Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# 1,1′-(2,5-Dimethylthiophene-3,4-diyl)-diethanone

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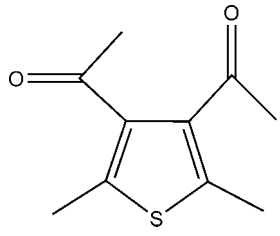
Received 24 June 2011; accepted 22 July 2011

Key indicators: single-crystal X-ray study; $T$ = 296 K; mean $\sigma$(C–C) = 0.007 Å; $R$ factor = 0.043; $wR$ factor = 0.092; data-to-parameter ratio = 14.9.

The title compound, $C_{10}H_{12}O_2S$, crystallizes with four molecules in the asymmetric unit. The main conformational difference between these molecules is the orientation of the acetyl groups with respect to the ring. Whereas one acetyl group is only slightly twisted with respect to the thiophene ring [C—C—C—O torsion angles = 165.7 (4), −164.6 (4), 164.3 (4) and −163.6 (4)°], the other acetyl group is markly twisted out of the ring plane [C—C—C—O torsion angles = −61.2 (6), 61.3 (7), −59.7 (7) and 59.9 (6)°]. In the crystal, molecules are linked by weak C—H···O interactions into infinite chains along the $c$ axis.

## Related literature

For the synthesis of the title compound, see: Li *et al.* (2011); Wang *et al.* (2004). For a related structure, see: Yu *et al.* (2010).




## Experimental

### Crystal data

$C_{10}H_{12}O_2S$
$M_r$ = 196.26
Monoclinic, $Cc$
$a$ = 12.142 (2) Å
$b$ = 12.129 (2) Å
$c$ = 27.446 (6) Å
$\beta$ = 99.387 (2)°
$V$ = 3987.8 (14) Å$^3$
$Z$ = 16
Mo $K\alpha$ radiation
$\mu$ = 0.29 mm$^{-1}$
$T$ = 296 K
0.38 × 0.30 × 0.21 mm

### Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
$T_{min}$ = 0.898, $T_{max}$ = 0.942
14665 measured reflections
7205 independent reflections
4969 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.031

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.092
$S$ = 1.02
7205 reflections
485 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.17 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.23 e Å$^{-3}$
Absolute structure: Flack (1983), 3486 Friedel pairs
Flack parameter: 0.05 (7)

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C35—H35$C$···O6$^{i}$ | 0.96 | 2.44 | 3.276 (6) | 145 |
| C39—H39$A$···O6$^{i}$ | 0.96 | 2.56 | 3.435 (6) | 152 |

Symmetry code: (i) $x-1, y, z$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; 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: *SHELXL97*.

This work was supported by the National Natural Science Foundation of China (No. 20802065), the Scientific Research Foundation for Returned Overseas Chinese Scholars, State Education Ministry (No. 2009–1001) and the Doctoral Special Funds of Zhanjiang Normal University (No. ZL0803).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5559).

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# supporting information

*Acta Cryst.* (2011). E**67**, o2219 [doi:10.1107/S1600536811029710]

## 1,1′-(2,5-Dimethylthiophene-3,4-diyl)diethanone

**Chengpeng Li, Qiaozheng Qi, Sheng Wang and Guohua Ding**

### S1. Comment

Azomethines are an important class of compounds which have been intensively investigated owning to their strong coordination capability, antibacterial activity, antitumor property and so on. Considering this, on our way to getting novel photochromic molecules on which we focused in the past few years, we first designed and synthesized a key intermediate 1-(2,5-Dimethylthiophen-3,4-yl) diethanone, which has two carbonyl groups. Usually, azomethines are obtained by the condensation of carbonyl compounds with primary amines. Herein, the design and synthesis of this compound provides a wide space for the new azomethines of thiophene. Recently the introduction of Schiff base ligands into photochromic diarylethene system and their photochromic properties in solution has been reported (Li *et al.*, 2011). We are trying to push forward that work through introducing the title compound to the system. Moreover, in our recent study we also found that the title compound played a good role in the synthesis of Schiff-base macrocycles. When we took different type or the length of chain diamines, we got varying size of the macrocycles and some of them had good ability of cooperation with metals.

### S2. Experimental

We used 2-methylthiophene as the starting material *via*, in turn, Vilsmeier, Wolff-Kishner-Huang, and Friedel-Crafts reactions and got the title compound. The synthetic processes are as follows:

**5-Methylthiophene-2-carbaldehyde**

To a 10 g anhydrous dimethylformamide solution of 2-methylthiophene (10 g, 0.1 mol), a (17 g, 0.11 mol) phosphorus oxychloride ($POCl_3$) was added drop by drop slowly at 0°C. After addition, the ice bath was removed and the mixture was stirred for 0.5 h at room temperature. Then, the reddish solution was heated slowly to reflux. After refluxed for 1 h and cooled to room temperature, the mixture was poured into ice water and $K_2CO_3$ was added until pH=10. The mixture was extracted with diethyl ether (3×25 ml). The combined organic layers were washed with a saturated NaCl solution (2×25 ml) and $H_2O$ (1×25 ml), dried ($MgSO_4$), filtered and the solvents evaporated in vacuum to yield: 10.8 g, 84.2%.

**2,5-Dimethylthiophene**

To a 360 ml e thyl glycol solution of 5-methyl-thiophene-2-carbaldehyde (112 g, 0.9 mol), a 120 ml hydrazine hydrate (85%) was added in 1000 ml flask. The mixture was refluxed for 0.5 h, and then evaporated the excessive water and hydrazine hydrate until the oil drops showed up. After the evaporation, KOH (20 g, 0.3 mol) was added in portions to the cooled mixture. Then refluxed for 0.5 h, distilled and the mixture of oil and water was washed with a saturated NaCl solution (3× 25 ml), After being extracted, the organic phase was distilled and the fraction boiling between 134 °C and 135 °C was collected to yield 110 g, 91%.

