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2-Bromo-2-methyl-1-[4-(methylsulfanyl)-phenyl]propan-1-one

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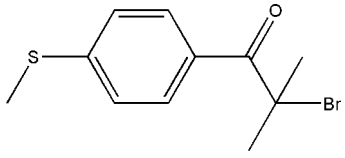
Key indicators: single-crystal X-ray study; T = 153 K; mean σ(C–C) = 0.002 Å; R factor = 0.032; wR factor = 0.073; data-to-parameter ratio = 27.9.

In the title compound, $C_{11}H_{13}BrOS$, the thioether unit and the phenyl ring adopt an essentially planar conformation, with a maximum deviation of 0.063 Å. In the crystal, molecules are linked by C—H···O hydrogen bonds, extending in zigzag chains along the b axis. A weak intramolecular C—H···Br hydrogen bond is also observed, which forms an S(6) ring motif.

Related literature

For general background to the properties of the title compound, a key intermediate for the preparation of a UV initiator, and its synthesis, see: Zhao *et al.* (2010); Liu *et al.* (2010). For related structures, see: Anuradha *et al.* (2008); Moreno-Fuquen *et al.* (2011).



Experimental

Crystal data

$C_{11}H_{13}BrOS$
M_r = 273.18
Monoclinic, $P2_1/n$
a = 11.061 (3) Å
b = 7.120 (2) Å
c = 14.721 (4) Å
β = 97.638 (3)°
V = 1149.1 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.73 mm^{-1}
T = 153 K
0.27 × 0.23 × 0.18 mm

Data collection

Rigaku AFC10/Saturn724+ diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.433, T_{max} = 0.551
9900 measured reflections
3625 independent reflections
2901 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.073
S = 1.00
3625 reflections
130 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.57 e Å^{-3}
$\Delta\rho_{min}$ = −0.72 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11A···O1^{i}	0.98	2.47	3.359 (2)	150
C5—H5···Br1	0.95	2.78	3.387 (2)	123

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

Data collection: *CrystalClear* (Rigaku/MSC, 2008); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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: *publCIF* (Westrip, 2010) and *PLATON* (Spek, 2009).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2458).

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supplementary materials

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2-Bromo-2-methyl-1-[4-(methylsulfanyl)phenyl]propan-1-one

Fei Liu, Shi-Ying Ren and Wei-Ji Yang

Comment

The title compound is a key intermediate for the preparation of 2-methyl-1-[4-(methylthio)phenyl]-2-(4-morpholinyl)-propanone, which is used as a UV initiator (Zhao *et al.*, 2010). It was prepared from thioanisole, which was reacted with isobutyryl chloride in the presence of aluminium cloride, followed by bromination with bromine/acetic acid (Liu *et al.*, 2010).

C—S bond lengths and the C—S—C angle agree with those in (*E*)-3-(4-fluorophenyl)-1-[4-(methylsulfanyl)phenyl]-prop-2-en-1-one (Anuradha *et al.*, 2008). The S—Csp^3 bond length (1.7954 Å) is longer than the S—Csp^2 one (1.7548 Å) and the C—Br distance length (1.9962 Å) is in the normal range for this type of bonds (Moreno-Fuquen *et al.*, 2011).

The thioether moiety and phenyl ring adopt an essentially planar conformation with a maximum deviation of 0.063 Å (Fig. 1). In the crystal, molecules are linked by C—H···O hydrogen bonds, extending as zigzag chains along the *b* axis (Fig. 2). In addition, a weak intramolecular C—H···Br hydrogen bond is also observed, forming an *S*(6) ring motif. This H-bond geometry is listed in Table 1.

Experimental

To a mixture of dichloroethane (50 ml) and aluminium cloride (17.4 g, 130 mmol) was added isobutyryl chloride (13.8 g, 130 mmol) at 298 K. Thioanisole (10.8 g, 100 mmol) was added dropwise to the mixture. After completion, it was poured into diluted hydrochloric acid and the organic layer was extracted.

