

(2E)-1-(3-Bromo-2-thienyl)-3-(4-methoxyphenyl)prop-2-en-1-one

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Key indicators

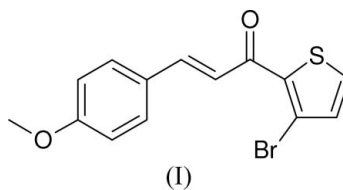
Single-crystal X-ray study
 $T = 120$ K
 Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.023
 wR factor = 0.056
 Data-to-parameter ratio = 16.4

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The molecules of the title compound, $\text{C}_{14}\text{H}_{11}\text{BrO}_2\text{S}$, display some distorted geometrical values that may be ascribed to an $\text{H}\cdots\text{Br}$ close contact. In the crystal structure, the molecules form translation-symmetry-generated infinite chains by way of a $\text{C}-\text{H}\cdots\text{O}$ interaction.

Comment

Chalcones and their heterocyclic derivatives show numerous biological effects (Opletalova & Sedivy, 1999). As part of our ongoing studies of these types of chalcones (Harrison *et al.*, 2006; Yathirajan *et al.*, 2006), the synthesis and structure of the title compound, (I) (Fig. 1), are presented here.



The bond lengths and angles in (I) mostly fall within their expected ranges (Cambridge Structural Database, Version 5.27; Allen, 2002). The terminal C14 methyl group is almost coplanar with its adjacent C8–C13 benzene ring mean plane [deviation of C14 = 0.015 (5) Å]. The dihedral angle between the C8–C13 benzene ring and C1–C4/S1 thiophene ring is 19.58 (9)°. The C5=O1 carbonyl group is also twisted with respect to the heterocycle, as reflected in the S1–C4–C5–O1 and C3–C4–C5–O1 torsion angles of –15.9 (3) and 164.0 (3)°, respectively.

The C3–C4–C5 angle of 135.8 (2)° is far more obtuse than the S1–C4–C5 angle of 114.52 (18)°, possibly as a result of a close intramolecular contact between Br1 and H6 (attached to C6): the separation of these atoms in (I) is 2.73 Å compared to the expected Bondi (1964) van der Waals separation of 3.05 Å. We presume that this represents a steric repulsion between Br and H rather than a $\text{C}-\text{H}\cdots\text{Br}$ 'bond'. The difference between the C4–C3–Br1 and C2–C3–Br1 bond angles [126.74 (18) and 119.08 (18)°, respectively] might also reflect this repulsive contact. Similar angular distortions have been seen in other 4-bromothiophenes such as 4-(4-bromo-5-methylthiophen-2-yl)pyridine (Xu *et al.*, 2005) and 3,4'-dibromo-2,2'-bithiophene (Antolini *et al.*, 1997).

The crystal packing in (I) is consolidated by $\text{C1}-\text{H1}\cdots\text{O2}^i$ interactions (Table 1) that link the molecules into chains propagating in [001]. A slightly short $\text{Br1}\cdots\text{O2}^{ii}$ [symmetry code: (ii) $1-x, \frac{1}{2}+y, 1-z$] contact of 3.2184 (18) Å arises; the expected Bondi separation is 3.37 Å.

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Experimental

3-Bromo-2-acetylthiophene (10 g, 0.048 mol) in methanol (50 ml) was mixed with 4-methoxybenzaldehyde (6.52 g, 0.048 mol) and the mixture was treated with 10 ml of 30% potassium hydroxide solution at 278 K. The reaction mixture was then brought to room temperature and stirred for 3 h. The precipitated solid was filtered and washed with water, dried and recrystallized from acetone to yield light yellow crystals of (I) (yield 80%; m.p. 383 K).

Crystal data

$C_{14}H_{11}BrO_2S$	$Z = 2$
$M_r = 323.20$	$D_x = 1.711 \text{ Mg m}^{-3}$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 4.0025 (1) \text{ \AA}$	$\mu = 3.43 \text{ mm}^{-1}$
$b = 10.7048 (3) \text{ \AA}$	$T = 120 (2) \text{ K}$
$c = 14.6451 (5) \text{ \AA}$	Slab, yellow
$\beta = 91.789 (2)^\circ$	$0.34 \times 0.18 \times 0.07 \text{ mm}$
$V = 627.18 (3) \text{ \AA}^3$	

