm

Data collection

 Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 1999)
 $T_{\min} = 0.455$, $T_{\max} = 0.740$
 19322 measured reflections
 6989 independent reflections
 4908 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.060$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.091$
 $S = 0.93$
 6989 reflections
 455 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.62$ e Å⁻³
 $\Delta\rho_{\min} = -0.55$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|-------|-------------|-------------|---------------|
| $\text{C4}-\text{H4}\cdots\text{S3}^i$ | 0.95 | 2.91 | 3.755 (3) | 149 |
| $\text{C33}-\text{H33A}\cdots\text{O7}^{ii}$ | 0.98 | 2.58 | 3.551 (5) | 169 |

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

Data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LD2052).

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Xu, W.-N., Yuan, J.-M., Liu, Y., Ma, J.-P. & Guo, D.-S. (2008). *Acta Cryst.* **C64**, o349–o352.

supporting information

Acta Cryst. (2012). E68, o1353–o1354 [doi:10.1107/S1600536812014559]

5,17-Dibromo-26,28-bis[(methoxycarbonyl)methoxy]-25,27-dipropoxy-2,8,14,20-tetrathiacalix[4]arene

Li-Jing Zhang, Ling-Ling Liu, Qi-Kui Liu and Dian-Shun Guo

S1. Comment

Thiacalix[4]arenes have attracted much interest because of their specific affinity, selectivity in molecular recognition, and supramolecular assembly (Shokova & Kovalev, 2003; Lhoták, 2004; Morohashi *et al.*, 2006; Kajiwara *et al.*, 2007; Guo *et al.*, 2007). Numerous crystal structures of thiacalix[4]arenes uniformly substituted at the lower rim or at the upper rim are known (Lhoták *et al.*, 2000, 2003; Himl *et al.*, 2005). Recently, we have presented structures of several dibromo and tetrabromothiacalix[4]arene derivatives that possess four identical or four different substituents at the lower rim (Xu *et al.*, 2008; Chen *et al.*, 2010; Liu *et al.*, 2011). Here we report the crystal structure of another dibromothiacalix[4]arene compound with different substituents at the lower rim – 5,17-dibromo-26,28-bis[(methoxycarbonyl)methoxy]-25,27-dipropoxy-2,8,14,20-tetrathiacalix[4]arene.

In the crystal structure of the title compound, C₃₆H₃₄Br₂O₈S₄, (Fig. 1), the thiacalix[4]arene unit adopts an unusual pinched cone conformation. Two opposite bromosubstituted phenolic rings are strongly bent outwards the thiacalix cavity with a Br⋯Br distance of 13.819 (3) Å [larger than that reported previously - 13.165 (2) Å (Liu *et al.*, 2011)]. The other two opposing phenolic rings are bent inwards. The phenolic rings form dihedral angles of 26.09 (7), 65.57 (7), 40.29 (6) and 81.18 (7)° with the virtual plane defined by the four bridging S atoms.

In the packing, there are several intermolecular short contacts (Table 1). The molecules are linked into an infinite zigzag one-dimensional chain along [001] (Hu *et al.*, 2009) by intermolecular C4—H4⋯S3(x, -y + 1/2, z - 1/2) hydrogen bonds, locally forming a C(8) motif (Bernstein *et al.*, 1995) (Fig. 2). Interestingly, in such a chain all 'tails' of the molecules extend to the same orientation and a significant S⋯S interaction between the adjacent thiacalix[4]arenes stabilizes the motif, with a S1⋯S3 distance of 3.492 (3) Å (S = 1.80 Å; Bondi, 1964). Finally, these chains are packed into a complex tail-to-tail-oriented bilayer system by a combination of interchain C—H⋯O hydrogen bonds, giving an R₂²(10) motif.

S2. Experimental

BrCH₂CO₂Me (0.08 ml, 0.84 mmol) was added to a suspension of 5,17-dibromo-26,28-dihydroxy-25,27-dipropoxy-2,8,14,20-tetrathiacalix[4]arene (0.080 g, 0.14 mmol) and anhydrous K₂CO₃ (0.022 g, 0.17 mmol) in dry acetone (15 ml). The resulting mixture was stirred for 3 h at 343 K and cooled to room temperature. The solvent was removed under reduced pressure. The residue was neutralized with 5% aqueous HCl and extracted with CH₂Cl₂. The organic layer was separated and washed with saturated sodium hydrogen carbonate and brine, and dried over anhydrous MgSO₄. The solvent was evaporated *in vacuo* and the residue was chromatographed on a silica gel column (CH₂Cl₂/petroleum ether = 1:1) to give the title compound as a white solid (yield 63%, R_f = 0.3) and another product (yield 28%, R_f = 0.45). ¹H NMR (300 MHz, CDCl₃) for the title product: δ 7.67 (s, 4H), 6.55 (d, 4H, J = 7.26 Hz), 6.46 (t, 2H, J = 7.57 Hz), 5.10 (s, 4H), 3.88 (t, 4H, J = 7.47 Hz), 3.74 (s, 6H), 1.89–1.77 (m, 4H), 1.05 (t, 6H, J = 7.39 Hz). IR (KBr pellets, cm⁻¹): 1763 (C=O). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution in CH₃OH

and CHCl_3 at 298 K.

S3. Refinement

All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were placed in geometrically idealized positions and refined as riding atoms with $\text{C—H} = 0.98 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$ (methyl); $\text{C—H} = 0.99 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ (methylene); $\text{C—H} = 0.95 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ (aromatic). The positions of methyl hydrogens were rotationally optimized.