**1-(2,5-Dimethylthiophen-3,4-yl) diethanone**

To a 200 ml dichloromethane solution of anhydrous aluminium chloride (41 g,0.3 mol), a 11 ml dichloromethane solution of acetyl chloride(16.4 g, 0.21 mol) and 15 ml dichloromethane solution of 2,5-Dimethylthiophene (23.5 g, 0.21

mol) was added dropwise in turn at 0°C. After addition, the reaction mixture was stirred for 8 h at room temperature. Then the mixture was poured into 45 ml ice-hydrochloric acid. The product was extracted with dichloromethane and the solution was dried ($MgSO_4$). After evaporation of the solvent, the pure product was obtained as a yellow solid (33.5 g, 81%) by column chromatography with petroleum/ethyl acetate(8:1) as eluent.

### S3. Refinement

H atoms were geometrically positioned with C-H = 0.96Å and $U(H)=1.5U_{eq}(C)$.

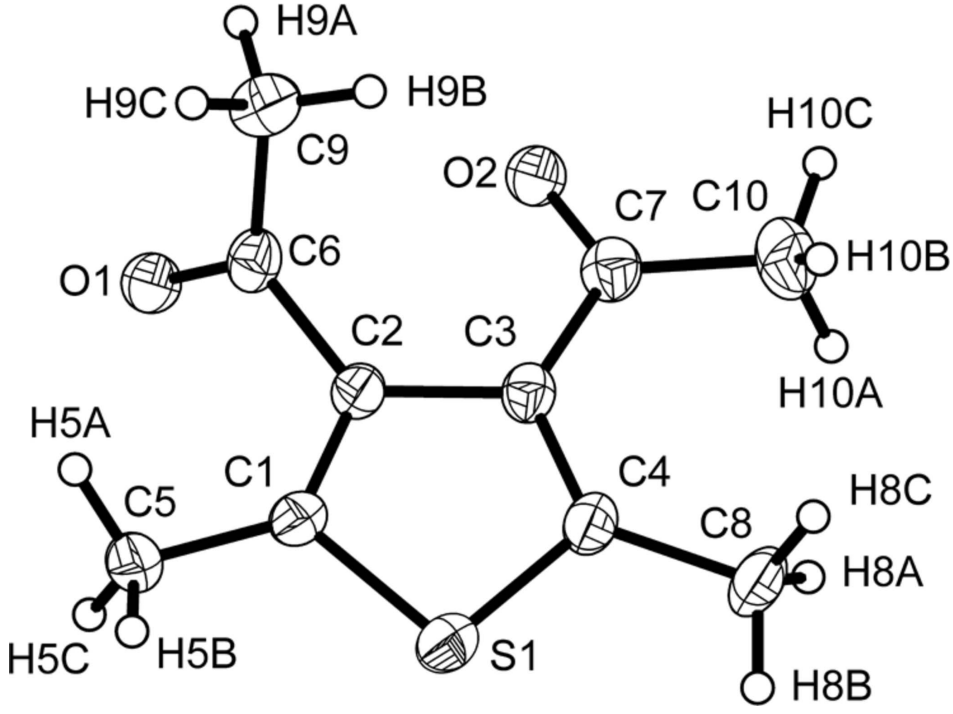


**Figure 1**

Molecular structure of one molecule in the asymmetric unit of the title compound, showing 30% probability displacement ellipsoids.

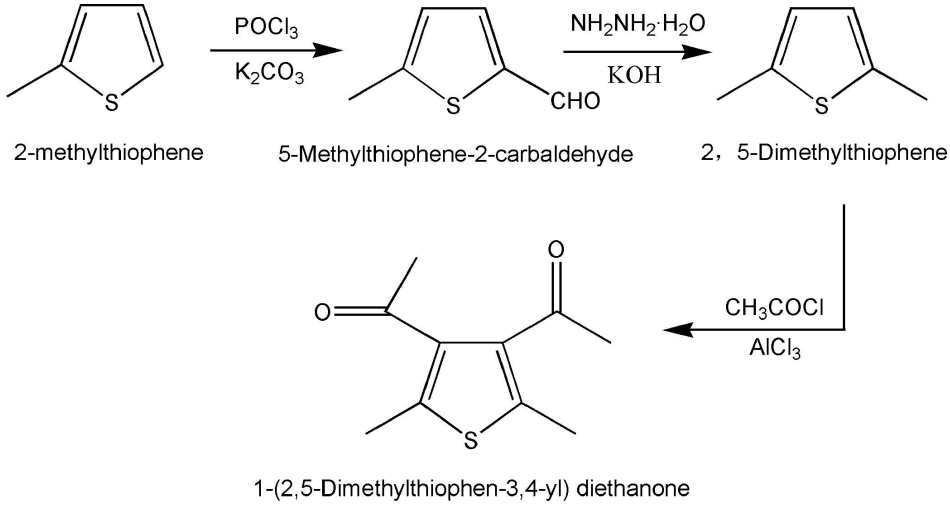


**Figure 2**

The synthetic route to the title compound.

### 1,1′-(2,5-Dimethylthiophene-3,4-diyl)diethanone

*Crystal data*

$C_{10}H_{12}O_2S$
$M_r = 196.26$
Monoclinic, *Cc*
$a = 12.142$ (2) Å
$b = 12.129$ (2) Å
$c = 27.446$ (6) Å
$\beta = 99.387$ (2)°
$V = 3987.8$ (14) Å$^3$
$Z = 16$
$F(000) = 1664$
$D_x = 1.308$ Mg m$^{-3}$
Melting point: 363 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3384 reflections
$\theta = 2.4$–23.9°
$\mu = 0.29$ mm$^{-1}$
$T = 296$ K
Block, colourless
0.38 × 0.30 × 0.21 mm

*Data collection*

Bruker SMART APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
$T_{min} = 0.898$, $T_{max} = 0.942$
14665 measured reflections
7205 independent reflections
4969 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 25.5°$, $\theta_{min} = 2.4°$
$h = -14\rightarrow14$
$k = -14\rightarrow14$
$l = -32\rightarrow33$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.092$
$S = 1.02$
7205 reflections
485 parameters
2 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
$w = 1/[\sigma^2(F_o^2) + (0.0329P)^2 + 1.3235P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.17 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.23 e Å$^{-3}$

