# research communications

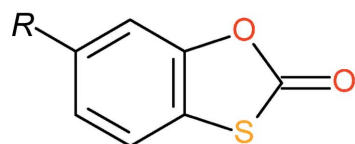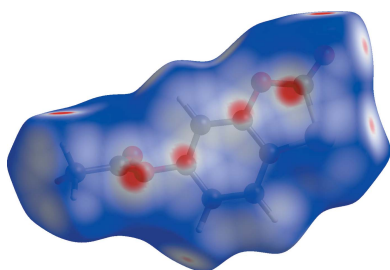# Crystal structures and Hirshfeld surfaces of two 1,3-benzoxathiol-2-one derivatives

**Eliza de L. Chazin,[a] Paola de S. Sanches,[a] Thatyana R. A. Vasconcelos,[a] Claudia R. B. Gomes,[b] James L. Wardell[b,c] and William T. A. Harrison[c]\***

[a]Universidade Federal Fluminense, Instituto de Química, Programa de Pós-Graduação em Química, Rua Outeiro de São João Batista s/no, Centro, Niterói, 24020-141, RJ, Brazil, [b]Instituto de Tecnologia em Fármacos − Farmanguinhos, Fiocruz. R. Sizenando, Nabuco, 100, Manguinhos, 21041-250, Rio de Janeiro, RJ, Brazil, and [c]Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland. *Correspondence e-mail: w.harrison@abdn.ac.uk

The crystal structures of 6-methoxy-1,3-benzoxathiol-2-one, $C_9H_8O_3S$, (I), and 2-oxo-1,3-benzoxathiol-6-yl acetate, $C_9H_6O_4S$, (II), are described. Compound (I) is almost planar (r.m.s. deviation for the non-H atoms = 0.011 Å), whereas (II) shows a substantial twist between the fused-ring system and the acetate substituent [dihedral angle = 74.42 (3)°]. For both structures, the bond distances in the heterocyclic ring suggest that little if any conjugation occurs. In the crystal of (I), C—H···O hydrogen bonds link the molecules into [$1\bar{1}1$] chains incorporating alternating $R_2^2(8)$ and $R_2^2(12)$ inversion dimers. The extended structure of (II) features $C(7)$ [201] chains linked by C—H···O hydrogen bonds, with further C—H···O bonds and weak $\pi$–$\pi$ stacking interactions connecting the chains into a three-dimensional network. Hirshfeld fingerprint analyses for (I) and (II) are presented and discussed.

## 1. Chemical context

1,3-Benzoxathiol-2-one and its derivatives have various biological properties including antibacterial, antimycotic, antioxidant, antitumor and anti-inflammatory activities (Vellasco Júnior *et al.*, 2011; Chazin *et al.*, 2015). They also act as inhibitors of carbonic anhydrase II (Barrese *et al.*, 2008) and monoamine oxidase (Mostert *et al.*, 2016). The first synthesized 1,3-benzoxathiol-2-one, 6-hydroxy-1,3-benzoxathiol-2-one $C_7H_4O_3S$, also known as tioxolone or thioxolone, has been used for many years in the treatment of acne and other skin diseases (*e.g.* psoriasis) (Berg & Fiedler, 1959).

A recent study reported the syntheses and antifungal activities of some derivatives of tioxolone (Terra *et al.*, 2018). In the present article we report the crystal structures and Hirshfeld surface analyses of two compounds with different substituents at the 6-position of the ring system obtained in that study, *viz.* 6-methoxy-1,3-benzoxathiol-2-one, $C_9H_8O_3S$, (I), and 2-oxo-1,3-benzoxathiol-6-yl acetate, $C_9H_8O_3S$, (II).
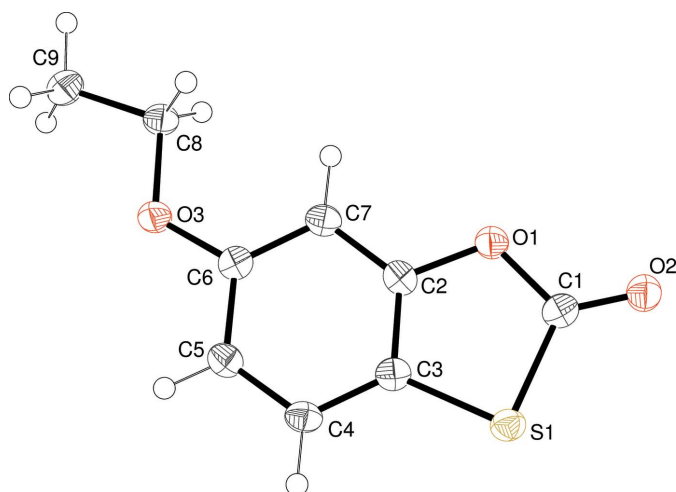


(I)  *R* = EtO

(II)  *R* = AcO

**Figure 1**
The molecular structure of (I), showing 50% displacement ellipsoids.

## 2. Structural commentary

Compound (I) crystallizes in space group $P\bar{1}$ with one molecule in the asymmetric unit (Fig. 1), which is almost planar (r.m.s. deviation for the non-hydrogen atoms = 0.011 Å): the ethoxy side chain adopts an extended conformation [C6—O3—C8—C9 = 179.82 (12)°]. Within the oxathiol-2-one ring system, the C1—O1, C1=O2 and C1—S1 bond lengths are 1.3732 (18), 1.1905 (19) and 1.7766 (16)Å, respectively, and the O1—C1—S1 and C1—S1—C3 bond angles are 111.07 (11) and 90.62 (7)°, respectively. These distance data suggest that there is little if any conjugation (*i.e.* partial double-bond character) involving the C1—O1 and C1—S1 bonds with the C1=O2 group.

