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5-[(4-Bromobenzyl)oxy]-4-(4-methylbenzenesulfonyl)-1,3-thiazole

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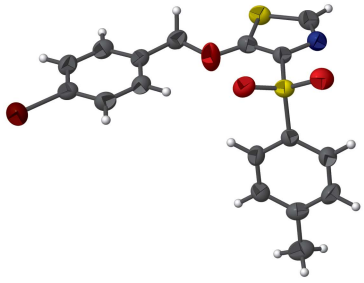
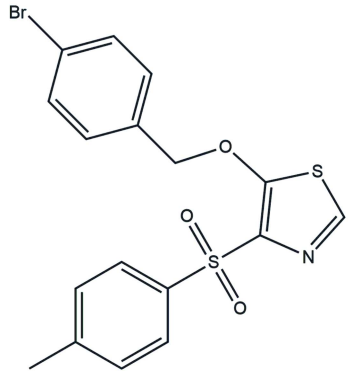
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{17}H_{14}BrNO_3S_2$, the mean plane of the thiazole ring subtends dihedral angles of 3.6 (2) and 79.9 (2)° with the bromobenzyl and toluyl rings, respectively. In the crystal, short S···O contacts [3.012 (3) Å] and aromatic π–π stacking between the thiazole and toluyl rings [centroid–centroid separation = 3.687 (2) Å] are observed.

3D view



Chemical scheme



Structure description

Thiazoles have many applications in the field of medicinal chemistry, for instance as antimicrobial (Liaras *et al.*, 2011), anti-cancer (Romagnoli *et al.*, 2012) and anti-mycobacterium tuberculosis (Shiradkar *et al.*, 2007) agents. As part of our studies of these compounds, we have synthesized the title compound to study its crystal structure.

In the molecular structure (Fig. 1), the mean plane of the thiazole moiety (C11/N12/C13/S14/C15), is approximately coplanar with the bromobenzyl ring [dihedral angle = 3.6 (2)°] and close to orthogonal to the toluyl ring [79.9 (2)°]. In the crystal, short S···O contacts [3.012 (3) Å] and aromatic π–π stacking between the thiazole and toluyl rings [centroid-centroid separation = 3.687 (2) Å] are observed. A packing diagram is shown in Fig. 2

Synthesis and crystallization

To a suspension of sodium hydride (60% suspension in paraffin; 4 mmol) in DMF (1.5 ml), a mixture of xanthate ester 2 (2 mmol), and active methylene isocyanide 3 (2 mmol) in DMF (1.5 ml) was added dropwise at 0°C. The mixture was allowed to stir at room temperature for 10–20 min (monitored by TLC). After completion of the reaction,

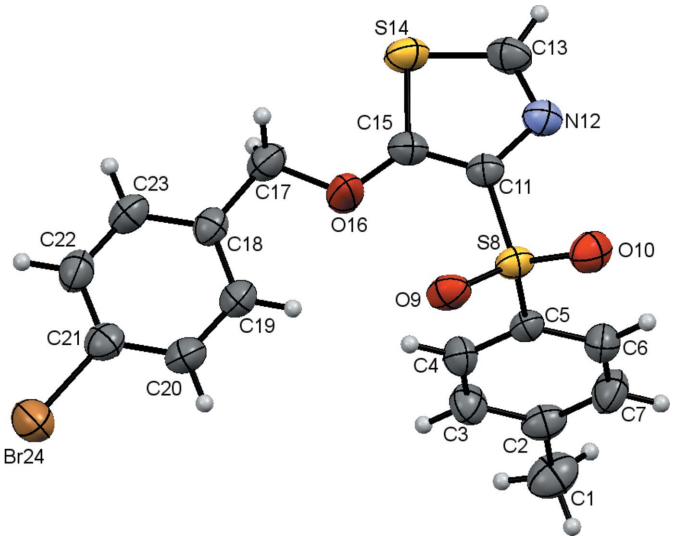


Figure 1
The molecular structure with 50% probability displacement ellipsoids.

the mixture was poured into a saturated solution of ammonium chloride (20 ml) and extracted with ethyl acetate (20 ml × 2). The combined ethyl acetate layer was washed with water (20 ml), brine (20 ml), dried over anhydrous sodium sulfate and concentrated under reduced pressure to get crude products, which were purified by column chromatography using ethyl acetate–hexane as eluent. Pale-yellow blocks of the title compound were recrystallized from ethyl acetate solution.