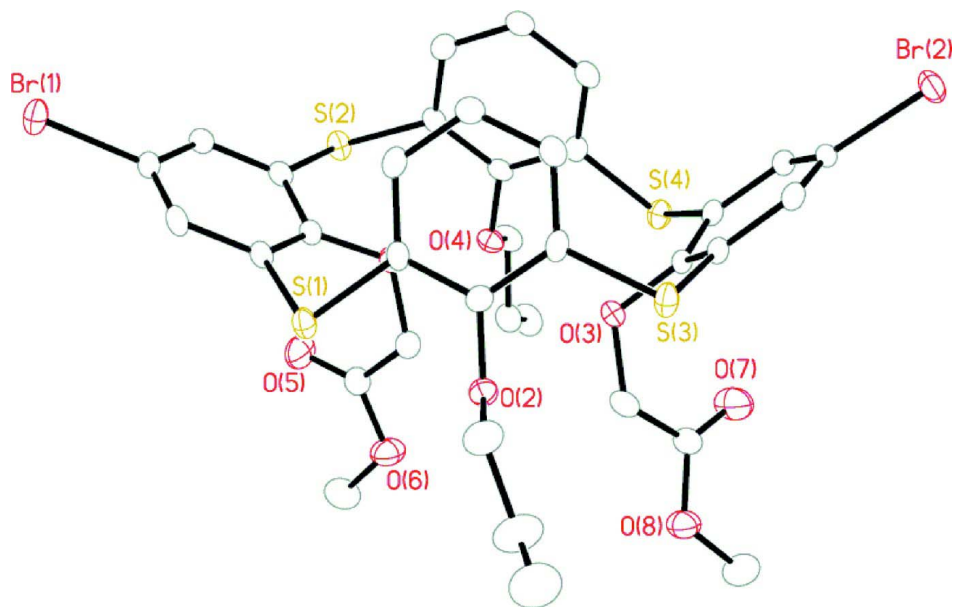
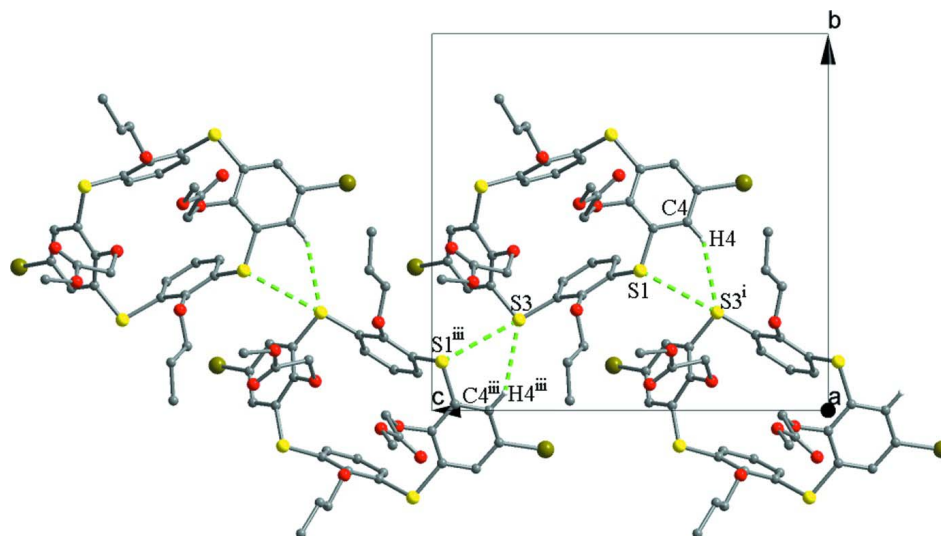


Figure 1

The molecular structure of the title compound with displacement ellipsoids drawn at the 30% probability level for non-H atoms. The hydrogen atoms have been omitted for clarity.

**Figure 2**

The hydrogen-bonded one-dimensional chain of the title compound, viewed along the crystallographic *a* axis, showing the *C*(8) motif. For the sake of clarity, H atoms not involved in the motifs have been omitted. [Symmetry codes: (i) *x*, *-y* + 1/2, *z* - 1/2; (iii) *x*, *-y* + 1/2, *z* + 1/2.]

5,17-Dibromo-26,28-bis[(methoxycarbonyl)methoxy]-25,27-dipropoxy-2,8,14,20-tetrathiacalix[4]arene

Crystal data

$C_{36}H_{34}Br_2O_8S_4$

$M_r = 882.69$

Monoclinic, $P2_1/c$

$a = 16.024$ (3) Å

$b = 14.808$ (3) Å

$c = 15.872$ (3) Å

$\beta = 100.065$ (3)°

$V = 3708.3$ (12) Å³

$Z = 4$

$F(000) = 1792$

$D_x = 1.581$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4762 reflections

$\theta = 2.4$ – 24.5 °

$\mu = 2.46$ mm⁻¹

$T = 173$ K

Block, colourless

$0.38 \times 0.18 \times 0.13$ mm

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ϕ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 1999)

$T_{\min} = 0.455$, $T_{\max} = 0.740$

19322 measured reflections

6989 independent reflections

4908 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.060$

$\theta_{\max} = 25.6$ °, $\theta_{\min} = 1.9$ °

$h = -19 \rightarrow 10$

$k = -18 \rightarrow 17$

$l = -17 \rightarrow 19$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.091$