A single molecule of compound (II) makes up the asymmetric unit in space group $P2_1/c$ (Fig. 2). The ring system is almost planar (r.m.s. deviation for C1–C7/O1/S1 = 0.032 Å) but there is a substantial twist about the C6—O3 bond, as indicated by the dihedral angle between the ring system and the acetate group of 74.42 (3)°. Key geometrical data for the heterocyclic ring are C1—O1 = 1.3864 (15), C1=O2 = 1.1936 (15), C1—S1 = 1.7709 (13) Å, O1—C1—S1 = 111.57 (8)
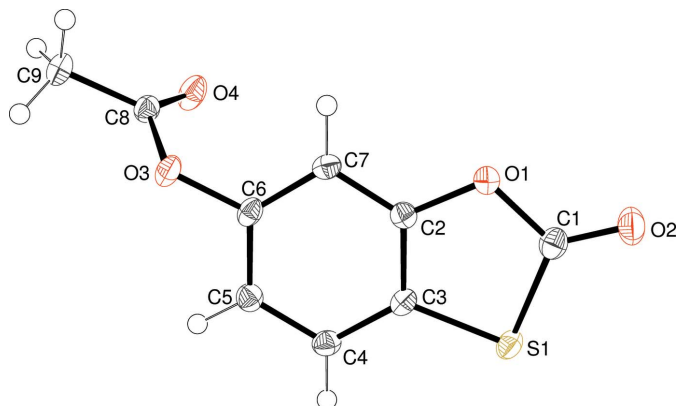
**Table 1**
Hydrogen-bond geometry (Å, °) for (I).

| $D—H\cdots A$ | $D—H$ | $H\cdots A$ | $D\cdots A$ | $D—H\cdots A$ |
|---|---|---|---|---|
| C5—H5$\cdots$O3$^i$ | 0.95 | 2.48 | 3.432 (2) | 175 |
| C7—H7$\cdots$O2$^{ii}$ | 0.95 | 2.66 | 3.5983 (19) | 170 |

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

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

| $D—H\cdots A$ | $D—H$ | $H\cdots A$ | $D\cdots A$ | $D—H\cdots A$ |
|---|---|---|---|---|
| C4—H4$\cdots$O4$^i$ | 0.95 | 2.35 | 3.2606 (15) | 159 |
| C9—H9$C\cdots$O2$^{ii}$ | 0.98 | 2.50 | 3.4030 (16) | 153 |

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

and C1—S1—C3 = 90.43 (6)°. These data are similar to the equivalent values for (I) and again indicate a lack of significant electronic delocalization within the oxathiol-2-one ring system.

## 3. Supramolecular features

In the crystal of (I), the molecules are linked by C—H$\cdots$O hydrogen bonds (Table 1). The C5—H5$\cdots$O3$^i$ [symmetry code: (i) $-x, 1-y, -z$] link generates inversion dimers featuring $R_2^2(8)$ loops. Based on its length, the C7—H7$\cdots$O2$^{ii}$ [symmetry code: (ii) $1-x, -y, 1-z$] bond is much weaker, but if it is considered significant, it generates a second inversion dimer [with an $R_2^2(12)$ graph-set symbol], which links the dimers into [1$\bar{1}$1] chains (Fig. 3). No C—H$\cdots\pi$ interactions could be identified in the crystal of (I) and any aromatic $\pi$–$\pi$ stacking must be extremely weak, as the shortest centroid–centroid separation is 3.9149 (10) Å.

In the crystal of (II), C4—H4$\cdots$O4$^i$ [symmetry code: (i) $x-1, \frac{1}{2}-y, z-\frac{1}{2}$] hydrogen bonds (Table 2) link the mol-



**Figure 2**
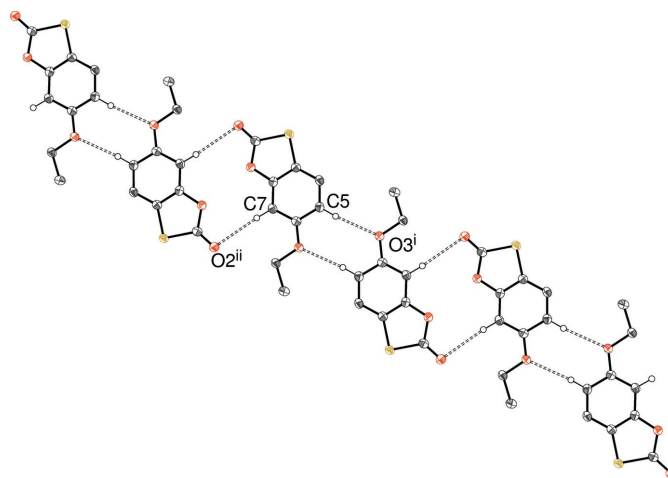The molecular structure of (II), showing 50% displacement ellipsoids.



**Figure 3**
Fragment of a [1$\bar{1}$1] hydrogen-bonded chain in (I); all hydrogen atoms except H5 and H7 have been omitted for clarity. Symmetry codes as in Table 1.
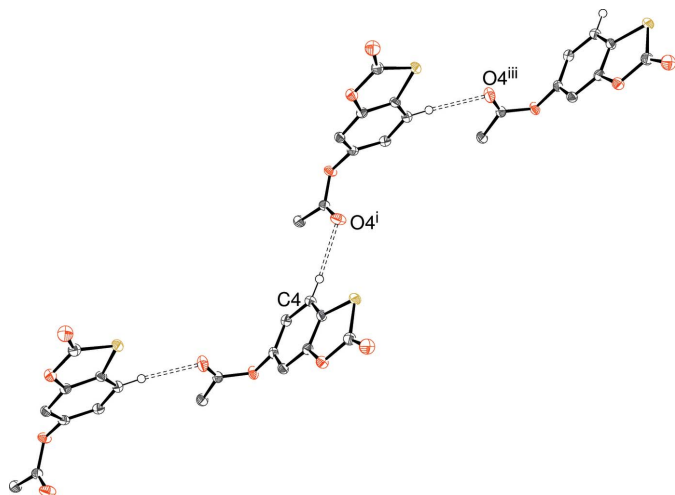
**Figure 4**
Fragment of a [201] hydrogen-bonded chain in (II); all hydrogen atoms except H4 omitted for clarity. Symmetry codes as in Table 2; additionally (iii) $x - 2, y, z - 1$.

