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# 3,5-Dimethoxyphenyl 4-methylbenzenesulfonate

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**Keywords:** crystal structure; tosylates; cross-coupling reactions.

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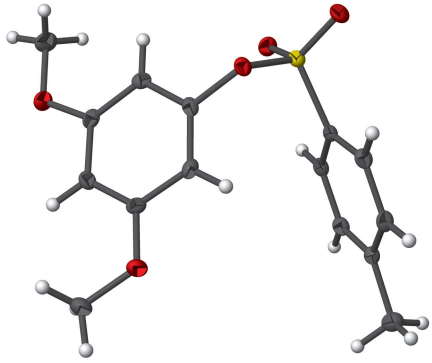
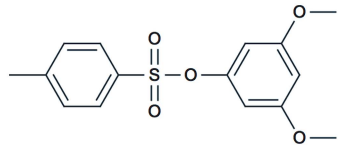
**Structural data**: full structural data are available from iucrdata.iucr.org

Molecules of the title compound, $C_{15}H_{16}O_5S$, are composed of a 3,5-dimethoxyphenyl moiety substituted with a toluene-4-sulfonate group. The dihedral angle between two aromatic rings is 57.23 (4)°. In the crystal, molecules are connected by weak C—H···O hydrogen bonds and S···O van der Waals interactions.

**3D view**



**Chemical scheme**



## Structure description

Aryl tosylates attract considerable attention as electrophiles in transition-metal-catalyzed cross-coupling reactions (Chen *et al.*, 2015; Nguyen *et al.*, 2003). 4-Methylbenzenesulfonate derivatives emerged as substrates for first-row transition metal catalysts. These non-precious transition metal elements are suitable alternatives to execute challenging cross-coupling with higher efficiency (Ananikov, 2015).

In the asymmetric unit of the title compound there is one independent molecule. The molecular structure is shown in Fig. 1. In the molecular structure, the bond lengths and angles are within normal ranges (Allen *et al.*, 2002). The dihedral angle between two aromatic moieties is 57.23 (4)°.

The crystal structure (Fig. 2) features weak C—H···O hydrogen bonds (Table 1) and S1···O1$^{i}$ van der Waals interactions [symmetry code: (i) $-x + 2, -y + 2, -z + 1$. The S1···O1$^{i}$ distance is 3.2929 (10) Å]. The S1···O1$^{i}$ contacts connect the molecules into dimers, while C—H···O bonds arrange the molecules into chains along *b* axis.

## Synthesis and crystallization

3,5-Dimethoxyphenyl 4-methylbenzenesulfonate was synthesized according to the procedure described by Murai and co-workers (Murai *et al.*, 2012). The crystallization was performed in a diethyl ether solution. Diethyl ether (0.6 ml) was placed in storage reaction vials (8 ml) with silicone septa. The title compound was placed in small portions