$S = 0.93$

6989 reflections

455 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0393P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.62 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.55 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| Br1 | 0.11682 (2) | 0.60398 (2) | 0.21293 (2) | 0.04232 (12) |
| Br2 | 0.03760 (2) | 0.38070 (3) | 1.04064 (3) | 0.04869 (13) |
| C1 | 0.20213 (19) | 0.6405 (2) | 0.4739 (2) | 0.0258 (7) |
| C2 | 0.16788 (18) | 0.6550 (2) | 0.38842 (19) | 0.0271 (7) |
| H2 | 0.1460 | 0.7128 | 0.3702 | 0.033* |
| C3 | 0.16546 (19) | 0.5857 (2) | 0.32980 (19) | 0.0274 (7) |
| C4 | 0.19244 (19) | 0.5003 (2) | 0.35546 (19) | 0.0285 (7) |
| H4 | 0.1884 | 0.4527 | 0.3148 | 0.034* |
| C5 | 0.22583 (19) | 0.48368 (19) | 0.44142 (19) | 0.0255 (7) |
| C6 | 0.23380 (18) | 0.5547 (2) | 0.49994 (19) | 0.0256 (7) |
| C7 | 0.17985 (19) | 0.3580 (2) | 0.54785 (18) | 0.0235 (7) |
| C8 | 0.1014 (2) | 0.4000 (2) | 0.5355 (2) | 0.0301 (8) |
| H8 | 0.0837 | 0.4348 | 0.4852 | 0.036* |
| C9 | 0.0489 (2) | 0.3920 (2) | 0.5948 (2) | 0.0324 (8) |
| H9 | -0.0048 | 0.4209 | 0.5852 | 0.039* |
| C10 | 0.0742 (2) | 0.3419 (2) | 0.6690 (2) | 0.0310 (8) |
| H10 | 0.0381 | 0.3367 | 0.7104 | 0.037* |
| C11 | 0.1524 (2) | 0.2996 (2) | 0.68202 (19) | 0.0271 (7) |
| C12 | 0.20550 (19) | 0.30606 (19) | 0.62144 (19) | 0.0242 (7) |
| C13 | 0.1789 (2) | 0.3319 (2) | 0.85101 (19) | 0.0272 (7) |
| C14 | 0.12273 (19) | 0.3240 (2) | 0.90827 (19) | 0.0298 (8) |
| H14 | 0.0927 | 0.2692 | 0.9118 | 0.036* |
| C15 | 0.1109 (2) | 0.3961 (2) | 0.9597 (2) | 0.0295 (8) |
| C16 | 0.1492 (2) | 0.4789 (2) | 0.95107 (19) | 0.0306 (8) |
| H16 | 0.1377 | 0.5292 | 0.9844 | 0.037* |
| C17 | 0.20401 (19) | 0.4872 (2) | 0.89340 (19) | 0.0267 (7) |
| C18 | 0.22386 (19) | 0.4120 (2) | 0.84720 (19) | 0.0246 (7) |
| C19 | 0.1805 (2) | 0.62323 (19) | 0.77646 (19) | 0.0270 (7) |
| C20 | 0.0935 (2) | 0.6079 (2) | 0.7646 (2) | 0.0320 (8) |
| H20 | 0.0688 | 0.5829 | 0.8096 | 0.038* |
| C21 | 0.0431 (2) | 0.6290 (2) | 0.6875 (2) | 0.0347 (8) |
| H21 | -0.0162 | 0.6181 | 0.6795 | 0.042* |