ecules into $C(7)$ chains propagating in [201], with adjacent molecules in the chain related by $c$-glide symmetry (plus translation) (Fig. 4). The C9—H9$C$···O2$^{ii}$ [symmetry code: (ii) $1 - x, -y, 1 - z$] bonds arising from the methyl group generate inversion dimers [$R_2^2(16)$ loops], which connect the chains into a three-dimensional network. There are no C—H···$\pi$ bonds in the crystal of (II) but the packing is consolidated by weak aromatic $\pi$–$\pi$ stacking between inversion-related C2–C7 benzene rings with a centroid–centroid separation of 3.7220 (8) Å.



**Figure 6**
Hirshfeld fingerprint plot for (II)

## 4. Hirshfeld analyses

Hirshfeld surface fingerprint plots for (I) (Fig. 5), (II) (Fig. 6) and tioxolone (refcode: EVOQEL), which features classical O—H···O hydrogen bonds (Byres & Cox, 2004) (Fig. 7) were calculated with *CrystalExplorer17* (Turner *et al.*, 2017). The plot for EVOQEL has very pronounced 'wingtip' features that



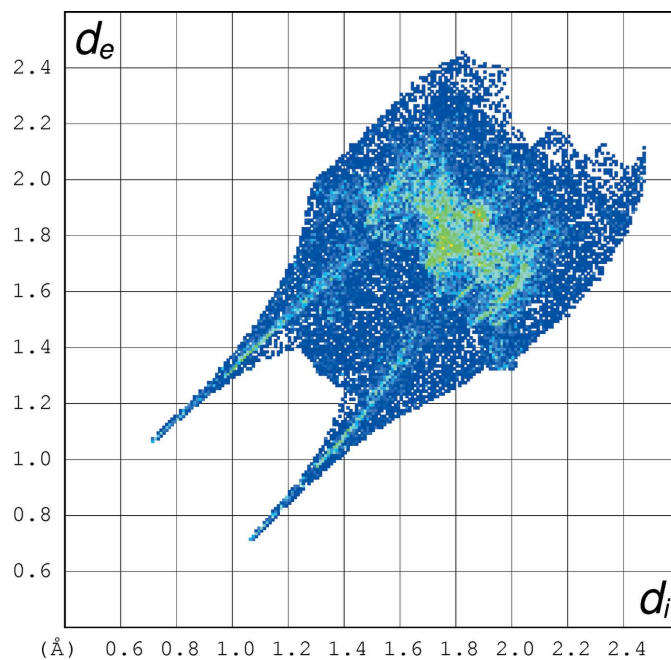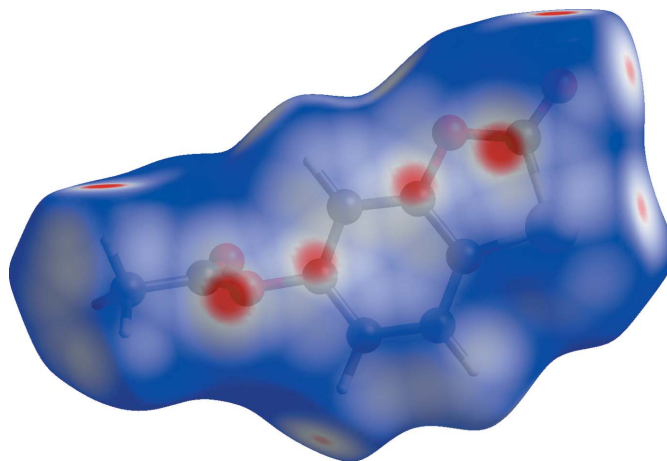**Figure 5**
Hirshfeld fingerprint plot for (I)



**Figure 7**
Hirshfeld fingerprint plot for tioxolone [atomic coordinates from Byres & Cox (2004)].

**Table 3**
Hirshfeld contact interactions (%).

| Contact type | (I) | (II) | EVOQEL |
|---|---|---|---|
| H⋯H | 28.7 | 14.8 | 13.5 |
| O⋯H/H⋯O | 30.1 | 39.5 | 36.0 |
| C⋯H/H⋯C | 11.3 | 13.4 | 8.6 |
| S⋯H/H⋯S | 11.1 | 10.8 | 8.8 |
| C⋯C | 5.9 | 4.4 | 10.4 |
| S⋯O/O⋯S | 1.5 | 7.0 | 10.1 |

correspond to the short, classical O—H⋯O hydrogen bond found in this structure (compare: McKinnon *et al.*, 2007). In (I) and (II), the wingtips associated with the longer and presumably weaker C—H⋯O bonds are far less pronounced.