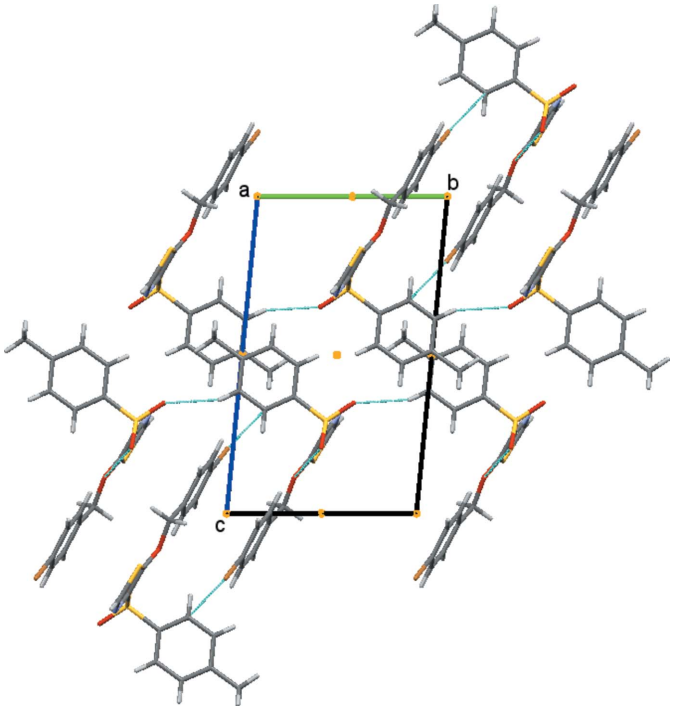


Figure 2
Packing diagram of the title compound viewed down [100].

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{17}H_{14}BrNO_3S_2$
M_r	424.31
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	293
a, b, c (Å)	7.6092 (4), 8.2768 (5), 13.8718 (8)
α, β, γ (°)	95.175 (5), 94.559 (5), 94.814 (5)
V (Å^3)	863.67 (9)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.64
Crystal size (mm)	0.28 × 0.25 × 0.22
Data collection	
Diffractometer	Bruker APEXII CCD
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7351, 3955, 2633
R_{int}	0.035
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.056, 0.144, 1.04
No. of reflections	3955
No. of parameters	218
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.35, −0.67

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXS97* and *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x171500 [https://doi.org/10.1107/S2414314617015000]

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Crystal data

$C_{17}H_{14}BrNO_3S_2$
M_r = 424.31
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 7.6092 (4) Å
b = 8.2768 (5) Å
c = 13.8718 (8) Å
α = 95.175 (5)°
β = 94.559 (5)°
γ = 94.814 (5)°
V = 863.67 (9) Å^3
Z = 2
$F(000)$ = 428
D_x = 1.632 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3955 reflections
θ = 2.5–27.5°
μ = 2.64 mm^{-1}
T = 293 K
Block, pale yellow
0.28 × 0.25 × 0.22 mm

Data collection

Bruker APEXII CCD diffractometer
Detector resolution: 18.4 pixels mm^{-1}
ω and φ scans
7351 measured reflections
3955 independent reflections
2633 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 27.5°, θ_{min} = 2.5°
h = −9→9
k = −10→8
l = −16→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.144
S = 1.04
3955 reflections
218 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\Sigma^2(FO^2) + (0.0501P)^2 + 0.4404P]$ where $P = (FO^2 + 2FC^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.67 e Å^{-3}