| | | | | |
|------|--------------|--------------|--------------|-------------|
| C22 | 0.0782 (2) | 0.6657 (2) | 0.6223 (2) | 0.0315 (8) |
| H22 | 0.0430 | 0.6797 | 0.5693 | 0.038* |
| C23 | 0.1646 (2) | 0.68234 (19) | 0.63296 (19) | 0.0264 (7) |
| C24 | 0.21621 (19) | 0.6616 (2) | 0.7109 (2) | 0.0249 (7) |
| C25 | 0.3470 (2) | 0.5133 (2) | 0.6152 (2) | 0.0320 (8) |
| H25A | 0.3524 | 0.4502 | 0.5965 | 0.038* |
| H25B | 0.3578 | 0.5140 | 0.6786 | 0.038* |
| C26 | 0.4131 (2) | 0.5699 (2) | 0.5838 (2) | 0.0358 (8) |
| C27 | 0.5595 (2) | 0.5920 (3) | 0.5987 (3) | 0.0608 (12) |
| H27A | 0.5548 | 0.5831 | 0.5369 | 0.091* |
| H27B | 0.6126 | 0.5655 | 0.6283 | 0.091* |
| H27C | 0.5588 | 0.6568 | 0.6113 | 0.091* |
| C28 | 0.2829 (2) | 0.1705 (2) | 0.6167 (2) | 0.0519 (11) |
| H28A | 0.2342 | 0.1425 | 0.6375 | 0.062* |
| H28B | 0.2753 | 0.1611 | 0.5541 | 0.062* |
| C29 | 0.3602 (3) | 0.1274 (3) | 0.6572 (3) | 0.0784 (16) |
| H29A | 0.3724 | 0.1453 | 0.7182 | 0.094* |
| H29B | 0.4075 | 0.1491 | 0.6300 | 0.094* |
| C30 | 0.3564 (3) | 0.0260 (3) | 0.6516 (3) | 0.0887 (17) |
| H30A | 0.3166 | 0.0032 | 0.6869 | 0.133* |
| H30B | 0.4129 | 0.0009 | 0.6722 | 0.133* |
| H30C | 0.3373 | 0.0079 | 0.5919 | 0.133* |
| C31 | 0.3558 (2) | 0.3663 (2) | 0.8103 (2) | 0.0387 (9) |
| H31A | 0.3885 | 0.3744 | 0.7634 | 0.046* |
| H31B | 0.3375 | 0.3024 | 0.8097 | 0.046* |
| C32 | 0.4124 (2) | 0.3854 (2) | 0.8935 (2) | 0.0351 (8) |
| C33 | 0.5475 (2) | 0.3478 (3) | 0.9742 (2) | 0.0577 (11) |
| H33A | 0.5603 | 0.4115 | 0.9871 | 0.087* |
| H33B | 0.5993 | 0.3163 | 0.9663 | 0.087* |
| H33C | 0.5250 | 0.3202 | 1.0217 | 0.087* |
| C34 | 0.3351 (2) | 0.7543 (2) | 0.7622 (2) | 0.0371 (9) |
| H34A | 0.3119 | 0.7636 | 0.8155 | 0.045* |
| H34B | 0.3190 | 0.8067 | 0.7241 | 0.045* |
| C35 | 0.4294 (2) | 0.7450 (2) | 0.7823 (2) | 0.0397 (9) |
| H35A | 0.4516 | 0.7370 | 0.7284 | 0.048* |
| H35B | 0.4443 | 0.6906 | 0.8179 | 0.048* |
| C36 | 0.4710 (2) | 0.8276 (3) | 0.8296 (2) | 0.0508 (10) |
| H36A | 0.4612 | 0.8806 | 0.7922 | 0.076* |
| H36B | 0.5321 | 0.8171 | 0.8459 | 0.076* |
| H36C | 0.4465 | 0.8381 | 0.8812 | 0.076* |
| O1 | 0.26345 (13) | 0.54324 (13) | 0.58541 (13) | 0.0284 (5) |
| O2 | 0.28416 (13) | 0.26639 (13) | 0.63464 (13) | 0.0300 (5) |
| O3 | 0.28207 (13) | 0.42264 (14) | 0.79386 (13) | 0.0307 (5) |
| O4 | 0.30214 (13) | 0.67228 (13) | 0.72072 (13) | 0.0302 (5) |
| O5 | 0.40072 (16) | 0.62414 (17) | 0.52780 (17) | 0.0546 (7) |
| O6 | 0.48904 (15) | 0.54881 (17) | 0.62764 (17) | 0.0510 (7) |
| O7 | 0.39604 (17) | 0.4311 (2) | 0.94997 (18) | 0.0649 (8) |
| O8 | 0.48456 (15) | 0.34097 (18) | 0.89600 (15) | 0.0484 (7) |