When the fingerprint plots are decomposed into the separate types of contacts (McKinnon *et al.*, 2007), some interesting differences arise (Table 3): as a percentage of surface interactions, H⋯H contacts (*i.e.* van der Waals interactions) are far more prominent in (I) than in (II), which is comparable with EVOQEL, whereas C⋯H/H⋯C contacts are similar for the three structures. The O⋯H/H⋯O contacts are the most important contributors in all three structures, and in (II) they actually contribute a higher percentage to the surface than in EVOQEL, despite the fact that EVOQEL features both O—H⋯O and C—H⋯O hydrogen bonds and only one of its hydrogen atoms is not involved in such bonds (Byres & Cox, 2004). The C⋯C contacts (associated with aromatic π–π stacking) contribute a small percentage in (I) and (II) and about twice the amount in EVOQEL where the shortest



**Figure 8**
Hirshfeld surface plot mapped over $d_{norm}$ for (II) showing red spots associated with short C⋯C and C⋯O contacts: the slightly smaller spots refer to the former.

centroid–centroid separation is 3.508 (2) Å. Despite the small percentage for (II), the Hirshfeld surface (Fig. 8) clearly shows red spots associated with these contacts. The S⋯H/H⋯S contacts are similar in the three structures, and not insignificant at ∼10% of the surfaces, but they can hardly represent directional C—H⋯S hydrogen bonds, as the shortest H⋯S separations (3.21, 3.11 and 3.28 Å in (I), (II) and EVOQEL, respectively) are much longer than the van der Waals contact distance (Bondi, 1964) of 3.00 Å for H and S. Finally, S⋯O/

**Table 4**
Experimental details.

| | (I) | (II) |
|---|---|---|
| Crystal data | | |
| Chemical formula | $C_9H_8O_3S$ | $C_9H_6O_4S$ |
| $M_r$ | 196.21 | 210.20 |
| Crystal system, space group | Triclinic, $P\bar{1}$ | Monoclinic, $P2_1/c$ |
| Temperature (K) | 100 | 100 |
| $a, b, c$ (Å) | 3.9149 (6), 10.3237 (12), 11.7003 (14) | 5.6232 (5), 14.5650 (14), 10.8572 (11) |
| $\alpha, \beta, \gamma$ (°) | 66.526 (6), 81.110 (9), 84.349 (9) | 90, 96.045 (2), 90 |
| $V$ (Å$^3$) | 428.18 (10) | 884.28 (15) |
| $Z$ | 2 | 4 |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.35 | 0.35 |
| Crystal size (mm) | $0.17 \times 0.17 \times 0.03$ | $0.26 \times 0.11 \times 0.08$ |
| | | |
| Data collection | | |
| Diffractometer | Rigaku Saturn CCD | Rigaku Saturn CCD |
| Absorption correction | Multi-scan (*FS_ABSCOR*; Rigaku, 2013) | Multi-scan (*FS_ABSCOR*; Rigaku, 2013) |
| $T_{min}, T_{max}$ | 0.714, 1.000 | 0.829, 1.000 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 5189, 1674, 1540 | 11487, 2028, 1903 |
| $R_{int}$ | 0.040 | 0.036 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.617 | 0.650 |
| | | |
| Refinement | | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.034, 0.094, 1.04 | 0.028, 0.081, 1.10 |
| No. of reflections | 1674 | 2028 |
| No. of parameters | 119 | 128 |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained |
| $\Delta\rho_{max}, \Delta\rho_{min}$ (e Å$^{-3}$) | 0.52, −0.20 | 0.33, −0.21 |

Computer programs: *CrystalClear* (Rigaku, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

# research communications

O···S contacts have very different contributions in the three structures: negligible in (I), but clearly present in (II) and EVOQEL. This seems to correlate with the shortest S···O contact distances of 3.623 (2), 3.2742 (10) and 3.341 (2) Å for (I), (II) and EVOQEL, respectively: the distance in (II) is actually slightly shorter than the van der Waals contact distance of 3.32Å for sulfur and oxygen,

## 5. Database survey

A survey of of the Cambridge Structural Database (Groom *et al.*, 2016: updated to September 2017) for the benzoxathiol-2-one fused ring system (any substituents) yielded just three matches, *viz.* 6-hydroxy-1,3-benzoxathiol-2-one (refcode: EVOQEL; Byres & Cox, 2004); *N*-(4,7-dimethyl-2-oxo-benzo[1,3]oxathiol-5-yl)-4-benzenesulfonamide (NAJQOG; Avdeenko *et al.*, 2009); 7-phenyl-1,3-benzoxathiol-2-one (JOSGUV; Zhao *et al.*, 2014). To this list may be added the structure of 6-methoxy-5-nitrobenzo[*d*][1,3]oxathiol-2-one (CCDC deposition number 1404755) as recently reported by Terra *et al.* (2017).

## 6. Synthesis and crystallization

Compounds (I) and (II) were prepared as described previously (Terra *et al.*, 2018) and recrystallized from methanol solution as colourless plates of (I) and colourless blocks of (II).

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The hydrogen atoms were geometrically placed (C—H = 0.95–0.99 Å) and refined as riding atoms. The constraint $U_{iso}(H) = 1.2U_{eq}$(carrier) or $1.5U_{eq}$(methyl carrier) was applied in all cases. The methyl groups were allowed to rotate, but not to tip, to best fit the electron density.

## References

Avdeenko, A. P., Pirozhenko, V. V., Konovalov, S. A., Roman'kov, D. A., Palamarchuk, G. V. & Shishkin, O. V. (2009). *Russ. J. Org. Chem.* **45**, 408–416.

Barrese, A. A. III, Genis, C., Fisher, S. Z., Orwenyo, J. N., Kumara, M. T., Dutta, S. K., Phillips, E., Kiddle, J. J., Tu, C., Silverman, D. N., Govindasamy, L., Agbandje-McKenna, M., McKenna, R. & Tripp, B. C. (2008). *Biochemistry*, **47**, 3174–3184.

Berg, A. H. & Fiedler, H. (1959). US Patent 2,886,488.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Byres, M. & Cox, P. J. (2004). *Acta Cryst.* C**60**, o395–o396.