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses 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 observed criterion of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating -R-factor-obs 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.
The H atoms were positioned geometrically and allowed to ride on their parent atom, with C–H distance in the range of 0.93 to 0.97 Å; $U_{iso}(H) = 1.2–1.5U_{eq}$ (carrier atom) for all H atoms.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br24	0.46321 (8)	0.97111 (7)	0.79555 (4)	0.0674 (2)
S8	0.12112 (14)	0.52364 (12)	1.29198 (8)	0.0382 (3)
S14	−0.39923 (15)	0.56970 (15)	1.16549 (9)	0.0508 (4)
O9	0.2178 (4)	0.5355 (4)	1.2075 (2)	0.0474 (10)
O10	0.1418 (4)	0.3884 (3)	1.3483 (2)	0.0516 (11)
O16	−0.0708 (5)	0.6623 (5)	1.1124 (3)	0.0779 (14)
N12	−0.2288 (5)	0.4619 (4)	1.3100 (3)	0.0450 (12)
C1	0.2819 (7)	1.1548 (6)	1.5513 (4)	0.0647 (19)
C2	0.2422 (6)	0.9961 (5)	1.4872 (3)	0.0458 (16)
C3	0.2264 (6)	0.9965 (5)	1.3866 (3)	0.0483 (16)
C4	0.1911 (6)	0.8518 (5)	1.3277 (3)	0.0445 (16)
C5	0.1718 (5)	0.7057 (5)	1.3686 (3)	0.0358 (12)
C6	0.1858 (6)	0.7040 (5)	1.4683 (3)	0.0458 (14)
C7	0.2221 (7)	0.8489 (6)	1.5267 (3)	0.0539 (16)
C11	−0.1060 (5)	0.5239 (5)	1.2538 (3)	0.0366 (12)
C13	−0.3864 (6)	0.4786 (6)	1.2722 (3)	0.0504 (17)
C15	−0.1693 (6)	0.5886 (5)	1.1725 (3)	0.0438 (14)
C17	−0.1435 (6)	0.7034 (6)	1.0217 (3)	0.0471 (16)
C18	0.0056 (6)	0.7718 (5)	0.9690 (3)	0.0393 (14)
C19	0.1812 (6)	0.7713 (5)	1.0047 (3)	0.0449 (14)
C20	0.3145 (6)	0.8305 (5)	0.9536 (3)	0.0490 (17)
C21	0.2766 (6)	0.8919 (5)	0.8658 (3)	0.0452 (14)
C22	0.1037 (7)	0.8947 (5)	0.8301 (3)	0.0496 (16)
C23	−0.0312 (6)	0.8358 (5)	0.8813 (3)	0.0473 (17)
H1A	0.20336	1.15773	1.60218	0.0970*
H1B	0.26522	1.24432	1.51311	0.0970*
H1C	0.40214	1.16313	1.57933	0.0970*
H3	0.23960	1.09451	1.35890	0.0580*
H4	0.18030	0.85259	1.26051	0.0540*
H6	0.17101	0.60604	1.49586	0.0550*
H7	0.23317	0.84745	1.59382	0.0650*
H13	−0.48714	0.44345	1.30113	0.0610*
H16A	−0.22813	0.78345	1.03150	0.0560*
H16B	−0.20413	0.60745	0.98417	0.0560*
H18	0.20832	0.73038	1.06380	0.0540*
H19	0.43168	0.82933	0.97807	0.0590*
H21	0.07767	0.93653	0.77112	0.0600*