Absolute structure: Flack (1983), 3486 Friedel pairs
Absolute structure parameter: 0.05 (7)

*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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.1299 (4) | 0.1176 (4) | 0.4644 (2) | 0.0439 (13) |
| C2 | 0.0669 (4) | 0.1446 (4) | 0.4207 (2) | 0.0401 (13) |
| C3 | −0.0256 (4) | 0.0686 (3) | 0.40549 (18) | 0.0402 (12) |
| C4 | −0.0279 (3) | −0.0142 (3) | 0.43893 (16) | 0.0451 (10) |
| C5 | 0.2301 (5) | 0.1710 (4) | 0.4926 (2) | 0.0554 (16) |
| H5A | 0.2746 | 0.2015 | 0.4700 | 0.083* |
| H5B | 0.2731 | 0.1173 | 0.5132 | 0.083* |
| H5C | 0.2076 | 0.2287 | 0.5128 | 0.083* |
| C6 | 0.0987 (4) | 0.2391 (4) | 0.3911 (2) | 0.0437 (13) |
| C7 | −0.1085 (4) | 0.0924 (4) | 0.36101 (17) | 0.0473 (10) |
| C8 | −0.1080 (4) | −0.1097 (3) | 0.44085 (17) | 0.0620 (13) |
| H8A | −0.1834 | −0.0828 | 0.4352 | 0.093* |
| H8B | −0.0927 | −0.1441 | 0.4727 | 0.093* |
| H8C | −0.0985 | −0.1626 | 0.4158 | 0.093* |
| C9 | 0.1385 (4) | 0.2160 (4) | 0.34303 (15) | 0.0575 (12) |
| H9A | 0.1178 | 0.2760 | 0.3206 | 0.086* |
| H9B | 0.1049 | 0.1491 | 0.3290 | 0.086* |
| H9C | 0.2182 | 0.2081 | 0.3488 | 0.086* |
| C10 | −0.1952 (4) | 0.0083 (4) | 0.34150 (19) | 0.0743 (15) |
| H10A | −0.2475 | 0.0008 | 0.3640 | 0.112* |
| H10B | −0.1598 | −0.0614 | 0.3381 | 0.112* |
| H10C | −0.2339 | 0.0316 | 0.3099 | 0.112* |
| C11 | 0.2336 (3) | 0.7569 (3) | 0.43718 (15) | 0.0421 (10) |
| C12 | 0.1384 (4) | 0.7388 (4) | 0.40351 (18) | 0.0393 (12) |
| C13 | 0.0706 (4) | 0.6523 (4) | 0.4191 (2) | 0.0379 (13) |
| C14 | 0.1126 (4) | 0.6077 (4) | 0.4636 (2) | 0.0433 (13) |
| C15 | 0.3259 (4) | 0.8407 (4) | 0.43894 (17) | 0.0675 (13) |
| H15A | 0.3723 | 0.8218 | 0.4150 | 0.101* |
| H15B | 0.3700 | 0.8411 | 0.4713 | 0.101* |
| H15C | 0.2941 | 0.9124 | 0.4316 | 0.101* |
| C16 | 0.0998 (4) | 0.8043 (3) | 0.35802 (16) | 0.0460 (10) |
| C17 | −0.0341 (4) | 0.6062 (4) | 0.38910 (18) | 0.0432 (12) |

| | | | | |
|---|---|---|---|---|
| C18 | 0.0672 (5) | 0.5167 (4) | 0.4928 (2) | 0.0597 (17) |
| H18A | 0.0370 | 0.4588 | 0.4707 | 0.090* |
| H18B | 0.0096 | 0.5460 | 0.5092 | 0.090* |
| H18C | 0.1264 | 0.4877 | 0.5169 | 0.090* |
| C19 | 0.1763 (4) | 0.8807 (4) | 0.33769 (18) | 0.0662 (13) |
| H19A | 0.1419 | 0.9050 | 0.3055 | 0.099* |
| H19B | 0.2448 | 0.8433 | 0.3353 | 0.099* |
| H19C | 0.1915 | 0.9433 | 0.3591 | 0.099* |
| C20 | −0.0254 (4) | 0.5480 (4) | 0.34209 (16) | 0.0579 (12) |
| H20A | −0.0164 | 0.4704 | 0.3483 | 0.087* |
| H20B | 0.0378 | 0.5756 | 0.3290 | 0.087* |
| H20C | −0.0922 | 0.5605 | 0.3187 | 0.087* |
| C21 | 0.3487 (3) | −0.0066 (3) | 0.13375 (16) | 0.0452 (10) |
| C22 | 0.4442 (4) | 0.0093 (4) | 0.16737 (18) | 0.0397 (12) |
| C23 | 0.5136 (4) | 0.0960 (4) | 0.1516 (2) | 0.0395 (14) |
| C24 | 0.4702 (4) | 0.1402 (4) | 0.1073 (2) | 0.0412 (13) |
| C25 | 0.2538 (4) | −0.0864 (4) | 0.13179 (18) | 0.0595 (12) |
| H25A | 0.2771 | −0.1578 | 0.1223 | 0.089* |
| H25B | 0.1918 | −0.0614 | 0.1081 | 0.089* |
| H25C | 0.2317 | −0.0911 | 0.1638 | 0.089* |
| C26 | 0.4849 (4) | −0.0570 (3) | 0.21115 (17) | 0.0468 (10) |
| C27 | 0.6200 (4) | 0.1393 (4) | 0.18038 (19) | 0.0457 (13) |
| C28 | 0.5153 (5) | 0.2308 (5) | 0.0799 (2) | 0.0621 (17) |
| H28A | 0.4779 | 0.2985 | 0.0851 | 0.093* |
| H28B | 0.5034 | 0.2137 | 0.0452 | 0.093* |
| H28C | 0.5939 | 0.2387 | 0.0915 | 0.093* |
| C29 | 0.4078 (4) | −0.1369 (4) | 0.23122 (17) | 0.0653 (13) |
| H29A | 0.3862 | −0.1943 | 0.2075 | 0.098* |
| H29B | 0.3425 | −0.0985 | 0.2375 | 0.098* |
| H29C | 0.4457 | −0.1687 | 0.2614 | 0.098* |
| C30 | 0.6137 (4) | 0.1957 (3) | 0.22774 (17) | 0.0581 (12) |
| H30A | 0.6874 | 0.2024 | 0.2465 | 0.087* |
| H30B | 0.5677 | 0.1535 | 0.2462 | 0.087* |
| H30C | 0.5820 | 0.2677 | 0.2212 | 0.087* |
| C31 | −0.0373 (4) | 0.1242 (4) | 0.1086 (2) | 0.0409 (13) |
| C32 | 0.0215 (4) | 0.0999 (4) | 0.1535 (2) | 0.0373 (13) |
| C33 | 0.1135 (4) | 0.1744 (3) | 0.16831 (18) | 0.0390 (12) |
| C34 | 0.1199 (3) | 0.2560 (3) | 0.13392 (15) | 0.0438 (10) |
| C35 | −0.1391 (5) | 0.0656 (4) | 0.0813 (2) | 0.0583 (17) |
| H35A | −0.1332 | −0.0119 | 0.0883 | 0.087* |
| H35B | −0.1435 | 0.0773 | 0.0464 | 0.087* |
| H35C | −0.2050 | 0.0943 | 0.0919 | 0.087* |
| C36 | −0.0130 (4) | 0.0059 (4) | 0.1833 (2) | 0.0445 (13) |
| C37 | 0.1960 (3) | 0.1528 (4) | 0.21315 (17) | 0.0464 (10) |
| C38 | 0.1999 (4) | 0.3480 (3) | 0.13055 (18) | 0.0620 (13) |
| H38A | 0.2176 | 0.3837 | 0.1621 | 0.093* |
| H38B | 0.1667 | 0.4004 | 0.1063 | 0.093* |
| H38C | 0.2670 | 0.3191 | 0.1211 | 0.093* |

