

The supramolecular structure of 6-hydroxy-1,3-benzoxathiol-2-one (tioxolone)

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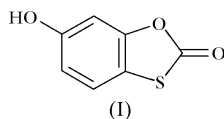
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The planar molecules of 6-hydroxy-1,3-benzoxathiol-2-one, $C_7H_4O_3S$, are linked by extensive $O-H\cdots O$ and $C-H\cdots O$ hydrogen bonding and are further stabilized by face-to-face $\pi-\pi$ interactions.

Comment

The title compound, (I), also known as tioxolone, has been used in the treatment of acne due to its sulfur content (Lius & Sennerfeldt, 1979). It is reported to possess cytostatic (Goeth & Wildfeuer, 1969), antipsoriatic, antibacterial and anti-mycotic properties (Wildfeuer, 1970). It is also added to some cosmetics (*e.g.* hair shampoos and skin cleansers), due to claims for its oil-regulating and antibacterial properties.



The bond lengths and angles in (I) are as expected (Table 1) for this almost planar molecule, where the greatest torsion angle deviation from zero or $\pm 180^\circ$ is seen for $C2-O1-C7-O2$ [-177.49 (18°)]. For simple molecules of this kind, with a hydrogen-bond donor group ($-OH$) at one end and an acceptor ($C=O$) at the other, it can be predicted that a continuous chain of hydrogen-bonded molecules will be present in the crystal lattice. Such is the case for 5-hydroxybenzofuran-(3*H*)-one (Bocelli & Grenier-Loustalot, 1982). For (I), this is indeed the case, and details of the classical $O3-H3\cdots O2^i$ hydrogen bond are given in Table 2 [symmetry code: (i) $1+x, \frac{1}{2}-y, z-\frac{1}{2}$].

Further examination of non-bonded contacts also reveals two intermolecular $C-H\cdots O$ bonds (Table 2). Hence, as shown in Fig. 2, each molecule of (I) is linked through six hydrogen bonds to five adjacent molecules. One $C-H\cdots O$ bond is arranged as described by graph set $R_2^2(8)$ about inversion centres, as shown in Fig. 3. The other $C-H\cdots O$ bond links the $O2$ keto group to $C4$; hence atom $O2$ acts as an

acceptor for two H atoms, with an $H3\cdots O2\cdots H4$ angle of 120° . The resultant $C-H\cdots O$ hydrogen-bonding motif may be described as zigzag ribbons. Hydroxy atom $O3$ acts as both a donor, in forming the continuous chain of classical hydrogen bonds in the $[20\bar{1}]$ direction, and an acceptor, in the formation of the $R_2^2(8)$ rings. Only one H atom in the molecule, namely $H5$, is not involved in hydrogen bonding.

The three-dimensional framework of (I) is further stabilized by $\pi-\pi$ interactions (Steed & Atwood, 2000) between the oxathiolone and benzene rings in partially overlapping molecules (Fig. 4). Here, the interplanar spacing is 3.377 (3) Å, the

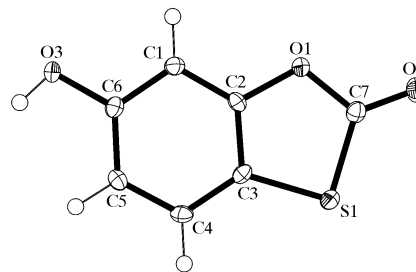


Figure 1
A view of the atomic arrangement in (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids.

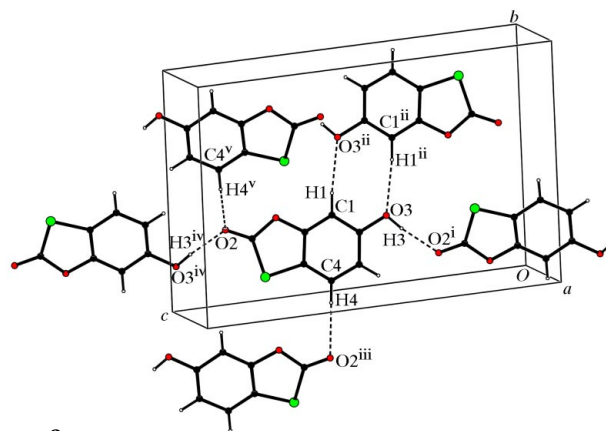


Figure 2
A partial packing diagram for (I), showing the intermolecular hydrogen bonding [symmetry codes: (i) $1+x, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $1-x, 1-y, 1-z$; (iii) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iv) $x-1, \frac{1}{2}-y, z+\frac{1}{2}$; (v) $1-x, y+\frac{1}{2}, \frac{3}{2}-z$].