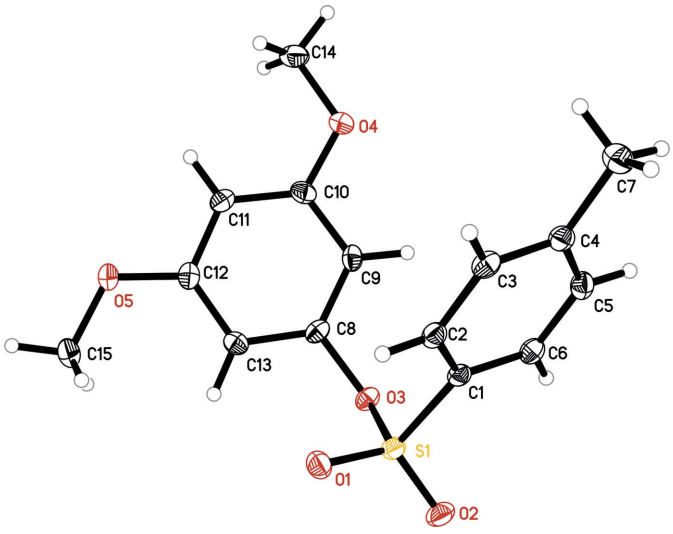



**Figure 1**
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level.

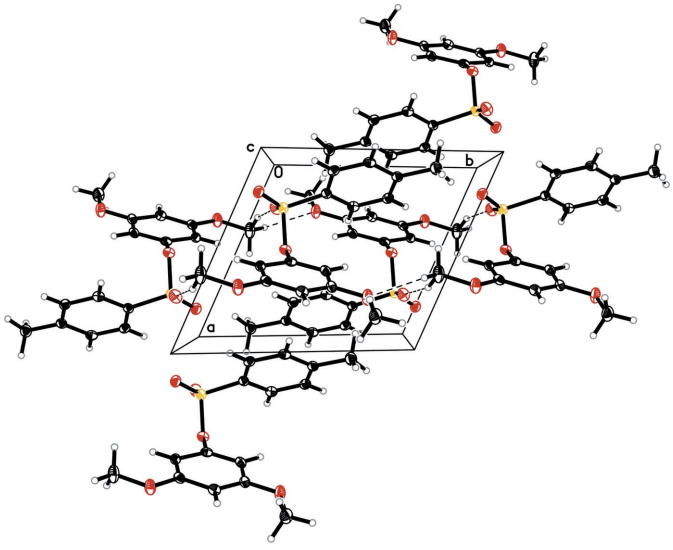



**Figure 2**
The crystal packing of the title compound, viewed along the *c* axis.

until a saturated solution was obtained. The solution was warmed, then left to stand in a refrigerator (−20°C).

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C15—H15*A*···O4$^{i}$ | 0.96 | 2.35 | 3.2051 (18) | 147 |
| C15—H15*C*···O2$^{ii}$ | 0.96 | 2.51 | 3.4063 (19) | 155 |

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

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{15}H_{16}O_5S$ |
| $M_r$ | 308.34 |
| Crystal system, space group | Triclinic, $P\overline{1}$ |
| Temperature (K) | 100 |
| $a, b, c$ (Å) | 7.8066 (2), 8.9238 (2), 11.9303 (3) |
| $\alpha, \beta, \gamma$ (°) | 106.583 (2), 94.701 (2), 111.358 (2) |
| $V$ (Å$^3$) | 725.58 (3) |
| $Z$ | 2 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.24 |
| Crystal size (mm) | 0.26 × 0.25 × 0.24 |
| | |
| Data collection | |
| Diffractometer | Oxford Diffraction Xcalibur |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 4805, 2795, 2316 |
| $R_{int}$ | 0.013 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.617 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.029, 0.077, 1.05 |
| No. of reflections | 2795 |
| No. of parameters | 193 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.38, −0.35 |

Computer programs: *CrysAlis CCD* and *CrysAlis RED* (Oxford Diffraction, 2008), *SHELXS2014* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *SHELXTL* (Sheldrick, 2008).

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# full crystallographic data

*IUCrData* (2017). **2**, x170980 [https://doi.org/10.1107/S2414314617009804]

## 3,5-Dimethoxyphenyl 4-methylbenzenesulfonate

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*Crystal data*

$C_{15}H_{16}O_5S$
$M_r$ = 308.34
Triclinic, $P\overline{1}$
$a$ = 7.8066 (2) Å
$b$ = 8.9238 (2) Å
$c$ = 11.9303 (3) Å
$\alpha$ = 106.583 (2)°
$\beta$ = 94.701 (2)°
$\gamma$ = 111.358 (2)°
$V$ = 725.58 (3) Å$^3$
$Z$ = 2
$F(000)$ = 324
$D_x$ = 1.411 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 4805 reflections
$\theta$ = 3.1–26.0°
$\mu$ = 0.24 mm$^{-1}$
$T$ = 100 K
Irregular, colourless
0.26 × 0.25 × 0.24 mm