Data collection

Nonius KappaCCD diffractometer	7197 measured reflections
φ and ω scans	2705 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 2003)	2555 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.388$, $T_{\max} = 0.795$	$R_{\text{int}} = 0.024$
	$\theta_{\max} = 27.5^\circ$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.023$	$\Delta\rho_{\max} = 0.70 \text{ e \AA}^{-3}$
$wR(F^2) = 0.056$	$\Delta\rho_{\min} = -0.55 \text{ e \AA}^{-3}$
$S = 1.08$	Extinction correction: <i>SHELXL97</i>
2705 reflections	Extinction coefficient: 0.016 (2)
165 parameters	Absolute structure: Flack (1983), 1198 Friedel pairs
H-atom parameters constrained	Flack parameter: 0.013 (7)
$w = 1/[\sigma^2(F_o^2) + 0.0736P]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 1

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C1-H1\cdots O2^i$	0.95	2.54	3.457 (3)	162

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

The H atoms were placed in idealized locations ($C-H = 0.95-0.99 \text{ \AA}$) and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$. The methyl group was rotated about its $C-O$ bond to best fit the electron density.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997), and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

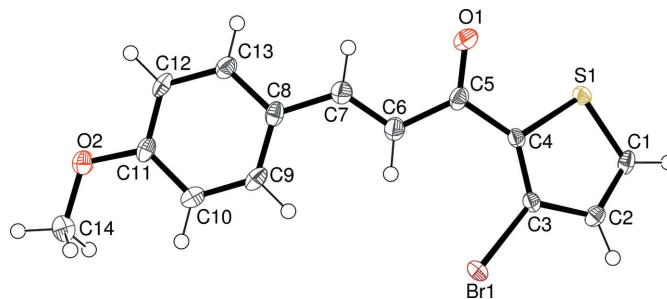


Figure 1

View of (I) showing 50% displacement ellipsoids and arbitrary spheres for the H atoms.

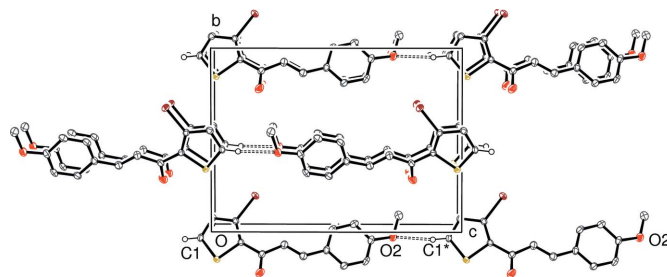


Figure 2

Unit-cell packing in (I), with all H atoms except H1 omitted for clarity and $C-H\cdots O$ interactions indicated by dashed lines. Atoms with an asterisk (*) are generated by the symmetry operation $(x, y, z + 1)$.

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supporting information

Acta Cryst. (2006). E62, o4164–o4165 [https://doi.org/10.1107/S1600536806033824]

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$M_r = 323.20$

Monoclinic, $P2_1$

Hall symbol: P 2yb

$a = 4.0025$ (1) Å

$b = 10.7048$ (3) Å

$c = 14.6451$ (5) Å

$\beta = 91.789$ (2)°

$V = 627.18$ (3) Å³

$Z = 2$

$F(000) = 324$

$D_x = 1.711$ Mg m⁻³

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

Cell parameters from 1442 reflections

$\theta = 1.0$ – 27.5 °

$\mu = 3.43$ mm⁻¹

$T = 120$ K

Slab, yellow

$0.34 \times 0.18 \times 0.07$ mm

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diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2003)

$T_{\min} = 0.388$, $T_{\max} = 0.795$

7197 measured reflections

2705 independent reflections

2555 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 3.4$ °

$h = -5 \rightarrow 5$

$k = -13 \rightarrow 13$

$l = -18 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.056$

$S = 1.08$

2705 reflections

165 parameters

1 restraint

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

$w = 1/[\sigma^2(F_o^2) + 0.0736P]$

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

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

$\Delta\rho_{\max} = 0.70$ e Å⁻³

$\Delta\rho_{\min} = -0.55$ e Å⁻³

Extinction correction: SHELXL97,

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.016 (2)