| | | | | |
|---|---|---|---|---|
| C39 | −0.0535 (4) | 0.0325 (4) | 0.22985 (16) | 0.0580 (12) |
| H39A | −0.1235 | 0.0707 | 0.2225 | 0.087* |
| H39B | 0.0001 | 0.0785 | 0.2500 | 0.087* |
| H39C | −0.0634 | −0.0345 | 0.2473 | 0.087* |
| C40 | 0.2819 (3) | 0.2373 (4) | 0.23302 (17) | 0.0615 (13) |
| H40A | 0.3211 | 0.2133 | 0.2645 | 0.092* |
| H40B | 0.2458 | 0.3064 | 0.2369 | 0.092* |
| H40C | 0.3339 | 0.2461 | 0.2104 | 0.092* |
| O1 | 0.1038 (3) | 0.3320 (2) | 0.40784 (13) | 0.0705 (9) |
| O2 | −0.1062 (2) | 0.1817 (3) | 0.34011 (12) | 0.0668 (9) |
| O3 | 0.0032 (3) | 0.7933 (3) | 0.33761 (11) | 0.0626 (9) |
| O4 | −0.1202 (2) | 0.6078 (3) | 0.40579 (13) | 0.0688 (9) |
| O5 | 0.5817 (3) | −0.0474 (2) | 0.23140 (12) | 0.0665 (9) |
| O6 | 0.7055 (2) | 0.1377 (3) | 0.16305 (12) | 0.0677 (9) |
| O7 | −0.0166 (3) | −0.0868 (2) | 0.16659 (12) | 0.0658 (8) |
| O8 | 0.1926 (2) | 0.0637 (2) | 0.23397 (12) | 0.0605 (8) |
| S1 | 0.07809 (11) | −0.00057 (11) | 0.48785 (5) | 0.0531 (4) |
| S2 | 0.23678 (11) | 0.67089 (12) | 0.48713 (5) | 0.0541 (4) |
| S3 | 0.34281 (10) | 0.08175 (12) | 0.08483 (5) | 0.0522 (4) |
| S4 | 0.01417 (10) | 0.23984 (11) | 0.08442 (5) | 0.0525 (4) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.043 (3) | 0.049 (3) | 0.041 (3) | −0.005 (2) | 0.011 (2) | 0.004 (3) |
| C2 | 0.041 (3) | 0.040 (3) | 0.041 (4) | −0.005 (3) | 0.010 (3) | −0.001 (3) |
| C3 | 0.036 (2) | 0.040 (3) | 0.046 (3) | −0.002 (2) | 0.009 (2) | −0.003 (2) |
| C4 | 0.046 (2) | 0.040 (2) | 0.052 (3) | −0.0078 (19) | 0.015 (2) | −0.003 (2) |
| C5 | 0.049 (3) | 0.073 (3) | 0.043 (4) | −0.018 (3) | 0.006 (3) | −0.005 (3) |
| C6 | 0.034 (3) | 0.043 (3) | 0.053 (3) | −0.002 (2) | 0.005 (2) | 0.003 (2) |
| C7 | 0.039 (2) | 0.051 (3) | 0.053 (3) | 0.001 (2) | 0.010 (2) | −0.002 (2) |
| C8 | 0.066 (3) | 0.053 (3) | 0.071 (3) | −0.023 (2) | 0.025 (3) | 0.003 (2) |
| C9 | 0.057 (3) | 0.062 (3) | 0.056 (3) | 0.002 (2) | 0.015 (2) | 0.009 (2) |
| C10 | 0.050 (3) | 0.087 (4) | 0.078 (4) | −0.015 (3) | −0.012 (3) | 0.000 (3) |
| C11 | 0.039 (2) | 0.045 (2) | 0.044 (2) | −0.0095 (19) | 0.0109 (19) | −0.005 (2) |
| C12 | 0.040 (3) | 0.036 (2) | 0.042 (3) | −0.003 (2) | 0.008 (2) | −0.0013 (19) |
| C13 | 0.040 (3) | 0.034 (3) | 0.039 (3) | −0.005 (2) | 0.005 (3) | −0.003 (2) |
| C14 | 0.044 (3) | 0.043 (3) | 0.042 (3) | −0.007 (2) | 0.005 (3) | −0.003 (2) |
| C15 | 0.057 (3) | 0.073 (3) | 0.069 (3) | −0.030 (3) | 0.002 (2) | −0.003 (3) |
| C16 | 0.051 (3) | 0.041 (3) | 0.046 (3) | 0.009 (2) | 0.009 (2) | 0.006 (2) |
| C17 | 0.043 (3) | 0.039 (3) | 0.047 (3) | 0.001 (2) | 0.003 (2) | 0.006 (2) |
| C18 | 0.070 (4) | 0.061 (3) | 0.049 (4) | −0.018 (3) | 0.012 (3) | 0.001 (3) |
| C19 | 0.069 (3) | 0.057 (3) | 0.072 (3) | −0.015 (2) | 0.010 (3) | 0.016 (3) |
| C20 | 0.059 (3) | 0.058 (3) | 0.052 (3) | −0.002 (2) | −0.004 (2) | −0.011 (2) |
| C21 | 0.041 (2) | 0.043 (2) | 0.053 (3) | −0.008 (2) | 0.010 (2) | −0.007 (2) |
| C22 | 0.033 (3) | 0.041 (3) | 0.046 (3) | 0.000 (2) | 0.011 (2) | −0.003 (2) |
| C23 | 0.032 (3) | 0.040 (3) | 0.047 (4) | 0.001 (2) | 0.009 (3) | −0.006 (3) |
| C24 | 0.039 (3) | 0.045 (3) | 0.040 (3) | −0.008 (2) | 0.008 (2) | −0.009 (3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C25 | 0.048 (2) | 0.061 (3) | 0.072 (3) | −0.024 (2) | 0.016 (2) | −0.004 (3) |
| C26 | 0.049 (3) | 0.041 (3) | 0.051 (3) | −0.004 (2) | 0.011 (2) | −0.007 (2) |
| C27 | 0.039 (3) | 0.042 (3) | 0.055 (3) | −0.005 (2) | 0.005 (2) | 0.002 (2) |
| C28 | 0.070 (4) | 0.064 (3) | 0.050 (4) | −0.016 (3) | 0.004 (3) | 0.005 (3) |
| C29 | 0.076 (3) | 0.052 (3) | 0.067 (3) | −0.005 (2) | 0.010 (3) | 0.020 (2) |
| C30 | 0.060 (3) | 0.054 (3) | 0.056 (3) | −0.006 (2) | −0.002 (2) | −0.006 (2) |
| C31 | 0.046 (3) | 0.039 (3) | 0.039 (3) | −0.006 (2) | 0.011 (3) | −0.002 (2) |
| C32 | 0.034 (3) | 0.037 (3) | 0.042 (4) | −0.002 (2) | 0.010 (3) | 0.000 (2) |
| C33 | 0.043 (3) | 0.034 (2) | 0.041 (3) | −0.002 (2) | 0.010 (2) | −0.003 (2) |
| C34 | 0.046 (2) | 0.041 (2) | 0.047 (3) | −0.0033 (19) | 0.012 (2) | 0.001 (2) |
| C35 | 0.064 (4) | 0.059 (3) | 0.050 (4) | −0.013 (3) | 0.002 (3) | 0.006 (3) |
| C36 | 0.040 (3) | 0.043 (3) | 0.050 (3) | −0.003 (2) | 0.004 (2) | 0.006 (2) |
| C37 | 0.037 (2) | 0.052 (3) | 0.050 (3) | 0.002 (2) | 0.008 (2) | −0.003 (2) |
| C38 | 0.062 (3) | 0.049 (3) | 0.075 (3) | −0.021 (2) | 0.012 (3) | 0.000 (2) |
| C39 | 0.053 (3) | 0.065 (3) | 0.057 (3) | −0.004 (2) | 0.013 (2) | 0.014 (2) |
| C40 | 0.046 (3) | 0.066 (3) | 0.070 (4) | −0.011 (2) | 0.000 (2) | 0.001 (3) |
| O1 | 0.089 (2) | 0.0401 (18) | 0.084 (3) | −0.0120 (17) | 0.0214 (19) | −0.0049 (17) |
| O2 | 0.061 (2) | 0.063 (2) | 0.071 (2) | 0.0018 (17) | −0.0037 (17) | 0.0143 (18) |
| O3 | 0.0558 (19) | 0.067 (2) | 0.060 (2) | −0.0011 (15) | −0.0072 (16) | 0.0114 (16) |
| O4 | 0.0389 (18) | 0.089 (2) | 0.080 (2) | −0.0106 (16) | 0.0149 (17) | −0.0050 (19) |
| O5 | 0.0523 (19) | 0.066 (2) | 0.077 (2) | 0.0014 (16) | 0.0002 (18) | 0.0154 (18) |
| O6 | 0.0384 (18) | 0.092 (2) | 0.073 (2) | −0.0116 (17) | 0.0114 (16) | −0.0069 (19) |
| O7 | 0.085 (2) | 0.0436 (18) | 0.071 (2) | −0.0106 (17) | 0.0194 (17) | −0.0003 (16) |
| O8 | 0.0559 (19) | 0.0557 (19) | 0.066 (2) | −0.0016 (15) | −0.0001 (15) | 0.0159 (16) |
| S1 | 0.0551 (9) | 0.0545 (8) | 0.0502 (9) | −0.0083 (6) | 0.0100 (7) | 0.0104 (6) |
| S2 | 0.0500 (8) | 0.0611 (8) | 0.0471 (9) | −0.0126 (6) | −0.0039 (6) | 0.0002 (7) |
| S3 | 0.0482 (8) | 0.0592 (8) | 0.0464 (9) | −0.0120 (6) | −0.0008 (6) | −0.0015 (7) |
| S4 | 0.0577 (9) | 0.0525 (8) | 0.0468 (9) | −0.0106 (7) | 0.0074 (7) | 0.0097 (7) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—C2 | 1.352 (7) | C21—C22 | 1.373 (6) |
| C1—C5 | 1.480 (7) | C21—C25 | 1.499 (5) |
| C1—S1 | 1.731 (5) | C21—S3 | 1.710 (4) |
| C2—C3 | 1.461 (7) | C22—C23 | 1.456 (6) |
| C2—C6 | 1.491 (7) | C22—C26 | 1.463 (6) |
| C3—C4 | 1.364 (6) | C23—C24 | 1.355 (7) |
| C3—C7 | 1.478 (6) | C23—C27 | 1.495 (7) |
| C4—C8 | 1.519 (5) | C24—C28 | 1.487 (7) |
| C4—S1 | 1.710 (5) | C24—S3 | 1.721 (5) |
| C5—H5A | 0.9600 | C25—H25A | 0.9600 |
| C5—H5B | 0.9600 | C25—H25B | 0.9600 |
| C5—H5C | 0.9600 | C25—H25C | 0.9600 |
| C6—O1 | 1.215 (5) | C26—O5 | 1.221 (5) |
| C6—C9 | 1.504 (6) | C26—C29 | 1.513 (6) |
| C7—O2 | 1.228 (5) | C27—O6 | 1.211 (5) |
| C7—C10 | 1.501 (6) | C27—C30 | 1.481 (6) |
| C8—H8A | 0.9600 | C28—H28A | 0.9600 |