To the organic layer, acetic acid (7.4 g, 123 mmol) and 30% hydrogen peroxide solution (7.4 g, 65 mmol) were added. Then, bromine (10.4 g, 65 mmol) was added at 303 K. After completion, water was added, and the organic layer was washed by 5% sodium bicarbonate solution and concentrated to yield the title compound with a yield of 77.3%. The crude product was recrystallized by slow evaporation from ethanol to give the single crystals used for data collection.

Refinement

C—bound H atoms were positioned geometrically with C—H 0.95 Å and 0.98 Å for Csp^2 and methyl C, respectively, and were treated as riding on their parent atoms, with U_{iso}(H)=1.2 U_{eq}(C).

Computing details

Data collection: *CrystalClear* (Rigaku/MSC, 2008); cell refinement: *CrystalClear* (Rigaku/MSC, 2008); data reduction: *CrystalClear* (Rigaku/MSC, 2008); 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: *publCIF* (Westrip, 2010) and *PLATON* (Spek, 2009).

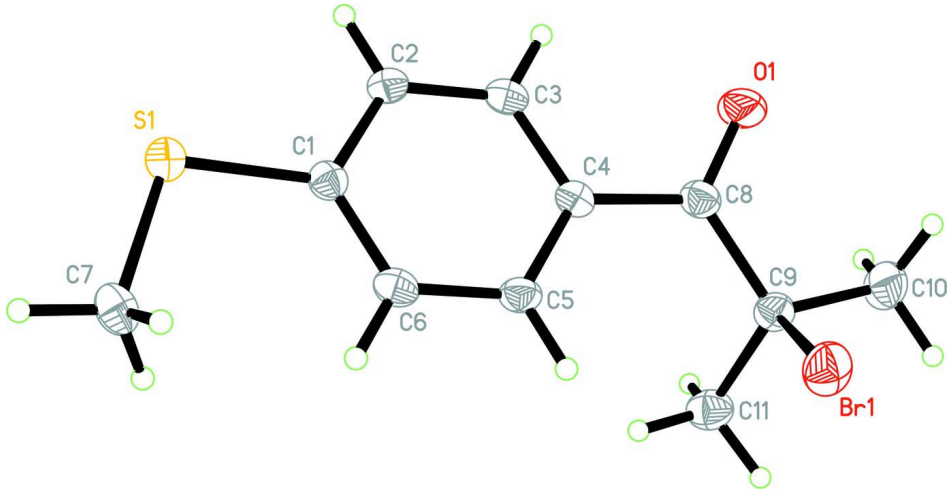

Figure 1

The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level.