Absolute structure: Flack (1983), 1198 Friedel
pairs

Absolute structure parameter: 0.013 (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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.2423 (6)	-0.0427 (2)	-0.04736 (17)	0.0193 (5)
H1	0.2683	-0.0523	-0.1112	0.023*
C2	0.3344 (6)	0.0614 (2)	-0.00015 (17)	0.0184 (5)
H2	0.4282	0.1337	-0.0269	0.022*
C3	0.2730 (6)	0.0486 (2)	0.09375 (16)	0.0164 (5)
C4	0.1342 (5)	-0.0634 (2)	0.11667 (16)	0.0156 (5)
C5	0.0263 (6)	-0.1228 (2)	0.20151 (18)	0.0207 (5)
C6	0.1591 (6)	-0.0777 (3)	0.29061 (18)	0.0224 (5)
H6	0.3067	-0.0082	0.2934	0.027*
C7	0.0716 (6)	-0.1346 (2)	0.36740 (18)	0.0221 (5)
H7	-0.0866	-0.2004	0.3608	0.026*
C8	0.1923 (6)	-0.1069 (2)	0.46063 (18)	0.0205 (5)
C9	0.3797 (6)	-0.0006 (2)	0.48433 (18)	0.0220 (5)
H9	0.4361	0.0566	0.4376	0.026*
C10	0.4853 (6)	0.0241 (2)	0.57303 (18)	0.0221 (5)
H10	0.6066	0.0981	0.5875	0.027*
C11	0.4104 (6)	-0.0621 (3)	0.64133 (18)	0.0194 (5)
C12	0.2243 (6)	-0.1685 (2)	0.62022 (18)	0.0207 (6)
H12	0.1722	-0.2264	0.6668	0.025*
C13	0.1154 (6)	-0.1897 (2)	0.53092 (17)	0.0215 (5)
H13	-0.0144	-0.2619	0.5171	0.026*
C14	0.6933 (6)	0.0627 (3)	0.75581 (19)	0.0251 (6)
H14A	0.7517	0.0604	0.8213	0.038*
H14B	0.5541	0.1361	0.7424	0.038*
H14C	0.8979	0.0673	0.7209	0.038*
O1	-0.1577 (5)	-0.2146 (2)	0.19520 (14)	0.0293 (4)
O2	0.5115 (4)	-0.04857 (17)	0.73066 (12)	0.0252 (4)
S1	0.07572 (15)	-0.15396 (5)	0.01985 (4)	0.01747 (14)
Br1	0.36561 (5)	0.18455 (3)	0.172837 (14)	0.02187 (9)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0257 (12)	0.0204 (12)	0.0121 (12)	0.0067 (10)	0.0037 (9)	0.0018 (10)
C2	0.0190 (11)	0.0179 (12)	0.0186 (13)	0.0024 (9)	0.0038 (9)	0.0024 (10)
C3	0.0173 (11)	0.0168 (12)	0.0148 (12)	0.0011 (9)	-0.0026 (9)	-0.0016 (10)

C4	0.0170 (10)	0.0155 (12)	0.0141 (12)	0.0008 (9)	-0.0026 (9)	-0.0009 (10)
C5	0.0266 (12)	0.0185 (13)	0.0170 (14)	0.0042 (10)	0.0006 (10)	0.0034 (10)
C6	0.0241 (12)	0.0245 (13)	0.0187 (14)	-0.0001 (11)	-0.0002 (10)	0.0014 (11)
C7	0.0230 (12)	0.0225 (13)	0.0207 (15)	0.0009 (11)	0.0004 (10)	0.0005 (11)
C8	0.0238 (12)	0.0227 (13)	0.0153 (13)	0.0068 (10)	0.0045 (10)	0.0018 (10)
C9	0.0245 (12)	0.0196 (13)	0.0223 (14)	0.0048 (10)	0.0068 (10)	0.0077 (11)
C10	0.0205 (11)	0.0201 (12)	0.0260 (15)	0.0002 (11)	0.0036 (10)	0.0050 (11)
C11	0.0167 (10)	0.0250 (13)	0.0167 (13)	0.0062 (10)	0.0046 (9)	0.0042 (11)
C12	0.0201 (12)	0.0251 (14)	0.0172 (14)	0.0040 (10)	0.0041 (10)	0.0100 (11)
C13	0.0259 (12)	0.0182 (12)	0.0206 (14)	0.0021 (10)	0.0041 (10)	0.0034 (10)
C14	0.0216 (12)	0.0295 (14)	0.0240 (15)	0.0039 (11)	-0.0014 (10)	-0.0022 (11)
O1	0.0318 (10)	0.0298 (11)	0.0262 (11)	-0.0097 (8)	0.0006 (8)	0.0079 (9)
O2	0.0282 (9)	0.0273 (10)	0.0199 (10)	-0.0009 (8)	-0.0034 (7)	0.0036 (8)
S1	0.0220 (3)	0.0143 (3)	0.0159 (3)	-0.0006 (2)	-0.0015 (2)	-0.0022 (2)
Br1	0.02817 (13)	0.01867 (13)	0.01862 (14)	-0.00414 (12)	-0.00191 (8)	-0.00505 (12)