*Data collection*

Oxford Diffraction Xcalibur diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 1024 x 1024 with blocks 2 x 2 pixels mm$^{-1}$
$\omega$–scan
4805 measured reflections
2795 independent reflections
2316 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.013
$\theta_{max}$ = 26.0°, $\theta_{min}$ = 3.1°
$h$ = −8→9
$k$ = −10→10
$l$ = −14→14

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.077
$S$ = 1.05
2795 reflections
193 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2 + 0.0255P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.38 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.35 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**. All H atoms were found in a difference map but set to idealized positions and treated as riding with $C_{Ar}$—H = 0.93 Å and $U_{iso}$(H) = 1.2$U_{eq}$(C) and with $C_{methyl}$—H = 0.96 Å and $U_{iso}$(H) = 1.5$U_{eq}$(C).

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| S1 | 0.73013 (5) | 0.83595 (4) | 0.47367 (3) | 0.01539 (11) |
| O1 | 0.81146 (14) | 0.96873 (12) | 0.42577 (9) | 0.0195 (2) |
| C1 | 0.80548 (19) | 0.67126 (18) | 0.41824 (12) | 0.0147 (3) |
| C2 | 0.91926 (19) | 0.68105 (18) | 0.33471 (12) | 0.0157 (3) |
| H2 | 0.9673 | 0.7794 | 0.3145 | 0.019* |
| O2 | 0.73567 (14) | 0.87416 (13) | 0.59863 (9) | 0.0217 (2) |
| O3 | 0.50777 (13) | 0.74229 (12) | 0.41772 (8) | 0.0157 (2) |
| C3 | 0.95988 (19) | 0.54111 (18) | 0.28197 (12) | 0.0168 (3) |
| H3 | 1.0349 | 0.5460 | 0.2253 | 0.020* |
| C4 | 0.89064 (19) | 0.39332 (18) | 0.31217 (12) | 0.0166 (3) |
| O4 | 0.26779 (15) | 0.29839 (13) | 0.04463 (9) | 0.0234 (3) |
| C5 | 0.78274 (19) | 0.39000 (18) | 0.39973 (12) | 0.0173 (3) |
| H5 | 0.7394 | 0.2940 | 0.4229 | 0.021* |
| O5 | 0.32254 (15) | 0.85268 (13) | 0.06289 (9) | 0.0221 (2) |
| C6 | 0.7393 (2) | 0.52739 (18) | 0.45258 (12) | 0.0165 (3) |
| H6 | 0.6665 | 0.5236 | 0.5105 | 0.020* |
| C8 | 0.44594 (18) | 0.69113 (18) | 0.29240 (12) | 0.0148 (3) |
| C7 | 0.9329 (2) | 0.24146 (19) | 0.25186 (14) | 0.0224 (3) |
| H7A | 0.8954 | 0.2084 | 0.1667 | 0.034* |
| H7B | 0.8649 | 0.1479 | 0.2774 | 0.034* |
| H7C | 1.0653 | 0.2714 | 0.2730 | 0.034* |
| C9 | 0.39824 (19) | 0.52299 (18) | 0.22586 (12) | 0.0163 (3) |
| H9 | 0.4173 | 0.4479 | 0.2607 | 0.020* |
| C10 | 0.3204 (2) | 0.46833 (18) | 0.10448 (13) | 0.0173 (3) |
| C11 | 0.29768 (19) | 0.58182 (18) | 0.05261 (12) | 0.0172 (3) |
| H11 | 0.2472 | 0.5449 | −0.0287 | 0.021* |
| C12 | 0.3511 (2) | 0.75243 (19) | 0.12328 (13) | 0.0163 (3) |
| C13 | 0.42417 (19) | 0.80989 (18) | 0.24526 (12) | 0.0157 (3) |
| H13 | 0.4570 | 0.9227 | 0.2931 | 0.019* |
| C14 | 0.1783 (2) | 0.2341 (2) | −0.07898 (13) | 0.0261 (4) |
| H14A | 0.2629 | 0.2905 | −0.1225 | 0.039* |
| H14B | 0.0668 | 0.2557 | −0.0868 | 0.039* |
| H14C | 0.1451 | 0.1132 | −0.1106 | 0.039* |
| C15 | 0.3825 (2) | 1.0314 (2) | 0.12916 (14) | 0.0275 (4) |
| H15A | 0.3640 | 1.0896 | 0.0759 | 0.041* |
| H15B | 0.5134 | 1.0791 | 0.1661 | 0.041* |
| H15C | 0.3102 | 1.0449 | 0.1897 | 0.041* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.01689 (19) | 0.01626 (19) | 0.01268 (19) | 0.00745 (15) | 0.00219 (13) | 0.00373 (14) |