| | | | | |
|----|-------------|-------------|-------------|------------|
| S1 | 0.25109 (5) | 0.37085 (5) | 0.47437 (5) | 0.0301 (2) |
| S2 | 0.20796 (5) | 0.73180 (5) | 0.54737 (5) | 0.0321 (2) |
| S3 | 0.18647 (6) | 0.24030 (5) | 0.77987 (5) | 0.0335 (2) |
| S4 | 0.24789 (5) | 0.59458 (6) | 0.87516 (5) | 0.0325 (2) |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|--------------|--------------|--------------|--------------|
| Br1 | 0.0565 (3) | 0.0436 (2) | 0.02588 (19) | 0.00021 (18) | 0.00459 (16) | 0.00639 (16) |
| Br2 | 0.0532 (3) | 0.0523 (3) | 0.0492 (2) | 0.01553 (19) | 0.03265 (19) | 0.0158 (2) |
| C1 | 0.0273 (19) | 0.0213 (16) | 0.0312 (18) | -0.0038 (14) | 0.0115 (14) | 0.0021 (15) |
| C2 | 0.0270 (19) | 0.0239 (17) | 0.0325 (18) | -0.0030 (14) | 0.0110 (14) | 0.0077 (15) |
| C3 | 0.0261 (19) | 0.0338 (19) | 0.0229 (17) | -0.0051 (15) | 0.0063 (13) | 0.0046 (15) |
| C4 | 0.039 (2) | 0.0250 (17) | 0.0244 (17) | -0.0048 (15) | 0.0142 (14) | -0.0011 (15) |
| C5 | 0.0321 (19) | 0.0210 (16) | 0.0260 (17) | -0.0008 (14) | 0.0121 (14) | 0.0032 (14) |
| C6 | 0.0243 (18) | 0.0281 (18) | 0.0257 (17) | -0.0035 (14) | 0.0082 (13) | 0.0027 (15) |
| C7 | 0.0315 (19) | 0.0198 (16) | 0.0197 (16) | -0.0062 (14) | 0.0055 (13) | -0.0032 (13) |
| C8 | 0.035 (2) | 0.0293 (18) | 0.0250 (17) | -0.0039 (16) | 0.0022 (14) | 0.0053 (15) |
| C9 | 0.029 (2) | 0.0337 (19) | 0.0345 (19) | 0.0021 (15) | 0.0055 (15) | -0.0005 (16) |
| C10 | 0.034 (2) | 0.0300 (18) | 0.0306 (19) | -0.0040 (16) | 0.0103 (15) | -0.0032 (16) |
| C11 | 0.039 (2) | 0.0210 (16) | 0.0211 (17) | -0.0035 (15) | 0.0035 (14) | 0.0017 (14) |
| C12 | 0.0273 (19) | 0.0165 (15) | 0.0277 (18) | -0.0018 (14) | 0.0016 (14) | -0.0037 (14) |
| C13 | 0.036 (2) | 0.0268 (18) | 0.0195 (16) | 0.0079 (15) | 0.0070 (14) | 0.0024 (14) |
| C14 | 0.034 (2) | 0.0289 (18) | 0.0265 (18) | 0.0023 (15) | 0.0046 (14) | 0.0085 (15) |
| C15 | 0.0284 (19) | 0.038 (2) | 0.0251 (17) | 0.0109 (16) | 0.0115 (14) | 0.0097 (16) |
| C16 | 0.035 (2) | 0.0345 (19) | 0.0229 (17) | 0.0092 (16) | 0.0076 (14) | 0.0015 (15) |
| C17 | 0.0302 (19) | 0.0282 (17) | 0.0212 (16) | 0.0005 (15) | 0.0031 (13) | 0.0029 (14) |
| C18 | 0.0244 (18) | 0.0294 (18) | 0.0202 (16) | 0.0012 (15) | 0.0046 (13) | 0.0049 (14) |
| C19 | 0.034 (2) | 0.0234 (17) | 0.0234 (17) | 0.0015 (14) | 0.0048 (14) | -0.0048 (14) |
| C20 | 0.032 (2) | 0.035 (2) | 0.0316 (19) | -0.0015 (15) | 0.0131 (15) | -0.0010 (16) |
| C21 | 0.024 (2) | 0.043 (2) | 0.038 (2) | -0.0020 (16) | 0.0079 (15) | -0.0034 (17) |
| C22 | 0.034 (2) | 0.0298 (19) | 0.0292 (18) | 0.0025 (15) | 0.0028 (15) | -0.0009 (15) |
| C23 | 0.034 (2) | 0.0200 (17) | 0.0274 (17) | 0.0011 (14) | 0.0107 (14) | -0.0061 (14) |
| C24 | 0.0236 (19) | 0.0209 (17) | 0.0316 (18) | -0.0014 (14) | 0.0090 (14) | -0.0056 (14) |
| C25 | 0.037 (2) | 0.0294 (18) | 0.0289 (18) | 0.0020 (16) | 0.0050 (15) | -0.0006 (15) |
| C26 | 0.039 (2) | 0.037 (2) | 0.031 (2) | -0.0001 (17) | 0.0063 (16) | -0.0057 (18) |
| C27 | 0.036 (3) | 0.080 (3) | 0.068 (3) | -0.004 (2) | 0.014 (2) | -0.002 (3) |
| C28 | 0.057 (3) | 0.047 (2) | 0.047 (2) | 0.013 (2) | -0.004 (2) | -0.013 (2) |
| C29 | 0.085 (4) | 0.065 (3) | 0.079 (4) | 0.032 (3) | -0.005 (3) | -0.006 (3) |
| C30 | 0.120 (4) | 0.050 (3) | 0.099 (4) | 0.039 (3) | 0.028 (3) | 0.011 (3) |
| C31 | 0.030 (2) | 0.052 (2) | 0.036 (2) | 0.0029 (17) | 0.0106 (15) | -0.0085 (18) |
| C32 | 0.031 (2) | 0.037 (2) | 0.038 (2) | 0.0011 (16) | 0.0076 (16) | -0.0040 (17) |
| C33 | 0.045 (3) | 0.067 (3) | 0.057 (3) | 0.006 (2) | -0.005 (2) | -0.001 (2) |
| C34 | 0.034 (2) | 0.0312 (19) | 0.048 (2) | -0.0075 (16) | 0.0108 (16) | -0.0112 (17) |
| C35 | 0.037 (2) | 0.046 (2) | 0.037 (2) | -0.0095 (17) | 0.0083 (16) | -0.0046 (18) |
| C36 | 0.046 (3) | 0.057 (3) | 0.050 (2) | -0.017 (2) | 0.0107 (19) | -0.012 (2) |
| O1 | 0.0318 (13) | 0.0296 (12) | 0.0246 (12) | 0.0010 (10) | 0.0075 (9) | 0.0009 (10) |
| O2 | 0.0325 (14) | 0.0259 (12) | 0.0321 (13) | 0.0025 (10) | 0.0067 (10) | 0.0012 (10) |

| | | | | | | |
|----|-------------|-------------|-------------|--------------|-------------|--------------|
| O3 | 0.0303 (14) | 0.0371 (13) | 0.0271 (12) | 0.0034 (10) | 0.0117 (10) | 0.0021 (11) |
| O4 | 0.0267 (13) | 0.0298 (12) | 0.0350 (13) | -0.0019 (10) | 0.0077 (10) | -0.0067 (10) |
| O5 | 0.0452 (17) | 0.0675 (19) | 0.0517 (17) | -0.0077 (14) | 0.0100 (13) | 0.0237 (15) |
| O6 | 0.0332 (16) | 0.0567 (17) | 0.0619 (18) | 0.0023 (13) | 0.0050 (13) | 0.0099 (14) |
| O7 | 0.0580 (19) | 0.086 (2) | 0.0473 (17) | 0.0177 (16) | 0.0002 (14) | -0.0265 (17) |
| O8 | 0.0379 (16) | 0.0612 (17) | 0.0436 (15) | 0.0107 (13) | 0.0006 (12) | -0.0088 (14) |
| S1 | 0.0435 (5) | 0.0230 (4) | 0.0264 (4) | 0.0019 (4) | 0.0135 (4) | 0.0013 (4) |
| S2 | 0.0447 (6) | 0.0226 (4) | 0.0313 (5) | -0.0038 (4) | 0.0131 (4) | -0.0007 (4) |
| S3 | 0.0530 (6) | 0.0247 (4) | 0.0237 (4) | 0.0024 (4) | 0.0095 (4) | 0.0026 (4) |
| S4 | 0.0393 (5) | 0.0310 (5) | 0.0258 (4) | -0.0033 (4) | 0.0023 (4) | -0.0023 (4) |