Chazin, E. L., Sanches, P. S., Lindgren, E. B., Vellasco Júnior, W. T., Pinto, L. C., Burbano, R. M. R., Yoneda, J. D., Leal, K. Z., Gomes, C. R. B., Wardell, J. L., Wardell, S. M. S. V., Montenegro, R. C. & Vasconcelos, T. R. A. (2015). *Molecules*, **20**, 1968–1983.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* 3814–3816.

Mostert, S., Petzer, A. & Petzer, J. P. (2016). *Bioorg. Med. Chem. Lett.* **26**, 1200–1204.

Rigaku (2013). *PS_ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Rigaku (2014). *CrysAlis PRO*. Rigaku Corporation, Tokyo, Japan.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Terra, L., Chazin, E. de L., Sanches, P. de S., Saito, M., de Souza, M. V. N., Gomes, C. R. B., Wardell, J. L., Wardell, S. M. S. V., Sathler, P. C., Silva, G. C. C., Lione, V. O., Kalil1, M., Joffily, A., Castro1, H. C. & Vasconcelos, T. R. A. (2018). *Med. Chem.* (Bentham) **14**, 1–7.

Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17. University of Western Australia, Nedlands, Western Australia*; http://hirshfeldsurface.net.

Vellasco, W. T., Gomes, C. F. B. & Vasconcelos, T. R. A. (2011). *Mini-Rev. Org. Chem.* **8**, 103–109.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Zhao, Y., Xie, Y., Xia, C. & Huang, H. (2014). *Adv. Synth. Catal.* **356**, 2471–2476.

## Crystal structures and Hirshfeld surfaces of two 1,3-benzoxathiol-2-one derivatives

**Eliza de L. Chazin, Paola de S. Sanches, Thatyana R. A. Vasconcelos, Claudia R. B. Gomes, James L. Wardell and William T. A. Harrison**

**Computing details**

For both structures, data collection: *CrystalClear* (Rigaku, 2014); cell refinement: *CrystalClear* (Rigaku, 2014); data reduction: *CrystalClear* (Rigaku, 2014); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

**6-Methoxy-1,3-benzoxathiol-2-one (I)**

*Crystal data*

| | |
|---|---|
| $C_9H_8O_3S$ | $Z = 2$ |
| $M_r = 196.21$ | $F(000) = 204$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.522$ Mg m$^{-3}$ |
| $a = 3.9149$ (6) Å | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $b = 10.3237$ (12) Å | Cell parameters from 1390 reflections |
| $c = 11.7003$ (14) Å | $\theta = 1.9–27.5°$ |
| $\alpha = 66.526$ (6)° | $\mu = 0.35$ mm$^{-1}$ |
| $\beta = 81.110$ (9)° | $T = 100$ K |
| $\gamma = 84.349$ (9)° | Plate, colourless |
| $V = 428.18$ (10) Å$^3$ | $0.17 \times 0.17 \times 0.03$ mm |

*Data collection*

| | |
|---|---|
| Rigaku Saturn CCD diffractometer | 1674 independent reflections |
| $\omega$ scans | 1540 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (*FS_ABSCOR*; Rigaku, 2013) | $R_{int} = 0.040$ |
| | $\theta_{max} = 26.0°$, $\theta_{min} = 1.9°$ |
| $T_{min} = 0.714$, $T_{max} = 1.000$ | $h = -4 \rightarrow 4$ |
| 5189 measured reflections | $k = -12 \rightarrow 12$ |
| | $l = -14 \rightarrow 14$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.034$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.094$ | |
| $S = 1.04$ | H-atom parameters constrained |
| 1674 reflections | $w = 1/[\sigma^2(F_o^2) + (0.0607P)^2 + 0.0766P]$ |
| 119 parameters | where $P = (F_o^2 + 2F_c^2)/3$ |
| 0 restraints | $(\Delta/\sigma)_{max} < 0.001$ |

$\Delta\rho_{max} = 0.52$ e Å$^{-3}$                                   $\Delta\rho_{min} = -0.20$ 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.

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

|  | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.0898 (4) | 0.15148 (16) | 0.62375 (14) | 0.0238 (3) |
| C2 | 0.1487 (4) | 0.21490 (16) | 0.40934 (14) | 0.0221 (3) |
| C3 | −0.0473 (4) | 0.33140 (16) | 0.41485 (14) | 0.0221 (3) |
| C4 | −0.1375 (4) | 0.43830 (16) | 0.30435 (15) | 0.0238 (3) |
| H4 | −0.2733 | 0.5190 | 0.3064 | 0.029* |
| C5 | −0.0252 (4) | 0.42431 (16) | 0.19181 (15) | 0.0245 (3) |
| H5 | −0.0854 | 0.4961 | 0.1157 | 0.029* |
| C6 | 0.1770 (4) | 0.30535 (16) | 0.18846 (14) | 0.0223 (3) |
| C7 | 0.2673 (4) | 0.19732 (16) | 0.29857 (14) | 0.0230 (3) |
| H7 | 0.4028 | 0.1161 | 0.2975 | 0.028* |
| C8 | 0.4817 (4) | 0.18554 (16) | 0.06172 (15) | 0.0240 (3) |
| H8A | 0.3576 | 0.0970 | 0.1095 | 0.029* |
| H8B | 0.7026 | 0.1773 | 0.0959 | 0.029* |
| C9 | 0.5494 (4) | 0.21106 (18) | −0.07580 (15) | 0.0283 (4) |
| H9A | 0.6977 | 0.1336 | −0.0867 | 0.042* |
| H9B | 0.6651 | 0.3005 | −0.1224 | 0.042* |
| H9C | 0.3294 | 0.2157 | −0.1077 | 0.042* |
| O1 | 0.2250 (3) | 0.11453 (11) | 0.52491 (10) | 0.0244 (3) |
| O2 | 0.1322 (3) | 0.07887 (11) | 0.72936 (10) | 0.0282 (3) |
| O3 | 0.2727 (3) | 0.30495 (11) | 0.07165 (10) | 0.0251 (3) |
| S1 | −0.14241 (9) | 0.31705 (4) | 0.57093 (3) | 0.02391 (16) |