| O1 | 0.0201 (5) | 0.0157 (5) | 0.0223 (6) | 0.0064 (4) | 0.0022 (4) | 0.0074 (4) |
| C1 | 0.0143 (7) | 0.0157 (7) | 0.0124 (7) | 0.0067 (6) | −0.0007 (5) | 0.0026 (6) |
| C2 | 0.0148 (7) | 0.0159 (7) | 0.0139 (7) | 0.0036 (6) | 0.0006 (6) | 0.0058 (6) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O2 | 0.0265 (6) | 0.0261 (6) | 0.0124 (5) | 0.0139 (5) | 0.0019 (4) | 0.0024 (4) |
| O3 | 0.0157 (5) | 0.0206 (5) | 0.0119 (5) | 0.0081 (4) | 0.0040 (4) | 0.0056 (4) |
| C3 | 0.0144 (7) | 0.0214 (8) | 0.0142 (7) | 0.0069 (6) | 0.0037 (6) | 0.0057 (6) |
| C4 | 0.0142 (7) | 0.0172 (7) | 0.0160 (7) | 0.0065 (6) | −0.0008 (6) | 0.0033 (6) |
| O4 | 0.0343 (6) | 0.0172 (6) | 0.0176 (6) | 0.0134 (5) | 0.0002 (5) | 0.0020 (4) |
| C5 | 0.0160 (7) | 0.0167 (7) | 0.0189 (7) | 0.0048 (6) | 0.0014 (6) | 0.0086 (6) |
| O5 | 0.0329 (6) | 0.0195 (6) | 0.0188 (5) | 0.0137 (5) | 0.0041 (5) | 0.0097 (4) |
| C6 | 0.0158 (7) | 0.0202 (8) | 0.0139 (7) | 0.0067 (6) | 0.0040 (6) | 0.0069 (6) |
| C8 | 0.0120 (7) | 0.0207 (8) | 0.0121 (7) | 0.0067 (6) | 0.0036 (5) | 0.0056 (6) |
| C7 | 0.0242 (8) | 0.0205 (8) | 0.0237 (8) | 0.0106 (7) | 0.0069 (7) | 0.0066 (7) |
| C9 | 0.0166 (7) | 0.0190 (7) | 0.0185 (8) | 0.0102 (6) | 0.0049 (6) | 0.0097 (6) |
| C10 | 0.0174 (7) | 0.0162 (7) | 0.0187 (8) | 0.0090 (6) | 0.0048 (6) | 0.0033 (6) |
| C11 | 0.0176 (7) | 0.0213 (8) | 0.0129 (7) | 0.0089 (6) | 0.0027 (6) | 0.0047 (6) |
| C12 | 0.0156 (7) | 0.0199 (8) | 0.0188 (7) | 0.0097 (6) | 0.0068 (6) | 0.0103 (6) |
| C13 | 0.0150 (7) | 0.0147 (7) | 0.0180 (7) | 0.0068 (6) | 0.0060 (6) | 0.0047 (6) |
| C14 | 0.0329 (9) | 0.0219 (8) | 0.0185 (8) | 0.0128 (7) | −0.0013 (7) | −0.0006 (7) |
| C15 | 0.0440 (10) | 0.0207 (8) | 0.0242 (9) | 0.0174 (8) | 0.0080 (7) | 0.0112 (7) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| S1—O2 | 1.4244 (10) | C6—H6 | 0.9300 |
| S1—O1 | 1.4254 (10) | C8—C9 | 1.373 (2) |
| S1—O3 | 1.6101 (10) | C8—C13 | 1.3871 (19) |
| S1—C1 | 1.7556 (14) | C7—H7A | 0.9600 |
| S1—O1$^{i}$ | 3.2929 (10) | C7—H7B | 0.9600 |
| C1—C2 | 1.3885 (19) | C7—H7C | 0.9600 |
| C1—C6 | 1.3910 (19) | C9—C10 | 1.3931 (19) |
| C2—C3 | 1.3887 (19) | C9—H9 | 0.9300 |
| C2—H2 | 0.9300 | C10—C11 | 1.382 (2) |
| O3—C8 | 1.4171 (15) | C11—C12 | 1.396 (2) |
| C3—C4 | 1.395 (2) | C11—H11 | 0.9300 |
| C3—H3 | 0.9300 | C12—C13 | 1.3896 (19) |
| C4—C5 | 1.3947 (19) | C13—H13 | 0.9300 |
| C4—C7 | 1.5070 (19) | C14—H14A | 0.9600 |
| O4—C10 | 1.3633 (17) | C14—H14B | 0.9600 |
| O4—C14 | 1.4313 (17) | C14—H14C | 0.9600 |
| C5—C6 | 1.383 (2) | C15—H15A | 0.9600 |
| C5—H5 | 0.9300 | C15—H15B | 0.9600 |
| O5—C12 | 1.3623 (17) | C15—H15C | 0.9600 |
| O5—C15 | 1.4366 (18) | | |
| | | | |
| O2—S1—O1 | 120.88 (6) | C4—C7—H7A | 109.5 |
| O2—S1—O3 | 102.37 (6) | C4—C7—H7B | 109.5 |
| O1—S1—O3 | 108.43 (5) | H7A—C7—H7B | 109.5 |
| O2—S1—C1 | 110.89 (6) | C4—C7—H7C | 109.5 |
| O1—S1—C1 | 110.05 (6) | H7A—C7—H7C | 109.5 |
| O3—S1—C1 | 102.28 (6) | H7B—C7—H7C | 109.5 |
| O2—S1—O1$^{i}$ | 80.61 (5) | C8—C9—C10 | 117.91 (13) |