Geometric parameters (Å, °)

| | | | |
|---------|-----------|----------|-----------|
| Br1—C3 | 1.902 (3) | C22—H22 | 0.9500 |
| Br2—C15 | 1.900 (3) | C23—C24 | 1.396 (4) |
| C1—C2 | 1.389 (4) | C23—S2 | 1.787 (3) |
| C1—C6 | 1.404 (4) | C24—O4 | 1.368 (3) |
| C1—S2 | 1.776 (3) | C25—O1 | 1.411 (3) |
| C2—C3 | 1.381 (4) | C25—C26 | 1.501 (5) |
| C2—H2 | 0.9500 | C25—H25A | 0.9900 |
| C3—C4 | 1.375 (4) | C25—H25B | 0.9900 |
| C4—C5 | 1.398 (4) | C26—O5 | 1.189 (4) |
| C4—H4 | 0.9500 | C26—O6 | 1.329 (4) |
| C5—C6 | 1.394 (4) | C27—O6 | 1.440 (4) |
| C5—S1 | 1.776 (3) | C27—H27A | 0.9800 |
| C6—O1 | 1.367 (3) | C27—H27B | 0.9800 |
| C7—C8 | 1.385 (4) | C27—H27C | 0.9800 |
| C7—C12 | 1.399 (4) | C28—C29 | 1.442 (5) |
| C7—S1 | 1.779 (3) | C28—O2 | 1.447 (4) |
| C8—C9 | 1.374 (4) | C28—H28A | 0.9900 |
| C8—H8 | 0.9500 | C28—H28B | 0.9900 |
| C9—C10 | 1.391 (4) | C29—C30 | 1.505 (5) |
| C9—H9 | 0.9500 | C29—H29A | 0.9900 |
| C10—C11 | 1.383 (4) | C29—H29B | 0.9900 |
| C10—H10 | 0.9500 | C30—H30A | 0.9800 |
| C11—C12 | 1.394 (4) | C30—H30B | 0.9800 |
| C11—S3 | 1.785 (3) | C30—H30C | 0.9800 |
| C12—O2 | 1.373 (3) | C31—O3 | 1.432 (4) |
| C13—C14 | 1.392 (4) | C31—C32 | 1.494 (4) |
| C13—C18 | 1.395 (4) | C31—H31A | 0.9900 |
| C13—S3 | 1.782 (3) | C31—H31B | 0.9900 |
| C14—C15 | 1.377 (4) | C32—O7 | 1.188 (4) |
| C14—H14 | 0.9500 | C32—O8 | 1.325 (4) |
| C15—C16 | 1.389 (4) | C33—O8 | 1.460 (4) |
| C16—C17 | 1.381 (4) | C33—H33A | 0.9800 |
| C16—H16 | 0.9500 | C33—H33B | 0.9800 |
| C17—C18 | 1.400 (4) | C33—H33C | 0.9800 |
| C17—S4 | 1.783 (3) | C34—O4 | 1.437 (3) |

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|-------------|-----------|---------------|-----------|
| C18—O3 | 1.374 (4) | C34—C35 | 1.496 (4) |
| C19—C24 | 1.393 (4) | C34—H34A | 0.9900 |
| C19—C20 | 1.393 (4) | C34—H34B | 0.9900 |
| C19—S4 | 1.791 (3) | C35—C36 | 1.526 (4) |
| C20—C21 | 1.379 (4) | C35—H35A | 0.9900 |
| C20—H20 | 0.9500 | C35—H35B | 0.9900 |
| C21—C22 | 1.373 (4) | C36—H36A | 0.9800 |
| C21—H21 | 0.9500 | C36—H36B | 0.9800 |
| C22—C23 | 1.388 (4) | C36—H36C | 0.9800 |
| | | | |
| C2—C1—C6 | 119.2 (3) | C26—C25—H25A | 108.9 |
| C2—C1—S2 | 119.4 (2) | O1—C25—H25B | 108.9 |
| C6—C1—S2 | 121.4 (2) | C26—C25—H25B | 108.9 |
| C3—C2—C1 | 120.2 (3) | H25A—C25—H25B | 107.7 |
| C3—C2—H2 | 119.9 | O5—C26—O6 | 124.6 (3) |
| C1—C2—H2 | 119.9 | O5—C26—C25 | 126.1 (3) |
| C4—C3—C2 | 120.9 (3) | O6—C26—C25 | 109.3 (3) |
| C4—C3—Br1 | 118.3 (2) | O6—C27—H27A | 109.5 |
| C2—C3—Br1 | 120.7 (2) | O6—C27—H27B | 109.5 |
| C3—C4—C5 | 119.9 (3) | H27A—C27—H27B | 109.5 |
| C3—C4—H4 | 120.1 | O6—C27—H27C | 109.5 |
| C5—C4—H4 | 120.1 | H27A—C27—H27C | 109.5 |
| C6—C5—C4 | 119.5 (3) | H27B—C27—H27C | 109.5 |
| C6—C5—S1 | 121.6 (2) | C29—C28—O2 | 111.4 (3) |
| C4—C5—S1 | 118.8 (2) | C29—C28—H28A | 109.3 |
| O1—C6—C5 | 122.9 (3) | O2—C28—H28A | 109.3 |
| O1—C6—C1 | 116.7 (3) | C29—C28—H28B | 109.3 |
| C5—C6—C1 | 120.1 (3) | O2—C28—H28B | 109.3 |
| C8—C7—C12 | 119.5 (3) | H28A—C28—H28B | 108.0 |
| C8—C7—S1 | 121.9 (2) | C28—C29—C30 | 113.1 (4) |
| C12—C7—S1 | 118.5 (2) | C28—C29—H29A | 108.9 |
| C9—C8—C7 | 120.9 (3) | C30—C29—H29A | 108.9 |
| C9—C8—H8 | 119.6 | C28—C29—H29B | 108.9 |
| C7—C8—H8 | 119.6 | C30—C29—H29B | 108.9 |
| C8—C9—C10 | 120.3 (3) | H29A—C29—H29B | 107.8 |
| C8—C9—H9 | 119.9 | C29—C30—H30A | 109.5 |
| C10—C9—H9 | 119.9 | C29—C30—H30B | 109.5 |
| C11—C10—C9 | 119.3 (3) | H30A—C30—H30B | 109.5 |
| C11—C10—H10 | 120.3 | C29—C30—H30C | 109.5 |
| C9—C10—H10 | 120.3 | H30A—C30—H30C | 109.5 |
| C10—C11—C12 | 120.8 (3) | H30B—C30—H30C | 109.5 |
| C10—C11—S3 | 118.9 (2) | O3—C31—C32 | 113.9 (3) |
| C12—C11—S3 | 120.2 (2) | O3—C31—H31A | 108.8 |
| O2—C12—C11 | 121.4 (3) | C32—C31—H31A | 108.8 |
| O2—C12—C7 | 119.4 (3) | O3—C31—H31B | 108.8 |
| C11—C12—C7 | 119.2 (3) | C32—C31—H31B | 108.8 |
| C14—C13—C18 | 119.8 (3) | H31A—C31—H31B | 107.7 |
| C14—C13—S3 | 118.3 (2) | O7—C32—O8 | 124.6 (3) |