*Atomic displacement parameters (Å$^2$)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0236 (8) | 0.0232 (7) | 0.0273 (8) | −0.0042 (6) | −0.0017 (6) | −0.0124 (6) |
| C2 | 0.0220 (7) | 0.0193 (7) | 0.0254 (8) | −0.0039 (6) | −0.0056 (6) | −0.0076 (6) |
| C3 | 0.0218 (7) | 0.0212 (7) | 0.0264 (8) | −0.0034 (6) | −0.0037 (6) | −0.0117 (6) |
| C4 | 0.0228 (7) | 0.0213 (8) | 0.0301 (8) | 0.0010 (6) | −0.0056 (6) | −0.0125 (6) |
| C5 | 0.0257 (8) | 0.0216 (7) | 0.0273 (8) | −0.0009 (6) | −0.0069 (6) | −0.0096 (6) |
| C6 | 0.0214 (7) | 0.0222 (8) | 0.0258 (7) | −0.0045 (6) | −0.0026 (6) | −0.0112 (6) |
| C7 | 0.0223 (7) | 0.0201 (7) | 0.0286 (8) | −0.0013 (6) | −0.0042 (6) | −0.0110 (6) |
| C8 | 0.0245 (7) | 0.0216 (7) | 0.0280 (8) | 0.0002 (6) | −0.0040 (6) | −0.0120 (6) |
| C9 | 0.0289 (8) | 0.0302 (8) | 0.0288 (8) | −0.0026 (7) | −0.0007 (6) | −0.0153 (7) |
| O1 | 0.0290 (6) | 0.0210 (5) | 0.0239 (6) | 0.0013 (4) | −0.0044 (4) | −0.0096 (4) |
| O2 | 0.0335 (6) | 0.0260 (6) | 0.0246 (6) | −0.0001 (5) | −0.0037 (5) | −0.0095 (5) |
| O3 | 0.0300 (6) | 0.0221 (6) | 0.0247 (6) | 0.0026 (4) | −0.0044 (4) | −0.0112 (5) |
| S1 | 0.0252 (2) | 0.0234 (2) | 0.0259 (2) | 0.00092 (16) | −0.00403 (16) | −0.01255 (17) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—O2 | 1.1905 (19) | C5—H5 | 0.9500 |
| C1—O1 | 1.3732 (18) | C6—O3 | 1.3617 (18) |
| C1—S1 | 1.7766 (16) | C6—C7 | 1.395 (2) |
| C2—C3 | 1.380 (2) | C7—H7 | 0.9500 |
| C2—C7 | 1.383 (2) | C8—O3 | 1.4452 (18) |
| C2—O1 | 1.3926 (18) | C8—C9 | 1.508 (2) |
| C3—C4 | 1.394 (2) | C8—H8A | 0.9900 |
| C3—S1 | 1.7552 (16) | C8—H8B | 0.9900 |
| C4—C5 | 1.381 (2) | C9—H9A | 0.9800 |
| C4—H4 | 0.9500 | C9—H9B | 0.9800 |
| C5—C6 | 1.405 (2) | C9—H9C | 0.9800 |
| | | | |
| O2—C1—O1 | 122.22 (14) | C2—C7—C6 | 116.34 (14) |
| O2—C1—S1 | 126.71 (12) | C2—C7—H7 | 121.8 |
| O1—C1—S1 | 111.07 (11) | C6—C7—H7 | 121.8 |
| C3—C2—C7 | 123.62 (14) | O3—C8—C9 | 107.02 (12) |
| C3—C2—O1 | 114.96 (13) | O3—C8—H8A | 110.3 |
| C7—C2—O1 | 121.41 (13) | C9—C8—H8A | 110.3 |
| C2—C3—C4 | 119.56 (14) | O3—C8—H8B | 110.3 |
| C2—C3—S1 | 110.37 (11) | C9—C8—H8B | 110.3 |
| C4—C3—S1 | 130.07 (12) | H8A—C8—H8B | 108.6 |
| C5—C4—C3 | 118.55 (14) | C8—C9—H9A | 109.5 |
| C5—C4—H4 | 120.7 | C8—C9—H9B | 109.5 |
| C3—C4—H4 | 120.7 | H9A—C9—H9B | 109.5 |
| C4—C5—C6 | 120.85 (14) | C8—C9—H9C | 109.5 |
| C4—C5—H5 | 119.6 | H9A—C9—H9C | 109.5 |
| C6—C5—H5 | 119.6 | H9B—C9—H9C | 109.5 |
| O3—C6—C7 | 123.91 (13) | C1—O1—C2 | 112.97 (12) |
| O3—C6—C5 | 115.01 (13) | C6—O3—C8 | 117.75 (12) |
| C7—C6—C5 | 121.08 (14) | C3—S1—C1 | 90.62 (7) |
| | | | |
| C7—C2—C3—C4 | 0.7 (2) | C5—C6—C7—C2 | −0.4 (2) |
| O1—C2—C3—C4 | 179.88 (13) | O2—C1—O1—C2 | −179.25 (14) |
| C7—C2—C3—S1 | −179.08 (11) | S1—C1—O1—C2 | 0.23 (15) |
| O1—C2—C3—S1 | 0.14 (16) | C3—C2—O1—C1 | −0.24 (18) |
| C2—C3—C4—C5 | −0.3 (2) | C7—C2—O1—C1 | 178.99 (12) |
| S1—C3—C4—C5 | 179.33 (12) | C7—C6—O3—C8 | −0.3 (2) |
| C3—C4—C5—C6 | −0.3 (2) | C5—C6—O3—C8 | 179.90 (13) |
| C4—C5—C6—O3 | −179.56 (13) | C9—C8—O3—C6 | 179.82 (12) |
| C4—C5—C6—C7 | 0.6 (2) | C2—C3—S1—C1 | −0.01 (11) |
| C3—C2—C7—C6 | −0.3 (2) | C4—C3—S1—C1 | −179.71 (15) |
| O1—C2—C7—C6 | −179.47 (13) | O2—C1—S1—C3 | 179.32 (15) |
| O3—C6—C7—C2 | 179.87 (13) | O1—C1—S1—C3 | −0.13 (11) |

