

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

6-Methoxy-1,3-benzothiazol-2-amine

Aamer Saeed,^{a*} Hummera Rafique^a and Ulrich Flörke^b

^aDepartment of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan, and ^bDepartment Chemie, Fakultät für Naturwissenschaften, Universität Paderborn, Warburgerstrasse 100, D-33098 Paderborn, Germany.

Correspondence e-mail: aamersaeed@yahoo.com

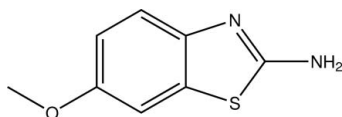
Received 13 June 2012; accepted 21 June 2012

Key indicators: single-crystal X-ray study; $T = 130$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.033; wR factor = 0.094; data-to-parameter ratio = 18.3.

The title compound, $\text{C}_8\text{H}_8\text{N}_2\text{OS}$, is almost planar, the C—C—O—C torsion angle associated with the methoxy group being 0.72 (1)°. Intermolecular amine N—H...N hydrogen-bonding interactions form inversion dimers [graph set $R_2^2(8)$] which are extended into chains along the b axis through amine N—H...O hydrogen bonds.

Related literature

For information on various important biological activities of aminobenzothiazoles, see: Hutchinson *et al.* (2002); Benavides *et al.* (1985); La'cova *et al.* (1991). For their pharmaceutical applications, see: Suter & Zutter (1967); Sawhney *et al.* (1978); Bensimon *et al.* (1994); Foscolos *et al.* (1977); Shirke *et al.* (1990); Paget *et al.* (1969); Domino *et al.* (1952). For antimicrobial and pesticidal activities, see: Pattan *et al.* (2002); Kaufmann (1935). For related structures see: Saeed *et al.* (2007); Sun *et al.* (2011). For graph-set analysis, see: Etter *et al.* (1990).



Experimental

Crystal data

$\text{C}_8\text{H}_8\text{N}_2\text{OS}$ $V = 1679.8$ (5) Å³
 $M_r = 180.23$ $Z = 8$
 Orthorhombic, $Pbca$ $\text{Mo } K\alpha$ radiation
 $a = 15.060$ (2) Å $\mu = 0.33$ mm⁻¹
 $b = 6.6997$ (11) Å $T = 130$ K
 $c = 16.649$ (3) Å $0.47 \times 0.23 \times 0.14$ mm

Data collection

Bruker SMART APEX CCD diffractometer 14745 measured reflections
 Absorption correction: multi-scan (SADABS; Sheldrick, 2004) 2010 independent reflections
 $T_{\min} = 0.859$, $T_{\max} = 0.955$ 1771 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$ 110 parameters
 $wR(F^2) = 0.094$ H-atom parameters constrained
 $S = 1.06$ $\Delta\rho_{\text{max}} = 0.40$ e Å⁻³
 2010 reflections $\Delta\rho_{\text{min}} = -0.20$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N2}-\text{H2A}\cdots\text{N1}^{\text{i}}$	0.88	2.13	2.9774 (16)	163
$\text{N2}-\text{H2B}\cdots\text{O1}^{\text{ii}}$	0.88	2.10	2.9655 (16)	170

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

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; 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: SHELXTL and local programs.

AS gratefully acknowledges a research grant from the Higher Education Commission of Pakistan under the project No. 4-279/PAK-US/HEC 2010-917 (Pakistan-US Science and Technology Cooperation Program).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZS2217).

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supporting information

Acta Cryst. (2012). E68, o2240 [https://doi.org/10.1107/S1600536812028152]

6-Methoxy-1,3-benzothiazol-2-amine

Aamer Saeed, Hummera Rafique and Ulrich Flörke

S1. Comment

2-Aminobenzothiazoles display a broad spectrum of important pharmaceutical applications and a number of derivatives are therapeutic agents for the treatment of various diseases e.g. diabetes (Suter & Zutter, 1967); inflammation (Sawhney *et al.*, 1978); amyotrophic lateral sclerosis (Bensimon *et al.*, 1994); analgesia (Foscolos *et al.*, 1977); tuberculosis (Shirke *et al.* 1990); viral infections (Paget *et al.*, 1969), and as central muscle relaxants (Domino *et al.*, 1952). Riluzole [6-(tri-fluoromethoxy)-2-benzothiazolamine] possesses potent anticonvulsant and neuroprotective effects (Benavides *et al.*, 1985). 6-Nitro or 6-amino 2-substituted benzothiazoles and fluorobenzothiazoles possess significant antimicrobial activity (Pattan *et al.*, 2002) and 6-ethoxy-2-amino benzothiazole is a strong local anesthetic agent (La'cova *et al.*, 1991).