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|--------------|------------|-----------------|-------------|
| C18—C13—S3 | 121.8 (2) | O7—C32—C31 | 126.5 (3) |
| C15—C14—C13 | 119.6 (3) | O8—C32—C31 | 108.9 (3) |
| C15—C14—H14 | 120.2 | O8—C33—H33A | 109.5 |
| C13—C14—H14 | 120.2 | O8—C33—H33B | 109.5 |
| C14—C15—C16 | 121.1 (3) | H33A—C33—H33B | 109.5 |
| C14—C15—Br2 | 118.3 (2) | O8—C33—H33C | 109.5 |
| C16—C15—Br2 | 120.6 (2) | H33A—C33—H33C | 109.5 |
| C17—C16—C15 | 119.2 (3) | H33B—C33—H33C | 109.5 |
| C17—C16—H16 | 120.4 | O4—C34—C35 | 107.3 (3) |
| C15—C16—H16 | 120.4 | O4—C34—H34A | 110.3 |
| C16—C17—C18 | 120.4 (3) | C35—C34—H34A | 110.3 |
| C16—C17—S4 | 120.1 (2) | O4—C34—H34B | 110.3 |
| C18—C17—S4 | 119.5 (2) | C35—C34—H34B | 110.3 |
| O3—C18—C13 | 122.4 (3) | H34A—C34—H34B | 108.5 |
| O3—C18—C17 | 118.2 (3) | C34—C35—C36 | 111.7 (3) |
| C13—C18—C17 | 119.2 (3) | C34—C35—H35A | 109.3 |
| C24—C19—C20 | 119.9 (3) | C36—C35—H35A | 109.3 |
| C24—C19—S4 | 119.1 (2) | C34—C35—H35B | 109.3 |
| C20—C19—S4 | 121.0 (3) | C36—C35—H35B | 109.3 |
| C21—C20—C19 | 120.0 (3) | H35A—C35—H35B | 107.9 |
| C21—C20—H20 | 120.0 | C35—C36—H36A | 109.5 |
| C19—C20—H20 | 120.0 | C35—C36—H36B | 109.5 |
| C22—C21—C20 | 120.4 (3) | H36A—C36—H36B | 109.5 |
| C22—C21—H21 | 119.8 | C35—C36—H36C | 109.5 |
| C20—C21—H21 | 119.8 | H36A—C36—H36C | 109.5 |
| C21—C22—C23 | 120.6 (3) | H36B—C36—H36C | 109.5 |
| C21—C22—H22 | 119.7 | C6—O1—C25 | 121.1 (2) |
| C23—C22—H22 | 119.7 | C12—O2—C28 | 114.1 (2) |
| C22—C23—C24 | 119.5 (3) | C18—O3—C31 | 116.6 (2) |
| C22—C23—S2 | 119.5 (2) | C24—O4—C34 | 115.6 (2) |
| C24—C23—S2 | 121.0 (2) | C26—O6—C27 | 115.2 (3) |
| O4—C24—C19 | 119.9 (3) | C32—O8—C33 | 117.4 (3) |
| O4—C24—C23 | 120.2 (3) | C5—S1—C7 | 98.88 (14) |
| C19—C24—C23 | 119.6 (3) | C1—S2—C23 | 101.78 (14) |
| O1—C25—C26 | 113.4 (3) | C13—S3—C11 | 97.62 (14) |
| O1—C25—H25A | 108.9 | C17—S4—C19 | 99.14 (14) |
| | | | |
| C6—C1—C2—C3 | -0.3 (4) | C20—C21—C22—C23 | -0.2 (5) |
| S2—C1—C2—C3 | 177.8 (2) | C21—C22—C23—C24 | 0.0 (5) |
| C1—C2—C3—C4 | 3.6 (5) | C21—C22—C23—S2 | -179.0 (2) |
| C1—C2—C3—Br1 | 178.8 (2) | C20—C19—C24—O4 | -176.6 (3) |
| C2—C3—C4—C5 | -2.4 (5) | S4—C19—C24—O4 | 3.6 (4) |
| Br1—C3—C4—C5 | -177.8 (2) | C20—C19—C24—C23 | -1.6 (4) |
| C3—C4—C5—C6 | -1.9 (5) | S4—C19—C24—C23 | 178.6 (2) |
| C3—C4—C5—S1 | 174.3 (2) | C22—C23—C24—O4 | 175.9 (3) |
| C4—C5—C6—O1 | 178.0 (3) | S2—C23—C24—O4 | -5.2 (4) |
| S1—C5—C6—O1 | 1.8 (4) | C22—C23—C24—C19 | 0.9 (4) |
| C4—C5—C6—C1 | 5.2 (4) | S2—C23—C24—C19 | 179.9 (2) |