Geometric parameters (Å, °)

C1—C2	1.357 (4)	C8—C13	1.400 (4)
C1—S1	1.695 (3)	C8—C9	1.401 (4)
C1—H1	0.9500	C9—C10	1.379 (4)
C2—C3	1.411 (3)	C9—H9	0.9500
C2—H2	0.9500	C10—C11	1.400 (4)
C3—C4	1.368 (3)	C10—H10	0.9500
C3—Br1	1.889 (2)	C11—O2	1.365 (3)
C4—C5	1.472 (3)	C11—C12	1.390 (4)
C4—S1	1.727 (2)	C12—C13	1.384 (4)
C5—O1	1.230 (3)	C12—H12	0.9500
C5—C6	1.475 (4)	C13—H13	0.9500
C6—C7	1.335 (4)	C14—O2	1.437 (3)
C6—H6	0.9500	C14—H14A	0.9800
C7—C8	1.464 (4)	C14—H14B	0.9800
C7—H7	0.9500	C14—H14C	0.9800
C2—C1—S1	112.75 (19)	C10—C9—C8	122.3 (2)
C2—C1—H1	123.6	C10—C9—H9	118.8
S1—C1—H1	123.6	C8—C9—H9	118.8
C1—C2—C3	111.4 (2)	C9—C10—C11	118.8 (2)
C1—C2—H2	124.3	C9—C10—H10	120.6
C3—C2—H2	124.3	C11—C10—H10	120.6
C4—C3—C2	114.1 (2)	O2—C11—C12	116.2 (2)
C4—C3—Br1	126.74 (18)	O2—C11—C10	123.4 (2)
C2—C3—Br1	119.08 (18)	C12—C11—C10	120.4 (2)
C3—C4—C5	135.8 (2)	C13—C12—C11	119.7 (2)
C3—C4—S1	109.64 (18)	C13—C12—H12	120.2
C5—C4—S1	114.52 (18)	C11—C12—H12	120.2
O1—C5—C4	118.2 (2)	C12—C13—C8	121.4 (2)
O1—C5—C6	121.8 (2)	C12—C13—H13	119.3

C4—C5—C6	119.9 (2)	C8—C13—H13	119.3
C7—C6—C5	119.9 (3)	O2—C14—H14A	109.5
C7—C6—H6	120.0	O2—C14—H14B	109.5
C5—C6—H6	120.0	H14A—C14—H14B	109.5
C6—C7—C8	127.2 (3)	O2—C14—H14C	109.5
C6—C7—H7	116.4	H14A—C14—H14C	109.5
C8—C7—H7	116.4	H14B—C14—H14C	109.5
C13—C8—C9	117.4 (2)	C11—O2—C14	117.8 (2)
C13—C8—C7	118.9 (2)	C1—S1—C4	92.12 (12)
C9—C8—C7	123.6 (2)		
S1—C1—C2—C3	1.2 (3)	C13—C8—C9—C10	-0.4 (3)
C1—C2—C3—C4	-0.4 (3)	C7—C8—C9—C10	178.9 (2)
C1—C2—C3—Br1	-177.62 (17)	C8—C9—C10—C11	1.8 (4)
C2—C3—C4—C5	179.6 (2)	C9—C10—C11—O2	178.0 (2)
Br1—C3—C4—C5	-3.5 (4)	C9—C10—C11—C12	-1.9 (3)
C2—C3—C4—S1	-0.5 (3)	O2—C11—C12—C13	-179.3 (2)
Br1—C3—C4—S1	176.42 (13)	C10—C11—C12—C13	0.6 (4)
C3—C4—C5—O1	164.0 (3)	C11—C12—C13—C8	0.9 (4)
S1—C4—C5—O1	-15.9 (3)	C9—C8—C13—C12	-1.0 (3)
C3—C4—C5—C6	-20.6 (4)	C7—C8—C13—C12	179.7 (2)
S1—C4—C5—C6	159.54 (18)	C12—C11—O2—C14	-177.6 (2)
O1—C5—C6—C7	-2.1 (4)	C10—C11—O2—C14	2.5 (3)
C4—C5—C6—C7	-177.4 (2)	C2—C1—S1—C4	-1.29 (19)
C5—C6—C7—C8	176.5 (2)	C3—C4—S1—C1	1.00 (18)
C6—C7—C8—C13	-169.4 (3)	C5—C4—S1—C1	-179.08 (18)
C6—C7—C8—C9	11.3 (4)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1 \cdots O2 ⁱ	0.95	2.54	3.457 (3)	162

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