2-(1,3-Benzothiazol-2-ylsulfanyl)-1-phenylethanone

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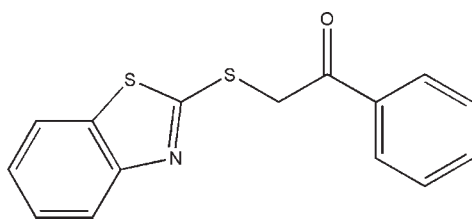Correspondence e-mail: loghmani_h@yahoo.com

In the molecule of the title compound, $C_{15}H_{11}NOS_2$, the 1,3-benzothiazole ring is oriented at a dihedral angle of 6.61 (6)° with respect to the phenyl ring. In the crystal structure, intermolecular C—H···O interactions link the molecules in a herring-bone arrangement along the b axis and π–π contacts between the thiazole and phenyl rings [centroid–centroid distance = 3.851 (1) Å] may further stabilize the structure.

Related literature

For applications of the title compound in organic synthesis, see: Marco *et al.* (1995); Fuju *et al.* (1988); Ni *et al.* (2006); Grossert *et al.* (1984); Oishi *et al.* (1988); Antane *et al.* (2004). For its biological activity, see: Padmavathi *et al.* (2008).

Experimental

Crystal data

$C_{15}H_{11}NOS_2$
$M_r = 285.37$
Orthorhombic, $P2_12_12_1$
$a = 5.1060$ (1) Å
$b = 14.6220$ (3) Å
$c = 17.3920$ (4) Å
$V = 1298.49$ (5) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.40$ mm^{-1}
$T = 295$ K
$0.45 \times 0.32 \times 0.17$ mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min} = 0.841$, $T_{max} = 0.935$
14309 measured reflections
3734 independent reflections
3576 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.068$
$S = 1.07$
3734 reflections
172 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}
Absolute structure: Flack (1983), 1550 Friedel pairs
Flack parameter: 0.01 (5)

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2A···O1^i	0.93	2.51	3.2299 (17)	135

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2004); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2008); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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supplementary materials

2-(1,3-Benzothiazol-2-ylsulfanyl)-1-phenylethanone

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Comment

2-(Benzo[d]thiaazol-2-ylthio)-1-phenylethanone is of great importance in organic synthesis and β-keto-sulfones are a very important group of intermediates as they are precursors for Michael and Knoevenagel reactions and are used in the preparation of acetylenes, allenes, chalcones, vinyl sulfones, polyfunctionalized 4H-pyrans and ketones (Marco *et al.*, 1995; Fuju *et al.*, 1988; Ni *et al.*, 2006). In addition, β-keto-sulfones can be converted into optically active β-hydroxy-sulfones, halomethyl and dihalomethyl sulfones. Halomethyl and dihalomethyl sulfones are very good α-carbanion stabilizing substituents and precursors for the preparation of alkenes, aziridines, epoxides and β-hydroxy-sulfones. Haloalkyl sulfones are useful in preventing aquatic organisms from attaching to fishing nets and ship hulls (Grossert *et al.*, 1984; Oishi *et al.*, 1988; Antane *et al.*, 2004). They also possess other biological properties such as herbicidal, bactericidal antifungal and insecticidal. Recently sulfone-linked heterocycles were prepared and have been showed antimicrobial activity (Padmavathi *et al.*, 2008). We prepared the title compound as a precursor for the synthesis of gem-difluoromethylene-containing heterocycle, and reported herein its crystal structure.

In the molecule of the title compound, (Fig. 1), the benzothiazole ring is oriented with respect to the phenyl ring at a dihedral angle of 6.61 (6)°. In the crystal structure, intermolecular C-H···O interactions (Table 1) link the molecules in herringbone mode along the b axis (Fig. 2), in which they may be effective in the stabilization of the structure. The π–π contact between the thiazole and phenyl rings, Cg1—Cg2[i], [symmetry code: (i) x - 1, y, z, where Cg1 and Cg2 are centroids of the rings (S1/N1/C1/C6/C7) and (C1-C6), respectively] may further stabilize the structure, with centroid-centroid distance of 3.851 (1) Å.