| | | | |
|---|---|---|---|
| C8—H8B | 0.9600 | C28—H28B | 0.9600 |
| C8—H8C | 0.9600 | C28—H28C | 0.9600 |
| C9—H9A | 0.9600 | C29—H29A | 0.9600 |
| C9—H9B | 0.9600 | C29—H29B | 0.9600 |
| C9—H9C | 0.9600 | C29—H29C | 0.9600 |
| C10—H10A | 0.9600 | C30—H30A | 0.9600 |
| C10—H10B | 0.9600 | C30—H30B | 0.9600 |
| C10—H10C | 0.9600 | C30—H30C | 0.9600 |
| C11—C12 | 1.374 (6) | C31—C32 | 1.353 (7) |
| C11—C15 | 1.508 (5) | C31—C35 | 1.514 (7) |
| C11—S2 | 1.718 (4) | C31—S4 | 1.713 (5) |
| C12—C13 | 1.441 (6) | C32—C33 | 1.443 (7) |
| C12—C16 | 1.490 (6) | C32—C36 | 1.502 (7) |
| C13—C14 | 1.358 (7) | C33—C34 | 1.379 (5) |
| C13—C17 | 1.505 (7) | C33—C37 | 1.478 (6) |
| C14—C18 | 1.519 (7) | C34—C38 | 1.492 (5) |
| C14—S2 | 1.720 (5) | C34—S4 | 1.722 (4) |
| C15—H15A | 0.9600 | C35—H35A | 0.9600 |
| C15—H15B | 0.9600 | C35—H35B | 0.9600 |
| C15—H15C | 0.9600 | C35—H35C | 0.9600 |
| C16—O3 | 1.221 (5) | C36—O7 | 1.213 (5) |
| C16—C19 | 1.484 (6) | C36—C39 | 1.477 (7) |
| C17—O4 | 1.209 (5) | C37—O8 | 1.226 (5) |
| C17—C20 | 1.489 (6) | C37—C40 | 1.500 (6) |
| C18—H18A | 0.9600 | C38—H38A | 0.9600 |
| C18—H18B | 0.9600 | C38—H38B | 0.9600 |
| C18—H18C | 0.9600 | C38—H38C | 0.9600 |
| C19—H19A | 0.9600 | C39—H39A | 0.9600 |
| C19—H19B | 0.9600 | C39—H39B | 0.9600 |
| C19—H19C | 0.9600 | C39—H39C | 0.9600 |
| C20—H20A | 0.9600 | C40—H40A | 0.9600 |
| C20—H20B | 0.9600 | C40—H40B | 0.9600 |
| C20—H20C | 0.9600 | C40—H40C | 0.9600 |