H22	−0.14821	0.83882	0.85688	0.0570*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br24	0.0677 (4)	0.0740 (4)	0.0582 (4)	−0.0139 (3)	0.0067 (3)	0.0127 (3)
S8	0.0301 (5)	0.0405 (5)	0.0433 (6)	0.0046 (4)	−0.0011 (4)	0.0023 (5)
S14	0.0309 (6)	0.0608 (7)	0.0595 (8)	0.0038 (5)	−0.0024 (5)	0.0055 (6)
O9	0.0313 (17)	0.0651 (19)	0.0448 (17)	0.0062 (15)	0.0058 (13)	−0.0036 (15)
O10	0.051 (2)	0.0425 (16)	0.061 (2)	0.0102 (15)	−0.0057 (16)	0.0080 (15)
O16	0.038 (2)	0.134 (3)	0.065 (2)	−0.007 (2)	−0.0069 (17)	0.052 (2)
N12	0.037 (2)	0.051 (2)	0.047 (2)	0.0018 (17)	0.0046 (17)	0.0055 (17)
C1	0.068 (4)	0.058 (3)	0.064 (3)	0.011 (3)	−0.006 (3)	−0.011 (3)
C2	0.038 (3)	0.044 (2)	0.053 (3)	0.007 (2)	−0.002 (2)	−0.006 (2)
C3	0.058 (3)	0.038 (2)	0.049 (3)	0.001 (2)	0.003 (2)	0.009 (2)
C4	0.046 (3)	0.052 (3)	0.036 (2)	0.002 (2)	0.0059 (19)	0.008 (2)
C5	0.029 (2)	0.040 (2)	0.038 (2)	0.0019 (17)	−0.0013 (17)	0.0069 (18)
C6	0.049 (3)	0.048 (2)	0.040 (2)	0.000 (2)	0.000 (2)	0.010 (2)
C7	0.065 (3)	0.061 (3)	0.034 (2)	0.005 (3)	−0.005 (2)	0.004 (2)
C11	0.033 (2)	0.037 (2)	0.039 (2)	0.0032 (18)	0.0028 (18)	0.0004 (17)
C13	0.037 (3)	0.058 (3)	0.056 (3)	0.000 (2)	0.012 (2)	0.001 (2)
C15	0.034 (2)	0.048 (2)	0.048 (3)	−0.002 (2)	0.001 (2)	0.004 (2)
C17	0.040 (3)	0.059 (3)	0.041 (2)	0.007 (2)	−0.005 (2)	0.003 (2)
C18	0.044 (3)	0.038 (2)	0.035 (2)	0.0059 (19)	−0.0009 (18)	0.0012 (18)
C19	0.045 (3)	0.050 (2)	0.038 (2)	0.001 (2)	−0.004 (2)	0.005 (2)
C20	0.041 (3)	0.055 (3)	0.048 (3)	−0.001 (2)	−0.007 (2)	0.004 (2)
C21	0.048 (3)	0.044 (2)	0.041 (2)	0.000 (2)	0.000 (2)	−0.003 (2)
C22	0.059 (3)	0.050 (2)	0.039 (3)	0.005 (2)	−0.005 (2)	0.008 (2)
C23	0.042 (3)	0.054 (3)	0.045 (3)	0.009 (2)	−0.006 (2)	0.004 (2)

Geometric parameters (Å, º)

Br24—C21	1.891 (4)	C18—C19	1.388 (6)
S8—O9	1.439 (3)	C18—C23	1.388 (6)
S8—O10	1.434 (3)	C19—C20	1.366 (6)
S8—C5	1.760 (4)	C20—C21	1.380 (6)
S8—C11	1.767 (4)	C21—C22	1.371 (7)
S14—C13	1.721 (5)	C22—C23	1.375 (7)
S14—C15	1.738 (5)	C1—H1A	0.9600
O16—C15	1.320 (6)	C1—H1B	0.9600
O16—C17	1.415 (6)	C1—H1C	0.9600
N12—C11	1.361 (6)	C3—H3	0.9300
N12—C13	1.294 (6)	C4—H4	0.9300
C1—C2	1.512 (7)	C6—H6	0.9300
C2—C3	1.391 (6)	C7—H7	0.9300
C2—C7	1.382 (6)	C13—H13	0.9300
C3—C4	1.382 (6)	C17—H16A	0.9700
C4—C5	1.383 (6)	C17—H16B	0.9700

C5—C6	1.380 (6)	C19—H18	0.9300
C6—C7	1.380 (6)	C20—H19	0.9300
C11—C15	1.363 (6)	C22—H21	0.9300
C17—C18	1.497 (6)	C23—H22	0.9300