Experimental

For the preparation of the title compound, sodium carbonate (4.5 mmol) was added to a stirred solution of 2-mercaptobenzothiazole (3 mmol) in ethanol (15 ml) and water (15 ml) and stirred at room temperature for 30 min. α-Bromoacetophenone (3 mmol) was added to the reaction mixture and stirring was continued for 1h. The reaction was monitored by TLC and after 60 min showed the complete disappearance of the starting material. The reaction mixture was poured into HCl (1M, 100 ml) containing crushed ice (50 g). The product was filtered under vacuum and filtrate washed with ice-cold ethanol (10 ml) and water (10 ml). Recrystalization from petrol ether and filtration gave the title compound (m.p. 387-389 K). ^{1}H NMR (400 MHz; CDCl$_3$): 8.15-7.75 (m, 4H), 7.55-7.32 (m, 5H), 5.10 (s, 2H). ^{13}C NMR (126 MHz; CDCl$_3$): 194.2 (C=O), 162.1, 151.8, 135.3, 134.2, 131.1, 126.7, 126.5, 124.7, 124.1, 119.8, 119.6, 37.5. Anal. Calcd. for CHNS: C, 63.13; H, 3.89; N, 4.91. Found: C, 63.07; H, 3.86; N, 4.93.

Refinement

H atoms were positioned geometrically with C-H = 0.93 and 0.97 Å for aromatic and methylene H atoms, respectively, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$.
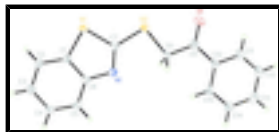
supplementary materials

Figures

Fig. 1. The molecular structure of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level
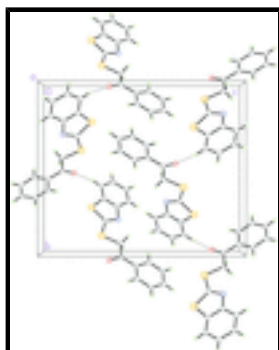

Fig. 2. A partial packing diagram. Hydrogen bonds are shown as dashed lines.

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Crystal data

$C_{15}H_{11}NOS_2$	$D_x = 1.460$ Mg m^{-3}
$M_r = 285.37$	Melting point: 388 K
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 8370 reflections
$a = 5.1060$ (1) Å	$\theta = 2.3–30.5º$
$b = 14.6220$ (3) Å	$\mu = 0.40$ mm^{-1}
$c = 17.3920$ (4) Å	$T = 295$ K
$V = 1298.49$ (5) Å^3	Block, pale-yellow
$Z = 4$	$0.45 \times 0.32 \times 0.17$ mm
$F_{000} = 592$	

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	3734 independent reflections
Radiation source: fine-focus sealed tube	3576 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.024$
$T = 295$ K	$\theta_{max} = 30.0º$
φ and ω scans	$\theta_{min} = 2.7º$
Absorption correction: multi-scan (SADABS; Bruker, 2005)	$h = -7\rightarrow6$
$T_{min} = 0.841$, $T_{max} = 0.935$	$k = -20\rightarrow20$
14309 measured reflections	$l = -24\rightarrow24$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.027$	$w = 1/[\sigma^2(F_o^2) + (0.0411P)^2 + 0.1348P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.068$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.07$	$\Delta\rho_{max} = 0.31$ e Å^{-3}
3734 reflections	$\Delta\rho_{min} = -0.16$ e Å^{-3}
172 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 1550 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.01 (5)

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. 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 $F^2 > 2\text{sigma}(F^2)$ 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	$U_{iso}*/U_{eq}$
S1	0.32503 (6)	0.26829 (2)	0.744608 (17)	0.02052 (8)
S2	0.01546 (7)	0.10723 (2)	0.799872 (17)	0.02062 (8)
O1	−0.3471 (2)	−0.02751 (8)	0.84299 (6)	0.0341 (3)
N1	0.3955 (2)	0.19530 (7)	0.87979 (6)	0.0178 (2)
C1	0.5575 (2)	0.31781 (8)	0.80443 (7)	0.0173 (2)
C2	0.7199 (3)	0.39273 (9)	0.79124 (8)	0.0226 (3)
H2A	0.7112	0.4252	0.7453	0.027*
C3	0.8936 (3)	0.41738 (9)	0.84818 (8)	0.0240 (3)
H3A	1.0056	0.4666	0.8402	0.029*
C4	0.9045 (3)	0.36954 (9)	0.91801 (8)	0.0223 (3)
H4A	1.0230	0.3876	0.9557	0.027*
C5	0.7413 (3)	0.29592 (9)	0.93148 (7)	0.0188 (2)
H5A	0.7477	0.2648	0.9781	0.023*
C6	0.5668 (2)	0.26908 (9)	0.87415 (6)	0.0159 (2)
C7	0.2610 (3)	0.18779 (9)	0.81703 (7)	0.0171 (2)
C8	0.0085 (3)	0.05695 (9)	0.89446 (7)	0.0219 (2)
H8A	0.1752	0.0279	0.9053	0.026*