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|---|---|---|---|
| C2—C1—C5 | 130.9 (5) | C25—C21—S3 | 116.3 (3) |
| C2—C1—S1 | 110.1 (4) | C21—C22—C23 | 111.6 (4) |
| C5—C1—S1 | 119.0 (4) | C21—C22—C26 | 127.6 (4) |
| C1—C2—C3 | 113.5 (4) | C23—C22—C26 | 120.4 (4) |
| C1—C2—C6 | 120.7 (5) | C24—C23—C22 | 113.2 (5) |
| C3—C2—C6 | 125.7 (5) | C24—C23—C27 | 120.7 (4) |
| C4—C3—C2 | 111.8 (4) | C22—C23—C27 | 126.1 (5) |
| C4—C3—C7 | 127.8 (4) | C23—C24—C28 | 128.7 (5) |
| C2—C3—C7 | 120.1 (4) | C23—C24—S3 | 110.7 (4) |
| C3—C4—C8 | 132.0 (4) | C28—C24—S3 | 120.5 (4) |
| C3—C4—S1 | 111.2 (3) | C21—C25—H25A | 109.5 |
| C8—C4—S1 | 116.8 (3) | C21—C25—H25B | 109.5 |
| C1—C5—H5A | 109.5 | H25A—C25—H25B | 109.5 |
| C1—C5—H5B | 109.5 | C21—C25—H25C | 109.5 |