O9—S8—O10	118.94 (19)	Br24—C21—C22	120.5 (3)
O9—S8—C5	108.10 (19)	C20—C21—C22	119.7 (4)
O9—S8—C11	107.43 (19)	C21—C22—C23	120.1 (4)
O10—S8—C5	108.85 (18)	C18—C23—C22	120.6 (4)
O10—S8—C11	108.17 (19)	C2—C1—H1A	109.00
C5—S8—C11	104.40 (19)	C2—C1—H1B	109.00
C13—S14—C15	88.4 (2)	C2—C1—H1C	110.00
C15—O16—C17	121.7 (4)	H1A—C1—H1B	109.00
C11—N12—C13	110.0 (4)	H1A—C1—H1C	109.00
C1—C2—C3	120.0 (4)	H1B—C1—H1C	109.00
C1—C2—C7	121.1 (4)	C2—C3—H3	120.00
C3—C2—C7	118.8 (4)	C4—C3—H3	120.00
C2—C3—C4	120.3 (4)	C3—C4—H4	120.00
C3—C4—C5	120.1 (4)	C5—C4—H4	120.00
S8—C5—C4	119.1 (3)	C5—C6—H6	120.00
S8—C5—C6	120.7 (3)	C7—C6—H6	120.00
C4—C5—C6	120.2 (4)	C2—C7—H7	119.00
C5—C6—C7	119.5 (4)	C6—C7—H7	119.00
C2—C7—C6	121.2 (4)	S14—C13—H13	122.00
S8—C11—N12	119.1 (3)	N12—C13—H13	122.00
S8—C11—C15	124.4 (3)	O16—C17—H16A	110.00
N12—C11—C15	116.5 (4)	O16—C17—H16B	110.00
S14—C13—N12	116.2 (3)	C18—C17—H16A	110.00
S14—C15—O16	125.8 (3)	C18—C17—H16B	110.00
S14—C15—C11	109.0 (3)	H16A—C17—H16B	108.00
O16—C15—C11	125.1 (4)	C18—C19—H18	120.00
O16—C17—C18	107.8 (4)	C20—C19—H18	120.00
C17—C18—C19	121.8 (4)	C19—C20—H19	120.00
C17—C18—C23	119.6 (4)	C21—C20—H19	120.00
C19—C18—C23	118.6 (4)	C21—C22—H21	120.00
C18—C19—C20	120.5 (4)	C23—C22—H21	120.00
C19—C20—C21	120.5 (4)	C18—C23—H22	120.00
Br24—C21—C20	119.8 (3)	C22—C23—H22	120.00

O9—S8—C5—C4	38.3 (4)	C3—C2—C7—C6	−0.4 (7)
O9—S8—C5—C6	−144.0 (3)	C2—C3—C4—C5	−0.2 (7)
O10—S8—C5—C4	168.8 (3)	C3—C4—C5—S8	178.3 (3)
O10—S8—C5—C6	−13.5 (4)	C3—C4—C5—C6	0.7 (7)
C11—S8—C5—C4	−75.8 (4)	S8—C5—C6—C7	−178.7 (4)
C11—S8—C5—C6	101.8 (4)	C4—C5—C6—C7	−1.1 (7)
O9—S8—C11—N12	158.7 (3)	C5—C6—C7—C2	1.0 (7)
O9—S8—C11—C15	−24.0 (4)	S8—C11—C15—S14	−177.6 (2)
O10—S8—C11—N12	29.2 (4)	S8—C11—C15—O16	−1.4 (7)

O10—S8—C11—C15	−153.6 (4)	N12—C11—C15—S14	−0.3 (5)
C5—S8—C11—N12	−86.7 (4)	N12—C11—C15—O16	176.0 (4)
C5—S8—C11—C15	90.6 (4)	O16—C17—C18—C19	6.7 (6)
C15—S14—C13—N12	−0.4 (4)	O16—C17—C18—C23	−174.2 (4)
C13—S14—C15—O16	−175.9 (4)	C17—C18—C19—C20	178.2 (4)
C13—S14—C15—C11	0.4 (3)	C23—C18—C19—C20	−1.0 (6)
C17—O16—C15—S14	−14.6 (6)	C17—C18—C23—C22	−178.0 (4)
C17—O16—C15—C11	169.8 (4)	C19—C18—C23—C22	1.2 (6)
C15—O16—C17—C18	−175.3 (4)	C18—C19—C20—C21	0.1 (6)
C13—N12—C11—S8	177.5 (3)	C19—C20—C21—Br24	−179.3 (3)
C13—N12—C11—C15	0.0 (5)	C19—C20—C21—C22	0.6 (6)
C11—N12—C13—S14	0.3 (5)	Br24—C21—C22—C23	179.5 (3)
C1—C2—C3—C4	179.7 (4)	C20—C21—C22—C23	−0.4 (6)
C7—C2—C3—C4	0.0 (7)	C21—C22—C23—C18	−0.5 (6)
C1—C2—C7—C6	180.0 (5)		