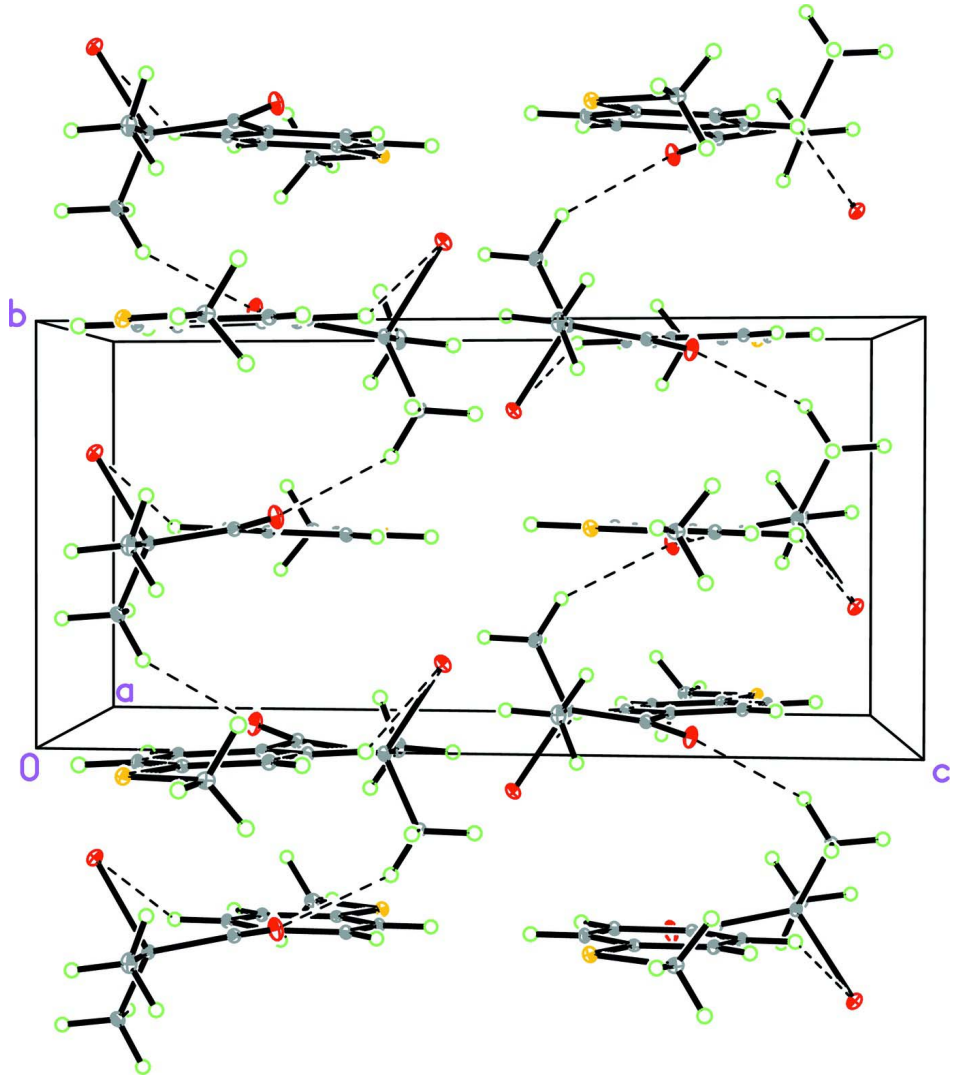

Figure 2

The packing of the crystal structure of (I), showing the intramolecular hydrogen bonds and the zigzag chains formed by C—H···O hydrogen bonds (dotted lines).

2-Bromo-2-methyl-1-[4-(methylsulfanyl)phenyl]propan-1-one

Crystal data

$C_{11}H_{13}BrOS$
$M_r = 273.18$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 11.061$ (3) Å
$b = 7.120$ (2) Å
$c = 14.721$ (4) Å
$\beta = 97.638$ (3)°
$V = 1149.1$ (5) Å^3
$Z = 4$

$F(000) = 552$
$D_x = 1.579$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4327 reflections
$\theta = 2.2$–31.0°
$\mu = 3.73$ mm^{-1}
$T = 153$ K
Block, colourless
0.27 × 0.23 × 0.18 mm

Data collection

Rigaku AFC10/Saturn724+ diffractometer
Radiation source: Rotating Anode
Graphite monochromator
Detector resolution: 28.5714 pixels mm^{-1}
phi and ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.433, T_{max} = 0.551

9900 measured reflections
3625 independent reflections
2901 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 31.0°, θ_{min} = 2.8°
h = −16→14
k = −10→8
l = −21→21

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.073
S = 1.00
3625 reflections
130 parameters
0 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
$w = 1/[\sigma^2(F_o^2) + (0.0339P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.57 e Å^{-3}
$\Delta\rho_{min}$ = −0.72 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.