*Hydrogen-bond geometry (Å, º)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| C5—H5···O3$^i$ | 0.95 | 2.48 | 3.432 (2) | 175 |
| C7—H7···O2$^{ii}$ | 0.95 | 2.66 | 3.5983 (19) | 170 |

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

**2-Oxo-1,3-benzoxathiol-6-yl acetate (II)**

*Crystal data*

| | |
|---|---|
| $C_9H_6O_4S$ | $F(000) = 432$ |
| $M_r = 210.20$ | $D_x = 1.579$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 5.6232$ (5) Å | Cell parameters from 3355 reflections |
| $b = 14.5650$ (14) Å | $\theta = 2.3–27.5°$ |
| $c = 10.8572$ (11) Å | $\mu = 0.35$ mm$^{-1}$ |
| $\beta = 96.045$ (2)° | $T = 100$ K |
| $V = 884.28$ (15) Å$^3$ | Block, colourless |
| $Z = 4$ | $0.26 \times 0.11 \times 0.08$ mm |

*Data collection*

| | |
|---|---|
| Rigaku Saturn CCD diffractometer | 2028 independent reflections |
| $\omega$ scans | 1903 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (*FS_ABSCOR*; Rigaku, 2013) | $R_{int} = 0.036$ |
| $T_{min} = 0.829$, $T_{max} = 1.000$ | $\theta_{max} = 27.5°$, $\theta_{min} = 2.4°$ |
| 11487 measured reflections | $h = -7 \rightarrow 7$ |
| | $k = -18 \rightarrow 18$ |
| | $l = -14 \rightarrow 14$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.028$ | H-atom parameters constrained |
| $wR(F^2) = 0.081$ | $w = 1/[\sigma^2(F_o^2) + (0.0423P)^2 + 0.328P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.10$ | |
| 2028 reflections | $(\Delta/\sigma)_{max} = 0.001$ |
| 128 parameters | $\Delta\rho_{max} = 0.33$ e Å$^{-3}$ |
| 0 restraints | $\Delta\rho_{min} = -0.21$ 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.

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

| | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.1830 (2) | 0.03032 (8) | 0.18546 (11) | 0.0210 (2) |
| C2 | 0.1514 (2) | 0.07946 (8) | 0.38446 (11) | 0.0167 (2) |
| C3 | −0.0602 (2) | 0.11624 (8) | 0.32717 (11) | 0.0174 (2) |

| | | | |
|---|---|---|---|
| C4 | −0.2186 (2) | 0.16130 (8) | 0.39666 (11) | 0.0194 (2) |
| H4 | −0.3625 | 0.1872 | 0.3580 | 0.023* |
| C5 | −0.1609 (2) | 0.16746 (8) | 0.52441 (11) | 0.0191 (2) |
| H5 | −0.2657 | 0.1979 | 0.5742 | 0.023* |
| C6 | 0.0505 (2) | 0.12894 (8) | 0.57848 (10) | 0.0175 (2) |
| C7 | 0.2139 (2) | 0.08489 (8) | 0.51080 (11) | 0.0175 (2) |
| H7 | 0.3595 | 0.0601 | 0.5491 | 0.021* |
| C8 | 0.2608 (2) | 0.18164 (8) | 0.76657 (11) | 0.0183 (2) |
| C9 | 0.2792 (2) | 0.16577 (9) | 0.90343 (11) | 0.0222 (3) |
| H9A | 0.1197 | 0.1535 | 0.9284 | 0.033* |
| H9B | 0.3465 | 0.2204 | 0.9467 | 0.033* |
| H9C | 0.3833 | 0.1129 | 0.9248 | 0.033* |
| O1 | 0.29007 (15) | 0.03350 (6) | 0.30638 (8) | 0.01950 (19) |
| O2 | 0.27313 (17) | −0.00958 (7) | 0.10631 (8) | 0.0282 (2) |
| O3 | 0.08651 (15) | 0.12684 (6) | 0.70829 (7) | 0.0207 (2) |
| O4 | 0.37694 (17) | 0.23332 (7) | 0.71088 (8) | 0.0275 (2) |
| S1 | −0.09135 (5) | 0.09103 (2) | 0.16863 (3) | 0.02017 (11) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0246 (6) | 0.0209 (6) | 0.0177 (6) | −0.0017 (5) | 0.0030 (4) | 0.0015 (4) |
| C2 | 0.0164 (5) | 0.0158 (5) | 0.0181 (6) | −0.0015 (4) | 0.0026 (4) | −0.0003 (4) |
| C3 | 0.0194 (5) | 0.0177 (5) | 0.0148 (5) | −0.0023 (4) | −0.0004 (4) | 0.0001 (4) |
| C4 | 0.0180 (5) | 0.0194 (6) | 0.0202 (6) | 0.0019 (4) | −0.0009 (4) | 0.0003 (4) |
| C5 | 0.0194 (5) | 0.0185 (6) | 0.0196 (6) | −0.0010 (4) | 0.0028 (4) | −0.0020 (4) |
| C6 | 0.0208 (5) | 0.0178 (5) | 0.0137 (5) | −0.0055 (4) | 0.0007 (4) | 0.0004 (4) |
| C7 | 0.0158 (5) | 0.0182 (6) | 0.0178 (6) | −0.0017 (4) | −0.0008 (4) | 0.0019 (4) |
| C8 | 0.0201 (5) | 0.0182 (5) | 0.0163 (5) | 0.0003 (4) | 0.0005 (4) | −0.0020 (4) |
| C9 | 0.0287 (6) | 0.0235 (6) | 0.0140 (5) | −0.0009 (5) | 0.0007 (4) | −0.0007 (4) |
| O1 | 0.0190 (4) | 0.0230 (4) | 0.0167 (4) | 0.0017 (3) | 0.0025 (3) | −0.0010 (3) |
| O2 | 0.0336 (5) | 0.0321 (5) | 0.0200 (5) | 0.0048 (4) | 0.0076 (4) | −0.0030 (4) |
| O3 | 0.0239 (4) | 0.0251 (5) | 0.0128 (4) | −0.0076 (3) | 0.0006 (3) | 0.0003 (3) |
| O4 | 0.0317 (5) | 0.0327 (5) | 0.0176 (4) | −0.0140 (4) | 0.0008 (4) | −0.0002 (4) |
| S1 | 0.02389 (18) | 0.02219 (18) | 0.01374 (17) | 0.00119 (11) | −0.00123 (12) | 0.00007 (10) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—O2 | 1.1936 (15) | C5—H5 | 0.9500 |
| C1—O1 | 1.3864 (15) | C6—C7 | 1.3923 (16) |
| C1—S1 | 1.7709 (13) | C6—O3 | 1.4030 (13) |
| C2—C7 | 1.3820 (17) | C7—H7 | 0.9500 |
| C2—O1 | 1.3835 (14) | C8—O4 | 1.2008 (15) |
| C2—C3 | 1.3905 (16) | C8—O3 | 1.3665 (14) |
| C3—C4 | 1.3908 (16) | C8—C9 | 1.4965 (16) |
| C3—S1 | 1.7506 (12) | C9—H9A | 0.9800 |
| C4—C5 | 1.3936 (16) | C9—H9B | 0.9800 |
| C4—H4 | 0.9500 | C9—H9C | 0.9800 |