| | | | |
|---|---|---|---|
| H5A—C5—H5B | 109.5 | H25A—C25—H25C | 109.5 |
| C1—C5—H5C | 109.5 | H25B—C25—H25C | 109.5 |
| H5A—C5—H5C | 109.5 | O5—C26—C22 | 119.5 (4) |
| H5B—C5—H5C | 109.5 | O5—C26—C29 | 120.1 (4) |
| O1—C6—C2 | 120.6 (5) | C22—C26—C29 | 120.3 (4) |
| O1—C6—C9 | 120.0 (5) | O6—C27—C30 | 121.5 (4) |
| C2—C6—C9 | 118.9 (4) | O6—C27—C23 | 120.6 (5) |
| O2—C7—C3 | 119.5 (4) | C30—C27—C23 | 117.5 (4) |
| O2—C7—C10 | 120.1 (4) | C24—C28—H28A | 109.5 |
| C3—C7—C10 | 120.4 (4) | C24—C28—H28B | 109.5 |
| C4—C8—H8A | 109.5 | H28A—C28—H28B | 109.5 |
| C4—C8—H8B | 109.5 | C24—C28—H28C | 109.5 |
| H8A—C8—H8B | 109.5 | H28A—C28—H28C | 109.5 |
| C4—C8—H8C | 109.5 | H28B—C28—H28C | 109.5 |
| H8A—C8—H8C | 109.5 | C26—C29—H29A | 109.5 |
| H8B—C8—H8C | 109.5 | C26—C29—H29B | 109.5 |
| C6—C9—H9A | 109.5 | H29A—C29—H29B | 109.5 |
| C6—C9—H9B | 109.5 | C26—C29—H29C | 109.5 |
| H9A—C9—H9B | 109.5 | H29A—C29—H29C | 109.5 |
| C6—C9—H9C | 109.5 | H29B—C29—H29C | 109.5 |
| H9A—C9—H9C | 109.5 | C27—C30—H30A | 109.5 |
| H9B—C9—H9C | 109.5 | C27—C30—H30B | 109.5 |
| C7—C10—H10A | 109.5 | H30A—C30—H30B | 109.5 |
| C7—C10—H10B | 109.5 | C27—C30—H30C | 109.5 |
| H10A—C10—H10B | 109.5 | H30A—C30—H30C | 109.5 |
| C7—C10—H10C | 109.5 | H30B—C30—H30C | 109.5 |
| H10A—C10—H10C | 109.5 | C32—C31—C35 | 128.0 (5) |
| H10B—C10—H10C | 109.5 | C32—C31—S4 | 111.1 (4) |
| C12—C11—C15 | 131.9 (4) | C35—C31—S4 | 120.8 (4) |
| C12—C11—S2 | 110.3 (3) | C31—C32—C33 | 112.9 (4) |
| C15—C11—S2 | 117.6 (3) | C31—C32—C36 | 120.7 (5) |
| C11—C12—C13 | 112.0 (4) | C33—C32—C36 | 126.4 (5) |
| C11—C12—C16 | 126.4 (4) | C34—C33—C32 | 112.6 (4) |
| C13—C12—C16 | 121.3 (4) | C34—C33—C37 | 126.2 (4) |
| C14—C13—C12 | 114.1 (5) | C32—C33—C37 | 120.8 (4) |
| C14—C13—C17 | 120.3 (4) | C33—C34—C38 | 133.6 (4) |
| C12—C13—C17 | 125.5 (5) | C33—C34—S4 | 109.9 (3) |
| C13—C14—C18 | 130.4 (5) | C38—C34—S4 | 116.4 (3) |
| C13—C14—S2 | 109.8 (4) | C31—C35—H35A | 109.5 |
| C18—C14—S2 | 119.8 (4) | C31—C35—H35B | 109.5 |
| C11—C15—H15A | 109.5 | H35A—C35—H35B | 109.5 |
| C11—C15—H15B | 109.5 | C31—C35—H35C | 109.5 |
| H15A—C15—H15B | 109.5 | H35A—C35—H35C | 109.5 |
| C11—C15—H15C | 109.5 | H35B—C35—H35C | 109.5 |
| H15A—C15—H15C | 109.5 | O7—C36—C39 | 122.2 (4) |
| H15B—C15—H15C | 109.5 | O7—C36—C32 | 119.5 (5) |
| O3—C16—C19 | 120.6 (4) | C39—C36—C32 | 117.9 (4) |
| O3—C16—C12 | 118.3 (4) | O8—C37—C33 | 118.3 (4) |

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| C19—C16—C12 | 121.2 (4) | O8—C37—C40 | 120.5 (4) |
| O4—C17—C20 | 121.6 (4) | C33—C37—C40 | 121.2 (4) |
| O4—C17—C13 | 119.5 (5) | C34—C38—H38A | 109.5 |
| C20—C17—C13 | 118.5 (4) | C34—C38—H38B | 109.5 |
| C14—C18—H18A | 109.5 | H38A—C38—H38B | 109.5 |
| C14—C18—H18B | 109.5 | C34—C38—H38C | 109.5 |
| H18A—C18—H18B | 109.5 | H38A—C38—H38C | 109.5 |
| C14—C18—H18C | 109.5 | H38B—C38—H38C | 109.5 |
| H18A—C18—H18C | 109.5 | C36—C39—H39A | 109.5 |
| H18B—C18—H18C | 109.5 | C36—C39—H39B | 109.5 |
| C16—C19—H19A | 109.5 | H39A—C39—H39B | 109.5 |
| C16—C19—H19B | 109.5 | C36—C39—H39C | 109.5 |
| H19A—C19—H19B | 109.5 | H39A—C39—H39C | 109.5 |
| C16—C19—H19C | 109.5 | H39B—C39—H39C | 109.5 |
| H19A—C19—H19C | 109.5 | C37—C40—H40A | 109.5 |
| H19B—C19—H19C | 109.5 | C37—C40—H40B | 109.5 |
| C17—C20—H20A | 109.5 | H40A—C40—H40B | 109.5 |
| C17—C20—H20B | 109.5 | C37—C40—H40C | 109.5 |
| H20A—C20—H20B | 109.5 | H40A—C40—H40C | 109.5 |
| C17—C20—H20C | 109.5 | H40B—C40—H40C | 109.5 |
| H20A—C20—H20C | 109.5 | C4—S1—C1 | 93.5 (2) |
| H20B—C20—H20C | 109.5 | C11—S2—C14 | 93.8 (2) |
| C22—C21—C25 | 132.4 (4) | C21—S3—C24 | 93.3 (2) |
| C22—C21—S3 | 111.2 (3) | C31—S4—C34 | 93.4 (2) |