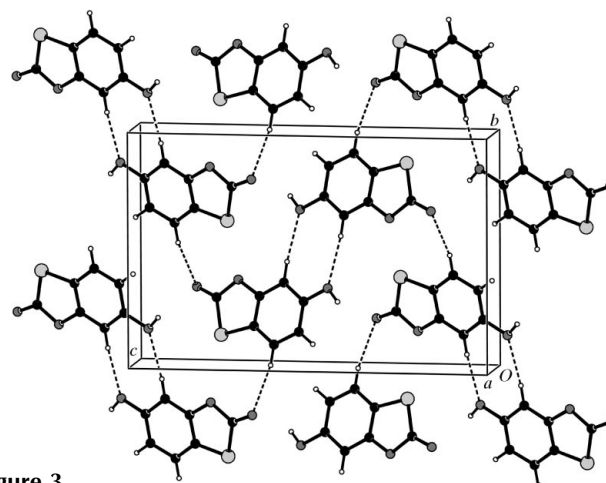


Figure 3
The $C-H\cdots O$ hydrogen bonding in the crystal structure of (I).

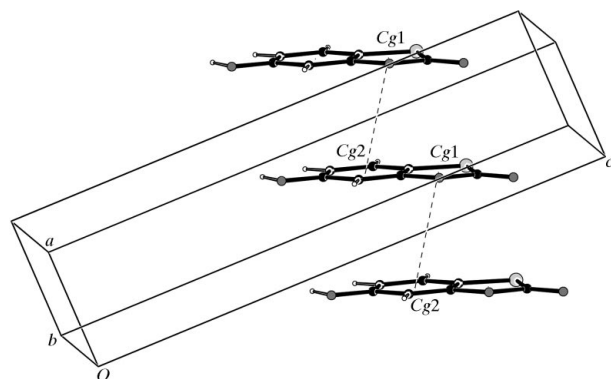


Figure 4
A partial packing diagram for (I), showing molecules stacked along the *a* axis. Ring centroids (*Cg1* for the oxathiolone ring and *Cg2* for the benzene ring) involved in the π - π interactions are joined by dashed lines.

distance between the centroids of the two rings is 3.508 (2) Å, the two centres are offset by 0.961 (2) Å and the interacting molecules are related by unit-cell translations along the short *a* axis.

A search of the Cambridge Structural Database (Version 5.25, January 2004 update; Allen, 2002) shows that the ring system in (I) is unique among crystal structures examined to date. Similar, but not identical, ring systems which lack classical hydrogen bonding are present in the crystal structures of 5,7-di-*tert*-butyl-3*H*-2,1-benzoxathiol-3-one (Krische *et al.*, 1982) and 3-oxo-3*H*-2,1-benzoxathiole-7-carboxylic acid methyl ester (Walter *et al.*, 1978).

Experimental

The title compound was purchased from Sigma and recrystallized from *n*-butanol. Data were collected on a very small crystal (2×10^{-5} mm³).

Crystal data

$C_7H_4O_3S$	$D_x = 1.69$ Mg m ⁻³
$M_r = 168.16$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 18 478 reflections
$a = 3.7620$ (2) Å	$\theta = 2.9$ – 27.5°
$b = 10.686$ (4) Å	$\mu = 0.43$ mm ⁻¹
$c = 16.447$ (9) Å	$T = 120$ (2) K
$\beta = 91.424$ (16) $^\circ$	Needle, colourless
$V = 661.0$ (4) Å ³	$0.10 \times 0.02 \times 0.01$ mm
$Z = 4$	

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer	1502 independent reflections
φ and ω scans to fill Ewald sphere	1174 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SORTAV; Blessing, 1997)	$R_{int} = 0.08$
$T_{min} = 0.965$, $T_{max} = 1.000$	$\theta_{max} = 27.5^\circ$
11 482 measured reflections	$h = -4 \rightarrow 4$
	$k = -13 \rightarrow 13$
	$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2 + 0.3671P]$
$R(F) = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.083$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.05$	$\Delta\rho_{max} = 0.33$ e Å ⁻³
1502 reflections	$\Delta\rho_{min} = -0.30$ e Å ⁻³
103 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