| | | | |
|---|---|---|---|
| O1—S1—O1$^{i}$ | 68.92 (5) | C8—C9—H9 | 121.0 |
| O3—S1—O1$^{i}$ | 176.85 (4) | C10—C9—H9 | 121.0 |
| C1—S1—O1$^{i}$ | 77.41 (5) | O4—C10—C11 | 124.24 (13) |
| C2—C1—C6 | 121.02 (13) | O4—C10—C9 | 115.06 (12) |
| C2—C1—S1 | 119.61 (11) | C11—C10—C9 | 120.70 (13) |
| C6—C1—S1 | 119.22 (11) | C10—C11—C12 | 119.46 (13) |
| C1—C2—C3 | 118.68 (13) | C10—C11—H11 | 120.3 |
| C1—C2—H2 | 120.7 | C12—C11—H11 | 120.3 |
| C3—C2—H2 | 120.7 | O5—C12—C13 | 124.31 (13) |
| C8—O3—S1 | 118.80 (8) | O5—C12—C11 | 114.44 (13) |
| C2—C3—C4 | 121.42 (13) | C13—C12—C11 | 121.24 (13) |
| C2—C3—H3 | 119.3 | C8—C13—C12 | 116.89 (13) |
| C4—C3—H3 | 119.3 | C8—C13—H13 | 121.6 |
| C5—C4—C3 | 118.48 (13) | C12—C13—H13 | 121.6 |
| C5—C4—C7 | 120.97 (13) | O4—C14—H14A | 109.5 |
| C3—C4—C7 | 120.55 (13) | O4—C14—H14B | 109.5 |
| C10—O4—C14 | 117.21 (11) | H14A—C14—H14B | 109.5 |
| C6—C5—C4 | 120.99 (13) | O4—C14—H14C | 109.5 |
| C6—C5—H5 | 119.5 | H14A—C14—H14C | 109.5 |
| C4—C5—H5 | 119.5 | H14B—C14—H14C | 109.5 |
| C12—O5—C15 | 117.31 (12) | O5—C15—H15A | 109.5 |
| C5—C6—C1 | 119.33 (13) | O5—C15—H15B | 109.5 |
| C5—C6—H6 | 120.3 | H15A—C15—H15B | 109.5 |
| C1—C6—H6 | 120.3 | O5—C15—H15C | 109.5 |
| C9—C8—C13 | 123.77 (13) | H15A—C15—H15C | 109.5 |
| C9—C8—O3 | 117.73 (12) | H15B—C15—H15C | 109.5 |
| C13—C8—O3 | 118.33 (12) | | |