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|---|---|---|---|
| C5—C1—C2—C3 | 179.5 (5) | C22—C23—C24—C28 | 178.8 (5) |
| S1—C1—C2—C3 | 0.0 (5) | C27—C23—C24—C28 | 1.3 (8) |
| C5—C1—C2—C6 | 3.7 (9) | C22—C23—C24—S3 | 2.1 (5) |
| S1—C1—C2—C6 | −175.8 (4) | C27—C23—C24—S3 | −175.4 (4) |
| C1—C2—C3—C4 | −0.3 (6) | C21—C22—C26—O5 | 164.3 (4) |
| C6—C2—C3—C4 | 175.2 (4) | C23—C22—C26—O5 | −7.8 (6) |
| C1—C2—C3—C7 | 174.2 (4) | C21—C22—C26—C29 | −15.6 (7) |
| C6—C2—C3—C7 | −10.2 (7) | C23—C22—C26—C29 | 172.2 (4) |
| C2—C3—C4—C8 | 177.8 (4) | C24—C23—C27—O6 | −59.7 (7) |
| C7—C3—C4—C8 | 3.8 (8) | C22—C23—C27—O6 | 123.1 (5) |
| C2—C3—C4—S1 | 0.4 (5) | C24—C23—C27—C30 | 113.2 (5) |
| C7—C3—C4—S1 | −173.6 (4) | C22—C23—C27—C30 | −64.0 (6) |
| C1—C2—C6—O1 | −61.2 (7) | C35—C31—C32—C33 | −179.4 (5) |
| C3—C2—C6—O1 | 123.5 (5) | S4—C31—C32—C33 | −2.1 (5) |
| C1—C2—C6—C9 | 111.0 (5) | C35—C31—C32—C36 | −1.3 (8) |
| C3—C2—C6—C9 | −64.2 (6) | S4—C31—C32—C36 | 176.1 (4) |
| C4—C3—C7—O2 | 165.7 (4) | C31—C32—C33—C34 | 1.5 (6) |
| C2—C3—C7—O2 | −7.9 (7) | C36—C32—C33—C34 | −176.6 (4) |
| C4—C3—C7—C10 | −14.1 (7) | C31—C32—C33—C37 | −172.0 (4) |
| C2—C3—C7—C10 | 172.3 (4) | C36—C32—C33—C37 | 9.9 (7) |
| C15—C11—C12—C13 | −176.3 (4) | C32—C33—C34—C38 | −177.1 (4) |
| S2—C11—C12—C13 | −1.2 (5) | C37—C33—C34—C38 | −4.0 (7) |
| C15—C11—C12—C16 | −1.7 (8) | C32—C33—C34—S4 | −0.2 (5) |

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|---|---|---|---|
| S2—C11—C12—C16 | 173.4 (4) | C37—C33—C34—S4 | 172.9 (4) |
| C11—C12—C13—C14 | 0.9 (6) | C31—C32—C36—O7 | 59.9 (6) |
| C16—C12—C13—C14 | −174.0 (4) | C33—C32—C36—O7 | −122.2 (5) |
| C11—C12—C13—C17 | −174.9 (4) | C31—C32—C36—C39 | −113.3 (5) |
| C16—C12—C13—C17 | 10.1 (7) | C33—C32—C36—C39 | 64.6 (6) |
| C12—C13—C14—C18 | 179.7 (5) | C34—C33—C37—O8 | −163.6 (4) |
| C17—C13—C14—C18 | −4.2 (8) | C32—C33—C37—O8 | 8.9 (6) |
| C12—C13—C14—S2 | −0.2 (6) | C34—C33—C37—C40 | 16.5 (7) |
| C17—C13—C14—S2 | 175.9 (4) | C32—C33—C37—C40 | −170.9 (4) |
| C11—C12—C16—O3 | −164.6 (4) | C3—C4—S1—C1 | −0.4 (4) |
| C13—C12—C16—O3 | 9.5 (6) | C8—C4—S1—C1 | −178.2 (3) |
| C11—C12—C16—C19 | 15.6 (7) | C2—C1—S1—C4 | 0.2 (4) |
| C13—C12—C16—C19 | −170.2 (4) | C5—C1—S1—C4 | −179.4 (4) |
| C14—C13—C17—O4 | 61.3 (7) | C12—C11—S2—C14 | 1.0 (3) |
| C12—C13—C17—O4 | −123.0 (5) | C15—C11—S2—C14 | 176.8 (3) |
| C14—C13—C17—C20 | −111.7 (5) | C13—C14—S2—C11 | −0.4 (4) |
| C12—C13—C17—C20 | 63.9 (6) | C18—C14—S2—C11 | 179.7 (4) |
| C25—C21—C22—C23 | 177.8 (4) | C22—C21—S3—C24 | 1.4 (4) |
| S3—C21—C22—C23 | −0.5 (5) | C25—C21—S3—C24 | −177.1 (3) |
| C25—C21—C22—C26 | 5.0 (8) | C23—C24—S3—C21 | −2.0 (4) |
| S3—C21—C22—C26 | −173.2 (4) | C28—C24—S3—C21 | −179.1 (4) |
| C21—C22—C23—C24 | −1.1 (6) | C32—C31—S4—C34 | 1.7 (4) |
| C26—C22—C23—C24 | 172.2 (4) | C35—C31—S4—C34 | 179.3 (4) |
| C21—C22—C23—C27 | 176.3 (4) | C33—C34—S4—C31 | −0.9 (3) |
| C26—C22—C23—C27 | −10.4 (7) | C38—C34—S4—C31 | 176.6 (3) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C30—H30*B*···O5 | 0.96 | 2.48 | 2.978 (4) | 112 |
| C35—H35*C*···O6$^{i}$ | 0.96 | 2.44 | 3.276 (6) | 145 |
| C39—H39*A*···O6$^{i}$ | 0.96 | 2.56 | 3.435 (6) | 152 |

Symmetry code: (i) *x*−1, *y*, *z*.