The title compound, C₈H₈N₂OS, is almost planar (Fig. 1) with the C4—C5—O1—C8 torsion angle associated with the methoxy group = 0.72 (1)° and the amine hydrogen atoms lying in the molecular plane. Intermolecular amine N—H···N hydrogen-bonding interactions (Table 1) form centrosymmetric cyclic dimers [graph set R²₂(8): Etter *et al.*, 1990] which are extended into one-dimensional chains along the *b* axis, through amine N—H···O hydrogen bonds (Fig. 2).

S2. Experimental

A mixture of *p*-anisidine (3.7 g, 0.03 mol) and potassium thiocyanate (11.6 g, 0.12 mol) in AcOH (45 ml) was stirred at 20 °C for 10 minutes. A solution of bromine (1.5 ml, 0.03 mol) in AcOH (20 ml) was added over 20 min and the reaction mixture was stirred for 21 h at room temperature. The reaction mixture was poured into cold NH₄OH (90 ml) and extracted with EtOAc. The organic phase was washed with water, dried, filtered and evaporated. The crude product obtained was recrystallized using ethanol as solvent. Yield = 83%; m.p. = 145-147 °C; IR (KBr) 3389 (NH), 2733 (C-S), 1644 (C=N), 1585 (C=C), 1442 (C-N) cm⁻¹; ¹H NMR (CDCl₃, ? p.p.m.): 7.47 (1H, d, J = 8.7 Hz, H-1), 7.14 (1H, d, J = 2.4 Hz, H-2), 6.93 (1H, dd, J = 8.7, 2.4 Hz, H-3), 5.41 (1H, bs, -NH), 3.81 (3H, s, -OCH₃); ¹³C NMR (CDCl₃, ppm): 166.2 (S-C=N), 145.1 (C-9), 138.6 (C-6), 126.5 (C-8), 124.6 (C-4), 121.4 (C-5), 116.5 (C-7), 56.8 (-OCH₃); EIMS (70 eV): *m/z* (%); [M⁺] 180 (51%); Anal. Calcd. for C₈H₈N₂OS; C, 52.33; H, 4.44; N, 15.55; S, 17.77. Found: C, 52.26; H, 4.35; N, 15.37; S, 17.61..

S3. Refinement

Hydrogen atoms were clearly identified in difference syntheses, and were refined at idealized positions [C—N = 0.88 Å; C—H(aromatic) = 0.93 Å and C—H(methyl) = 0.96 Å], riding on the nitrogen or carbon atoms with isotropic displacement parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N}, \text{C}_{\text{ar}})$ or $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$. The hydrogen atoms were allowed to rotate but not to tip.

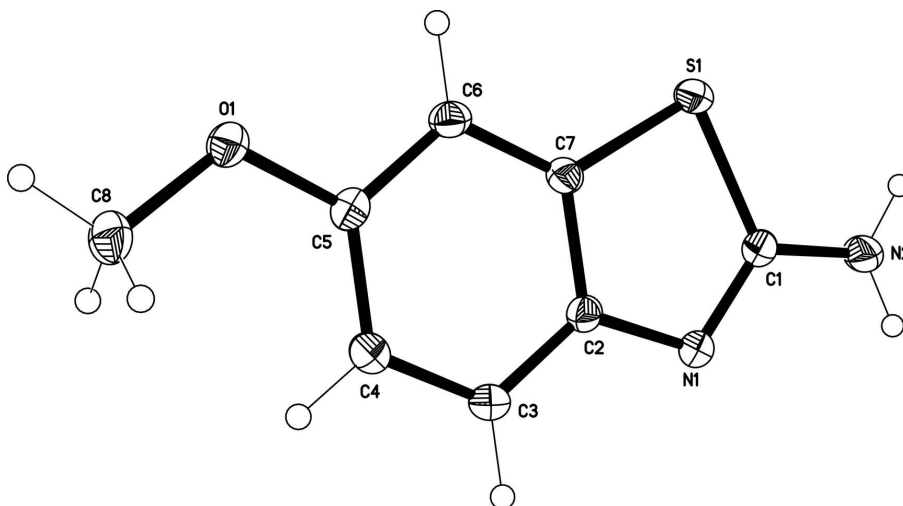


Figure 1

Molecular structure of title compound showing atom numbering scheme and displacement ellipsoids drawn at the 50% probability level.