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}
Br1	0.327247 (17)	0.69311 (3)	0.037381 (13)	0.03062 (7)
S1	0.86419 (4)	0.48317 (6)	0.36691 (3)	0.02352 (10)
O1	0.25965 (11)	0.5378 (2)	0.26208 (9)	0.0358 (3)
C1	0.71222 (15)	0.4889 (2)	0.31441 (12)	0.0184 (3)
C2	0.62070 (15)	0.4850 (2)	0.37198 (12)	0.0211 (3)
H2	0.6426	0.4798	0.4366	0.025*
C3	0.49965 (15)	0.4886 (2)	0.33555 (12)	0.0213 (3)
H3	0.4389	0.4856	0.3755	0.026*
C4	0.46416 (15)	0.4968 (2)	0.24059 (11)	0.0186 (3)
C5	0.55563 (15)	0.5004 (2)	0.18392 (12)	0.0201 (3)
H5	0.5339	0.5061	0.1193	0.024*
C6	0.67786 (16)	0.4957 (2)	0.22041 (12)	0.0212 (3)
H6	0.7387	0.4972	0.1805	0.025*
C7	0.94956 (16)	0.4878 (3)	0.27138 (13)	0.0256 (4)
H7A	0.9245	0.3824	0.2303	0.031*
H7B	1.0368	0.4773	0.2937	0.031*

H7C	0.9340	0.6063	0.2380	0.031*
C8	0.33064 (16)	0.5063 (2)	0.20746 (12)	0.0214 (4)
C9	0.27806 (15)	0.4717 (2)	0.10720 (12)	0.0213 (4)
C10	0.13996 (16)	0.4720 (3)	0.09560 (14)	0.0325 (4)
H10A	0.1084	0.4581	0.0305	0.039*
H10B	0.1110	0.5908	0.1185	0.039*
H10C	0.1111	0.3673	0.1303	0.039*
C11	0.32472 (17)	0.2949 (2)	0.06566 (13)	0.0264 (4)
H11A	0.3003	0.1846	0.0987	0.032*
H11B	0.4139	0.2998	0.0705	0.032*
H11C	0.2900	0.2861	0.0010	0.032*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.03163 (12)	0.03130 (13)	0.02925 (11)	0.00122 (8)	0.00520 (8)	0.00951 (8)
S1	0.0197 (2)	0.0277 (2)	0.0229 (2)	0.00113 (17)	0.00177 (16)	−0.00186 (17)
O1	0.0213 (7)	0.0622 (10)	0.0251 (7)	0.0015 (7)	0.0078 (5)	−0.0100 (7)
C1	0.0189 (8)	0.0163 (8)	0.0201 (8)	0.0003 (6)	0.0028 (6)	−0.0008 (6)
C2	0.0234 (9)	0.0247 (9)	0.0155 (8)	0.0015 (7)	0.0036 (6)	−0.0007 (6)
C3	0.0230 (8)	0.0229 (9)	0.0194 (8)	0.0001 (7)	0.0077 (6)	−0.0014 (7)
C4	0.0193 (8)	0.0178 (8)	0.0193 (8)	0.0004 (6)	0.0054 (6)	−0.0005 (6)
C5	0.0213 (8)	0.0240 (9)	0.0158 (8)	−0.0008 (7)	0.0060 (6)	−0.0001 (6)
C6	0.0218 (8)	0.0230 (9)	0.0204 (8)	−0.0011 (7)	0.0085 (6)	0.0001 (7)
C7	0.0187 (8)	0.0266 (10)	0.0323 (10)	−0.0008 (7)	0.0063 (7)	0.0006 (8)
C8	0.0207 (8)	0.0234 (9)	0.0209 (8)	0.0004 (7)	0.0058 (6)	−0.0006 (7)
C9	0.0199 (8)	0.0253 (9)	0.0192 (8)	−0.0021 (7)	0.0047 (6)	0.0019 (7)
C10	0.0189 (9)	0.0487 (13)	0.0294 (10)	−0.0018 (8)	0.0018 (7)	0.0004 (9)
C11	0.0278 (10)	0.0273 (11)	0.0244 (9)	−0.0048 (7)	0.0045 (7)	−0.0039 (7)

Geometric parameters (Å, º)