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

S1–C7	1.747 (2)	O1–C7	1.362 (2)
S1–C3	1.748 (2)	O2–C7	1.207 (2)
C7–S1–C3	90.11 (9)	O2–C7–S1	127.03 (16)
C7–O1–C2	112.08 (15)	O1–C7–S1	112.63 (13)
C2–C3–S1	110.61 (14)		
C2–O1–C7–O2	–177.49 (18)	C2–O1–C7–S1	2.3 (2)

Table 2

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O3–H3 \cdots O2 ⁱ	0.86 (2)	1.91 (2)	2.767 (2)	172 (2)
C1–H1 \cdots O3 ⁱⁱ	0.95	2.42	3.365 (3)	174
C4–H4 \cdots O2 ⁱⁱⁱ	0.95	2.53	3.437 (3)	161

Symmetry codes: (i) $1+x, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $1-x, 1-y, 1-z$; (iii) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$.

Due to the small amount of scattering material, it was necessary to stabilize the position of the hydroxy H atom using distance restraints [$O3-H3 = 0.90$ (2) Å and $H3 \cdots O2 = 1.90$ (2) Å] that led to acceptable geometries. The remaining H atoms were allowed to ride on their attached atoms, with C–H distances constrained to 0.95 Å. For all H atoms, $U_{iso}(H) = 1.2U_{eq}(\text{parent atom})$.

Data collection: DENZO (Otwinowski & Minor, 1997) and COLLECT (Nonius, 1998); cell refinement: DENZO and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: WinGX (Farrugia, 1999).

The authors thank the EPSRC National X-ray Crystallography Service at Southampton University for collecting the data.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1566). Services for accessing these data are described at the back of the journal.

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supporting information

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Computing details

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

(I)

Crystal data

C₇H₄O₃S

$M_r = 168.16$

Monoclinic, *P*2₁/*c*

Hall symbol: -P 2ybc

$a = 3.7620$ (2) Å

$b = 10.686$ (4) Å

$c = 16.447$ (9) Å

$\beta = 91.424$ (16)°

$V = 661.0$ (4) Å³

$Z = 4$

$F(000) = 344$

$D_x = 1.69$ Mg m⁻³

Mo *K*α radiation, $\lambda = 0.71073$ Å

Cell parameters from 18478 reflections

$\theta = 2.9$ – 27.5 °

$\mu = 0.43$ mm⁻¹

$T = 120$ K

Needle, colourless

$0.1 \times 0.02 \times 0.01$ mm

Data collection

Enraf Nonius KappaCCD area-detector diffractometer

φ and ω scans to fill Ewald sphere

Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)

$T_{\min} = 0.965$, $T_{\max} = 1.000$

11482 measured reflections

1502 independent reflections

1174 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.08$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 3.1$ °

$h = -4 \rightarrow 4$

$k = -13 \rightarrow 13$

$l = -21 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.083$

$S = 1.05$

1502 reflections

103 parameters

2 restraints

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2 + 0.3671P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.33$ e Å⁻³

$\Delta\rho_{\min} = -0.30$ e Å⁻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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.31869 (13)	0.12103 (4)	0.76562 (3)	0.01635 (16)
O1	0.2310 (4)	0.35210 (12)	0.72071 (8)	0.0161 (3)
O2	0.0223 (4)	0.31042 (13)	0.84351 (8)	0.0215 (4)
O3	0.6947 (4)	0.34264 (13)	0.45481 (8)	0.0211 (4)
H3	0.802 (6)	0.2907 (19)	0.4239 (12)	0.025*
C1	0.4639 (5)	0.35334 (18)	0.58528 (11)	0.0151 (4)
H1	0.4152	0.4399	0.5781	0.018*
C2	0.3875 (5)	0.29119 (17)	0.65601 (11)	0.0135 (4)
C3	0.4551 (5)	0.16607 (18)	0.66909 (11)	0.0137 (4)
C4	0.6082 (5)	0.09592 (18)	0.60835 (11)	0.0156 (4)
H4	0.6574	0.0095	0.6161	0.019*
C5	0.6879 (5)	0.15485 (18)	0.53593 (11)	0.0151 (4)
H5	0.7918	0.1082	0.4935	0.018*
C6	0.6171 (5)	0.28151 (18)	0.52483 (11)	0.0152 (4)
C7	0.1683 (5)	0.27299 (18)	0.78366 (11)	0.0157 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0207 (3)	0.0143 (3)	0.0141 (2)	−0.0007 (2)	0.00184 (18)	0.0018 (2)
O1	0.0218 (8)	0.0138 (7)	0.0129 (7)	0.0011 (5)	0.0037 (5)	0.0001 (5)
O2	0.0278 (9)	0.0192 (8)	0.0178 (7)	−0.0048 (6)	0.0093 (6)	−0.0035 (6)
O3	0.0330 (9)	0.0181 (8)	0.0125 (7)	0.0052 (6)	0.0082 (6)	0.0022 (6)
C1	0.0178 (10)	0.0123 (10)	0.0154 (9)	0.0002 (8)	0.0000 (8)	0.0002 (7)
C2	0.0142 (10)	0.0136 (10)	0.0129 (9)	−0.0005 (8)	0.0004 (7)	−0.0040 (7)
C3	0.0141 (10)	0.0144 (10)	0.0124 (9)	−0.0016 (7)	−0.0019 (8)	0.0030 (7)
C4	0.0160 (10)	0.0121 (10)	0.0186 (10)	0.0035 (8)	−0.0025 (8)	0.0005 (8)
C5	0.0153 (10)	0.0164 (10)	0.0135 (9)	0.0011 (8)	−0.0001 (8)	−0.0034 (7)
C6	0.0164 (11)	0.0173 (10)	0.0119 (9)	0.0001 (8)	−0.0009 (8)	0.0012 (8)
C7	0.0165 (10)	0.0161 (10)	0.0144 (9)	−0.0038 (8)	0.0005 (8)	−0.0003 (8)