H8B	−0.0207	0.1041	0.9327	0.026*
C9	−0.2085 (3)	−0.01289 (9)	0.89821 (8)	0.0208 (3)
C10	−0.2437 (3)	−0.06360 (9)	0.97210 (8)	0.0197 (2)
C11	−0.4423 (3)	−0.12874 (9)	0.97723 (9)	0.0255 (3)
H11A	−0.5527	−0.1388	0.9355	0.031*
C12	−0.4758 (3)	−0.17854 (10)	1.04421 (9)	0.0296 (3)
H12A	−0.6096	−0.2215	1.0476	0.036*
C13	−0.3103 (3)	−0.16447 (9)	1.10627 (9)	0.0271 (3)
H13A	−0.3309	−0.1991	1.1507	0.032*
C14	−0.1145 (3)	−0.09906 (10)	1.10233 (8)	0.0271 (3)
H14A	−0.0055	−0.0891	1.1443	0.032*
C15	−0.0816 (3)	−0.04858 (10)	1.03552 (8)	0.0240 (3)
H15A	0.0493	−0.0044	1.0329	0.029*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.02236 (15)	0.02516 (15)	0.01403 (13)	−0.00182 (12)	−0.00251 (11)	0.00181 (11)
S2	0.02335 (15)	0.02168 (14)	0.01685 (13)	−0.00322 (13)	−0.00214 (12)	−0.00344 (11)
O1	0.0360 (6)	0.0339 (5)	0.0323 (5)	−0.0120 (5)	−0.0132 (5)	0.0001 (4)
N1	0.0199 (5)	0.0188 (5)	0.0148 (5)	−0.0008 (4)	0.0011 (4)	−0.0018 (4)
C1	0.0166 (5)	0.0199 (5)	0.0154 (5)	0.0016 (4)	−0.0003 (4)	−0.0011 (4)
C2	0.0233 (6)	0.0220 (6)	0.0224 (6)	0.0001 (5)	0.0012 (5)	0.0051 (5)
C3	0.0223 (6)	0.0193 (6)	0.0303 (7)	−0.0026 (5)	−0.0002 (5)	0.0022 (5)
C4	0.0202 (6)	0.0231 (6)	0.0237 (6)	0.0003 (5)	−0.0041 (5)	−0.0042 (5)
C5	0.0207 (6)	0.0197 (6)	0.0160 (5)	0.0021 (5)	−0.0016 (4)	−0.0006 (4)
C6	0.0168 (5)	0.0164 (5)	0.0144 (5)	0.0018 (5)	0.0012 (4)	−0.0015 (4)
C7	0.0188 (6)	0.0175 (5)	0.0150 (5)	0.0002 (4)	0.0019 (4)	−0.0021 (4)
C8	0.0226 (6)	0.0233 (6)	0.0199 (5)	−0.0065 (6)	−0.0036 (5)	0.0005 (5)
C9	0.0197 (6)	0.0173 (6)	0.0253 (6)	−0.0004 (5)	−0.0011 (5)	−0.0033 (5)
C10	0.0172 (6)	0.0155 (5)	0.0265 (6)	0.0010 (4)	0.0018 (5)	−0.0026 (5)
C11	0.0211 (7)	0.0221 (6)	0.0333 (7)	−0.0042 (5)	−0.0012 (5)	−0.0039 (5)
C12	0.0255 (7)	0.0225 (6)	0.0409 (8)	−0.0054 (6)	0.0072 (6)	−0.0009 (6)
C13	0.0282 (7)	0.0229 (6)	0.0301 (7)	0.0020 (6)	0.0098 (6)	0.0020 (5)
C14	0.0280 (7)	0.0280 (7)	0.0253 (6)	−0.0025 (6)	−0.0006 (5)	0.0005 (6)
C15	0.0206 (6)	0.0228 (6)	0.0285 (6)	−0.0051 (5)	−0.0006 (5)	0.0006 (5)

Geometric parameters (Å, °)

S1—C1	1.7365 (13)	C5—H5A	0.9300
S1—C7	1.7548 (13)	C8—C9	1.5080 (18)
S2—C7	1.7459 (13)	C8—H8A	0.9700
S2—C8	1.8022 (13)	C8—H8B	0.9700
O1—C9	1.2122 (16)	C9—C10	1.4945 (19)
N1—C7	1.2944 (16)	C10—C11	1.3943 (18)
N1—C6	1.3923 (17)	C10—C15	1.3964 (19)
C1—C2	1.3929 (18)	C11—C12	1.384 (2)
C1—C6	1.4073 (17)	C11—H11A	0.9300
C2—C3	1.3774 (19)	C12—C13	1.386 (2)