Br1—C9	1.9962 (17)	C6—H6	0.9500
S1—C1	1.7548 (17)	C7—H7A	0.9800
S1—C7	1.7954 (19)	C7—H7B	0.9800
O1—C8	1.217 (2)	C7—H7C	0.9800
C1—C6	1.386 (2)	C8—C9	1.533 (2)
C1—C2	1.404 (2)	C9—C10	1.514 (2)
C2—C3	1.375 (2)	C9—C11	1.520 (2)
C2—H2	0.9500	C10—H10A	0.9800
C3—C4	1.402 (2)	C10—H10B	0.9800
C3—H3	0.9500	C10—H10C	0.9800
C4—C5	1.395 (2)	C11—H11A	0.9800
C4—C8	1.494 (2)	C11—H11B	0.9800
C5—C6	1.387 (2)	C11—H11C	0.9800
C5—H5	0.9500		
C1—S1—C7	103.15 (9)	H7A—C7—H7C	109.5
C6—C1—C2	118.63 (16)	H7B—C7—H7C	109.5
C6—C1—S1	124.05 (13)	O1—C8—C4	119.29 (16)

C2—C1—S1	117.32 (13)	O1—C8—C9	118.05 (16)
C3—C2—C1	120.47 (16)	C4—C8—C9	122.63 (14)
C3—C2—H2	119.8	C10—C9—C11	110.31 (15)
C1—C2—H2	119.8	C10—C9—C8	110.88 (14)
C2—C3—C4	121.25 (15)	C11—C9—C8	114.50 (15)
C2—C3—H3	119.4	C10—C9—Br1	106.31 (12)
C4—C3—H3	119.4	C11—C9—Br1	108.46 (12)
C5—C4—C3	117.90 (16)	C8—C9—Br1	105.95 (11)
C5—C4—C8	124.62 (16)	C9—C10—H10A	109.5
C3—C4—C8	117.45 (14)	C9—C10—H10B	109.5
C6—C5—C4	121.01 (16)	H10A—C10—H10B	109.5
C6—C5—H5	119.5	C9—C10—H10C	109.5
C4—C5—H5	119.5	H10A—C10—H10C	109.5
C1—C6—C5	120.74 (15)	H10B—C10—H10C	109.5
C1—C6—H6	119.6	C9—C11—H11A	109.5
C5—C6—H6	119.6	C9—C11—H11B	109.5
S1—C7—H7A	109.5	H11A—C11—H11B	109.5
S1—C7—H7B	109.5	C9—C11—H11C	109.5
H7A—C7—H7B	109.5	H11A—C11—H11C	109.5
S1—C7—H7C	109.5	H11B—C11—H11C	109.5

C7—S1—C1—C6	−0.14 (17)	C4—C5—C6—C1	−0.5 (3)
C7—S1—C1—C2	179.45 (13)	C5—C4—C8—O1	−166.18 (16)
C6—C1—C2—C3	−0.2 (3)	C3—C4—C8—O1	12.1 (2)
S1—C1—C2—C3	−179.84 (13)	C5—C4—C8—C9	15.8 (3)
C1—C2—C3—C4	−0.2 (3)	C3—C4—C8—C9	−165.99 (15)
C2—C3—C4—C5	0.2 (3)	O1—C8—C9—C10	−3.6 (2)
C2—C3—C4—C8	−178.13 (15)	C4—C8—C9—C10	174.51 (16)
C3—C4—C5—C6	0.1 (2)	O1—C8—C9—C11	−129.15 (17)
C8—C4—C5—C6	178.36 (16)	C4—C8—C9—C11	48.9 (2)
C2—C1—C6—C5	0.6 (3)	O1—C8—C9—Br1	111.37 (16)
S1—C1—C6—C5	−179.83 (13)	C4—C8—C9—Br1	−70.55 (18)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11*A*···O1^{i}	0.98	2.47	3.359 (2)	150
C5—H5···Br1	0.95	2.78	3.387 (2)	123

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