Geometric parameters (\AA , $^\circ$)

S1—C7	1.747 (2)	C1—C6	1.392 (3)
S1—C3	1.748 (2)	C1—H1	0.95
O1—C7	1.362 (2)	C2—C3	1.377 (3)
O1—C2	1.391 (2)	C3—C4	1.386 (3)
O2—C7	1.207 (2)	C4—C5	1.387 (3)
O3—C6	1.362 (2)	C4—H4	0.95

O3—H3	0.860 (15)	C5—C6	1.391 (3)
C1—C2	1.376 (3)	C5—H5	0.95
C7—S1—C3	90.11 (9)	C3—C4—C5	118.44 (18)
C7—O1—C2	112.08 (15)	C3—C4—H4	120.8
C6—O3—H3	107.7 (15)	C5—C4—H4	120.8
C2—C1—C6	115.89 (18)	C4—C5—C6	120.66 (18)
C2—C1—H1	122.1	C4—C5—H5	119.7
C6—C1—H1	122.1	C6—C5—H5	119.7
C1—C2—C3	123.99 (17)	O3—C6—C5	122.24 (17)
C1—C2—O1	121.49 (17)	O3—C6—C1	116.15 (17)
C3—C2—O1	114.52 (16)	C5—C6—C1	121.62 (18)
C2—C3—C4	119.41 (17)	O2—C7—O1	120.34 (18)
C2—C3—S1	110.61 (14)	O2—C7—S1	127.03 (16)
C4—C3—S1	129.97 (15)	O1—C7—S1	112.63 (13)
C6—C1—C2—C3	0.3 (3)	S1—C3—C4—C5	179.12 (15)
C6—C1—C2—O1	-179.38 (17)	C3—C4—C5—C6	0.3 (3)
C7—O1—C2—C1	178.14 (17)	C4—C5—C6—O3	179.41 (18)
C7—O1—C2—C3	-1.6 (2)	C4—C5—C6—C1	-0.2 (3)
C1—C2—C3—C4	-0.2 (3)	C2—C1—C6—O3	-179.74 (17)
O1—C2—C3—C4	179.49 (17)	C2—C1—C6—C5	-0.1 (3)
C1—C2—C3—S1	-179.59 (16)	C2—O1—C7—O2	-177.49 (18)
O1—C2—C3—S1	0.1 (2)	C2—O1—C7—S1	2.3 (2)
C7—S1—C3—C2	0.98 (15)	C3—S1—C7—O2	177.9 (2)
C7—S1—C3—C4	-178.3 (2)	C3—S1—C7—O1	-1.90 (15)
C2—C3—C4—C5	-0.1 (3)		

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O3—H3...O2 ⁱ	0.86 (2)	1.91 (2)	2.767 (2)	172 (2)
C1—H1...O3 ⁱⁱ	0.95	2.42	3.365 (3)	174
C4—H4...O2 ⁱⁱⁱ	0.95	2.53	3.437 (3)	161

Symmetry codes: (i) $x+1, -y+1/2, z-1/2$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+1, y-1/2, -z+3/2$.