C2—H2A	0.9300	C12—H12A	0.9300
C3—C4	1.4026 (19)	C13—C14	1.385 (2)
C3—H3A	0.9300	C13—H13A	0.9300
C4—C5	1.3813 (19)	C14—C15	1.387 (2)
C4—H4A	0.9300	C14—H14A	0.9300
C5—C6	1.3934 (17)	C15—H15A	0.9300
C1—S1—C7	88.68 (6)	S2—C8—H8A	109.8
C7—S2—C8	97.66 (6)	C9—C8—H8B	109.8
C7—N1—C6	109.87 (11)	S2—C8—H8B	109.8
C2—C1—C6	121.32 (12)	H8A—C8—H8B	108.3
C2—C1—S1	129.51 (10)	O1—C9—C10	121.56 (13)
C6—C1—S1	109.17 (9)	O1—C9—C8	120.95 (12)
C3—C2—C1	118.08 (12)	C10—C9—C8	117.49 (11)
C3—C2—H2A	121.0	C11—C10—C15	119.22 (13)
C1—C2—H2A	121.0	C11—C10—C9	118.78 (12)
C2—C3—C4	121.17 (13)	C15—C10—C9	121.99 (12)
C2—C3—H3A	119.4	C12—C11—C10	120.20 (14)
C4—C3—H3A	119.4	C12—C11—H11A	119.9
C5—C4—C3	120.77 (12)	C10—C11—H11A	119.9
C5—C4—H4A	119.6	C11—C12—C13	120.13 (13)
C3—C4—H4A	119.6	C11—C12—H12A	119.9
C4—C5—C6	118.93 (12)	C13—C12—H12A	119.9
C4—C5—H5A	120.5	C14—C13—C12	120.25 (13)
C6—C5—H5A	120.5	C14—C13—H13A	119.9
N1—C6—C5	124.71 (11)	C12—C13—H13A	119.9
N1—C6—C1	115.57 (10)	C13—C14—C15	119.76 (14)
C5—C6—C1	119.71 (12)	C13—C14—H14A	120.1
N1—C7—S2	125.63 (10)	C15—C14—H14A	120.1
N1—C7—S1	116.71 (10)	C14—C15—C10	120.42 (13)
S2—C7—S1	117.63 (7)	C14—C15—H15A	119.8
C9—C8—S2	109.28 (9)	C10—C15—H15A	119.8
C9—C8—H8A	109.8		
C7—S1—C1—C2	179.53 (13)	C8—S2—C7—S1	−172.57 (8)
C7—S1—C1—C6	0.04 (9)	C1—S1—C7—N1	0.00 (11)
C6—C1—C2—C3	0.86 (19)	C1—S1—C7—S2	177.93 (8)
S1—C1—C2—C3	−178.59 (11)	C7—S2—C8—C9	175.74 (9)
C1—C2—C3—C4	−1.0 (2)	S2—C8—C9—O1	−0.42 (16)
C2—C3—C4—C5	0.2 (2)	S2—C8—C9—C10	179.05 (10)
C3—C4—C5—C6	0.7 (2)	O1—C9—C10—C11	−0.4 (2)
C7—N1—C6—C5	−179.59 (12)	C8—C9—C10—C11	−179.87 (12)
C7—N1—C6—C1	0.07 (15)	O1—C9—C10—C15	178.67 (13)
C4—C5—C6—N1	178.80 (12)	C8—C9—C10—C15	−0.79 (18)
C4—C5—C6—C1	−0.84 (19)	C15—C10—C11—C12	−0.7 (2)
C2—C1—C6—N1	−179.62 (11)	C9—C10—C11—C12	178.35 (13)
S1—C1—C6—N1	−0.07 (13)	C10—C11—C12—C13	−0.6 (2)
C2—C1—C6—C5	0.06 (19)	C11—C12—C13—C14	1.5 (2)
S1—C1—C6—C5	179.61 (10)	C12—C13—C14—C15	−1.0 (2)
C6—N1—C7—S2	−177.78 (9)	C13—C14—C15—C10	−0.3 (2)

| C6—N1—C7—S1 | −0.04 (14) | C11—C10—C15—C14 | 1.2 (2) |
| C8—S2—C7—N1 | 5.15 (13) | C9—C10—C15—C14 | −177.84 (13) |

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2A···O1[i]	0.93	2.51	3.2299 (17)	135

Symmetry codes: (i) −*x*, *y*+1/2, −*z*+3/2.

Fig. 1

Fig. 2