| C5—C6 | 1.3875 (16) | | |
|---|---|---|---|
| O2—C1—O1 | 121.54 (12) | C7—C6—O3 | 119.12 (10) |
| O2—C1—S1 | 126.88 (10) | C2—C7—C6 | 115.92 (11) |
| O1—C1—S1 | 111.57 (8) | C2—C7—H7 | 122.0 |
| C7—C2—O1 | 122.33 (10) | C6—C7—H7 | 122.0 |
| C7—C2—C3 | 122.57 (11) | O4—C8—O3 | 122.31 (11) |
| O1—C2—C3 | 115.05 (10) | O4—C8—C9 | 127.77 (11) |
| C2—C3—C4 | 120.37 (11) | O3—C8—C9 | 109.92 (10) |
| C2—C3—S1 | 110.57 (9) | C8—C9—H9A | 109.5 |
| C4—C3—S1 | 128.97 (9) | C8—C9—H9B | 109.5 |
| C3—C4—C5 | 118.37 (11) | H9A—C9—H9B | 109.5 |
| C3—C4—H4 | 120.8 | C8—C9—H9C | 109.5 |
| C5—C4—H4 | 120.8 | H9A—C9—H9C | 109.5 |
| C6—C5—C4 | 119.62 (11) | H9B—C9—H9C | 109.5 |
| C6—C5—H5 | 120.2 | C2—O1—C1 | 112.32 (9) |
| C4—C5—H5 | 120.2 | C8—O3—C6 | 118.24 (9) |
| C5—C6—C7 | 123.14 (11) | C3—S1—C1 | 90.43 (6) |
| C5—C6—O3 | 117.42 (10) | | |
| | | | |
| C7—C2—C3—C4 | 0.48 (18) | C7—C2—O1—C1 | 174.88 (10) |
| O1—C2—C3—C4 | 177.81 (10) | C3—C2—O1—C1 | −2.46 (14) |
| C7—C2—C3—S1 | −176.35 (9) | O2—C1—O1—C2 | −177.20 (11) |
| O1—C2—C3—S1 | 0.98 (13) | S1—C1—O1—C2 | 2.77 (12) |
| C2—C3—C4—C5 | −0.77 (18) | O4—C8—O3—C6 | 2.67 (17) |
| S1—C3—C4—C5 | 175.41 (9) | C9—C8—O3—C6 | −177.05 (10) |
| C3—C4—C5—C6 | −0.02 (17) | C5—C6—O3—C8 | −111.17 (12) |
| C4—C5—C6—C7 | 1.17 (18) | C7—C6—O3—C8 | 75.10 (14) |
| C4—C5—C6—O3 | −172.28 (10) | C2—C3—S1—C1 | 0.52 (9) |
| O1—C2—C7—C6 | −176.54 (10) | C4—C3—S1—C1 | −175.96 (12) |
| C3—C2—C7—C6 | 0.60 (17) | O2—C1—S1—C3 | 178.09 (12) |
| C5—C6—C7—C2 | −1.43 (17) | O1—C1—S1—C3 | −1.88 (9) |
| O3—C6—C7—C2 | 171.91 (10) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C4—H4···O4[i] | 0.95 | 2.35 | 3.2606 (15) | 159 |
| C9—H9*C*···O2[ii] | 0.98 | 2.50 | 3.4030 (16) | 153 |

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