| | | | |
|---|---|---|---|
| O2—S1—C1—C2 | −139.74 (11) | S1—C1—C6—C5 | 173.38 (11) |
| O1—S1—C1—C2 | −3.35 (13) | S1—O3—C8—C9 | 98.87 (13) |
| O3—S1—C1—C2 | 111.74 (11) | S1—O3—C8—C13 | −85.70 (13) |
| O1$^{i}$—S1—C1—C2 | −65.06 (11) | C13—C8—C9—C10 | −1.2 (2) |
| O2—S1—C1—C6 | 44.73 (13) | O3—C8—C9—C10 | 173.96 (11) |
| O1—S1—C1—C6 | −178.88 (11) | C14—O4—C10—C11 | −2.0 (2) |
| O3—S1—C1—C6 | −63.80 (12) | C14—O4—C10—C9 | 176.90 (13) |
| O1$^{i}$—S1—C1—C6 | 119.40 (11) | C8—C9—C10—O4 | −176.98 (12) |
| C6—C1—C2—C3 | 2.6 (2) | C8—C9—C10—C11 | 1.9 (2) |
| S1—C1—C2—C3 | −172.83 (10) | O4—C10—C11—C12 | 177.91 (12) |
| O2—S1—O3—C8 | 177.23 (9) | C9—C10—C11—C12 | −0.9 (2) |
| O1—S1—O3—C8 | 48.40 (11) | C15—O5—C12—C13 | 3.8 (2) |
| C1—S1—O3—C8 | −67.86 (10) | C15—O5—C12—C11 | −177.20 (12) |
| C1—C2—C3—C4 | −0.7 (2) | C10—C11—C12—O5 | 179.96 (12) |
| C2—C3—C4—C5 | −1.7 (2) | C10—C11—C12—C13 | −1.0 (2) |
| C2—C3—C4—C7 | 178.63 (13) | C9—C8—C13—C12 | −0.6 (2) |
| C3—C4—C5—C6 | 2.3 (2) | O3—C8—C13—C12 | −175.70 (11) |
| C7—C4—C5—C6 | −178.07 (13) | O5—C12—C13—C8 | −179.37 (13) |

| | | | |
|---|---|---|---|
| C4—C5—C6—C1 | −0.4 (2) | C11—C12—C13—C8 | 1.7 (2) |
| C2—C1—C6—C5 | −2.1 (2) | | |

Symmetry code: (i) −*x*+2, −*y*+2, −*z*+1.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C15—H15*A*···O4$^{ii}$ | 0.96 | 2.35 | 3.2051 (18) | 147 |
| C15—H15*C*···O2$^{iii}$ | 0.96 | 2.51 | 3.4063 (19) | 155 |

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