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|-----------------|------------|----------------|------------|
| S1—C5—C6—C1 | -170.9 (2) | O1—C25—C26—O5 | -13.4 (5) |
| C2—C1—C6—O1 | -177.3 (3) | O1—C25—C26—O6 | 167.7 (2) |
| S2—C1—C6—O1 | 4.7 (4) | O2—C28—C29—C30 | 171.2 (4) |
| C2—C1—C6—C5 | -4.1 (4) | O3—C31—C32—O7 | 12.0 (5) |
| S2—C1—C6—C5 | 177.9 (2) | O3—C31—C32—O8 | -169.7 (3) |
| C12—C7—C8—C9 | 0.7 (4) | O4—C34—C35—C36 | -178.0 (3) |
| S1—C7—C8—C9 | -177.3 (2) | C5—C6—O1—C25 | 63.4 (4) |
| C7—C8—C9—C10 | 0.4 (5) | C1—C6—O1—C25 | -123.6 (3) |
| C8—C9—C10—C11 | -0.5 (5) | C26—C25—O1—C6 | 54.1 (4) |
| C9—C10—C11—C12 | -0.6 (5) | C11—C12—O2—C28 | 80.2 (4) |
| C9—C10—C11—S3 | 176.8 (2) | C7—C12—O2—C28 | -103.3 (3) |
| C10—C11—C12—O2 | 178.3 (3) | C29—C28—O2—C12 | -160.9 (3) |
| S3—C11—C12—O2 | 0.9 (4) | C13—C18—O3—C31 | -64.3 (4) |
| C10—C11—C12—C7 | 1.7 (4) | C17—C18—O3—C31 | 121.5 (3) |
| S3—C11—C12—C7 | -175.7 (2) | C32—C31—O3—C18 | -66.1 (4) |
| C8—C7—C12—O2 | -178.3 (3) | C19—C24—O4—C34 | -86.5 (3) |
| S1—C7—C12—O2 | -0.3 (4) | C23—C24—O4—C34 | 98.5 (3) |
| C8—C7—C12—C11 | -1.7 (4) | C35—C34—O4—C24 | 169.0 (3) |
| S1—C7—C12—C11 | 176.3 (2) | O5—C26—O6—C27 | -4.5 (5) |
| C18—C13—C14—C15 | 1.1 (4) | C25—C26—O6—C27 | 174.4 (3) |
| S3—C13—C14—C15 | -175.3 (2) | O7—C32—O8—C33 | 0.9 (5) |
| C13—C14—C15—C16 | 5.0 (5) | C31—C32—O8—C33 | -177.5 (3) |
| C13—C14—C15—Br2 | -177.2 (2) | C6—C5—S1—C7 | 58.3 (3) |
| C14—C15—C16—C17 | -4.0 (5) | C4—C5—S1—C7 | -117.9 (3) |
| Br2—C15—C16—C17 | 178.2 (2) | C8—C7—S1—C5 | 33.4 (3) |
| C15—C16—C17—C18 | -3.0 (4) | C12—C7—S1—C5 | -144.6 (2) |
| C15—C16—C17—S4 | 175.4 (2) | C2—C1—S2—C23 | 131.6 (3) |
| C14—C13—C18—O3 | 178.0 (3) | C6—C1—S2—C23 | -50.4 (3) |
| S3—C13—C18—O3 | -5.8 (4) | C22—C23—S2—C1 | -72.7 (3) |
| C14—C13—C18—C17 | -7.9 (4) | C24—C23—S2—C1 | 108.3 (3) |
| S3—C13—C18—C17 | 168.4 (2) | C14—C13—S3—C11 | 118.2 (3) |
| C16—C17—C18—O3 | -176.7 (3) | C18—C13—S3—C11 | -58.1 (3) |
| S4—C17—C18—O3 | 4.9 (4) | C10—C11—S3—C13 | -56.9 (3) |
| C16—C17—C18—C13 | 8.9 (4) | C12—C11—S3—C13 | 120.5 (3) |
| S4—C17—C18—C13 | -169.5 (2) | C16—C17—S4—C19 | -101.1 (3) |
| C24—C19—C20—C21 | 1.3 (5) | C18—C17—S4—C19 | 77.2 (3) |
| S4—C19—C20—C21 | -178.8 (2) | C24—C19—S4—C17 | -137.2 (3) |
| C19—C20—C21—C22 | -0.4 (5) | C20—C19—S4—C17 | 43.0 (3) |

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------------|-------|-------------|-------------|---------------|
| C4—H4 \cdots S3 ⁱ | 0.95 | 2.91 | 3.755 (3) | 149 |
| C33—H33A \cdots O7 ⁱⁱ | 0.98 | 2.58 | 3.551 (5) | 169 |

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