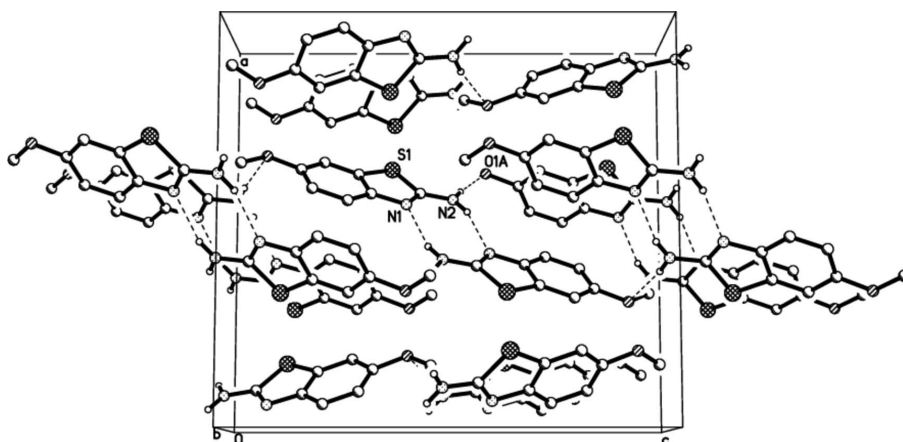


Figure 2

Crystal packing viewed along (010) with intermolecular hydrogen bonds indicated as dashed lines. H-atoms not involved in hydrogen bonding are omitted.

6-Methoxy-1,3-benzothiazol-2-amine

Crystal data

$C_8H_8N_2OS$

$M_r = 180.23$

Orthorhombic, *Pbca*

Hall symbol: $-P\ 2ac\ 2ab$

$a = 15.060\ (2)\ \text{\AA}$

$b = 6.6997\ (11)\ \text{\AA}$

$c = 16.649\ (3)\ \text{\AA}$

$V = 1679.8\ (5)\ \text{\AA}^3$

$Z = 8$

$F(000) = 752$

$D_x = 1.425\ \text{Mg m}^{-3}$

Melting point = 418–420 K

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3739 reflections

$\theta = 2.5\text{--}28.3^\circ$

$\mu = 0.33\ \text{mm}^{-1}$

$T = 130\ \text{K}$

Prism, colourless

$0.47 \times 0.23 \times 0.14\ \text{mm}$

Data collection

Bruker SMART APEX CCD diffractometer	14745 measured reflections
Radiation source: sealed tube	2010 independent reflections
Graphite monochromator	1771 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.029$
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	$\theta_{\text{max}} = 27.9^\circ$, $\theta_{\text{min}} = 2.5^\circ$
$T_{\text{min}} = 0.859$, $T_{\text{max}} = 0.955$	$h = -19 \rightarrow 19$
	$k = -8 \rightarrow 8$
	$l = -21 \rightarrow 20$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.033$	H-atom parameters constrained
$wR(F^2) = 0.094$	$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 0.5583P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
2010 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
110 parameters	$\Delta\rho_{\text{max}} = 0.40 \text{ e } \text{\AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.20 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.67080 (2)	0.21698 (5)	0.37026 (2)	0.02447 (13)
O1	0.68079 (6)	0.55013 (14)	0.09070 (6)	0.0234 (2)
N1	0.56180 (7)	0.50795 (17)	0.40573 (6)	0.0217 (2)
N2	0.58824 (8)	0.28778 (19)	0.51177 (7)	0.0292 (3)
H2A	0.5525	0.3536	0.5442	0.035*
H2B	0.6160	0.1805	0.5290	0.035*
C1	0.60027 (9)	0.3510 (2)	0.43608 (8)	0.0220 (3)
C2	0.58749 (8)	0.53507 (19)	0.32593 (8)	0.0191 (3)
C3	0.56017 (9)	0.6894 (2)	0.27627 (8)	0.0225 (3)
H3A	0.5211	0.7892	0.2962	0.027*
C4	0.58993 (9)	0.6982 (2)	0.19719 (8)	0.0220 (3)
H4A	0.5710	0.8036	0.1630	0.026*
C5	0.64762 (8)	0.55186 (19)	0.16817 (8)	0.0193 (3)
C6	0.67681 (8)	0.3964 (2)	0.21681 (8)	0.0209 (3)
H6A	0.7162	0.2973	0.1968	0.025*
C7	0.64648 (8)	0.39071 (19)	0.29540 (8)	0.0193 (3)

C8	0.65274 (10)	0.7074 (2)	0.03804 (9)	0.0281 (3)
H8A	0.5878	0.7068	0.0340	0.042*
H8B	0.6786	0.6867	-0.0153	0.042*
H8C	0.6726	0.8360	0.0595	0.042*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0272 (2)	0.0253 (2)	0.0208 (2)	0.00985 (13)	0.00107 (13)	0.00191 (12)
O1	0.0249 (5)	0.0256 (5)	0.0195 (5)	0.0008 (4)	0.0041 (4)	0.0015 (4)
N1	0.0242 (5)	0.0232 (5)	0.0177 (5)	0.0041 (4)	-0.0009 (4)	-0.0017 (4)
N2	0.0358 (7)	0.0314 (7)	0.0203 (6)	0.0133 (5)	0.0027 (5)	0.0039 (5)
C1	0.0220 (6)	0.0253 (7)	0.0187 (6)	0.0030 (5)	-0.0011 (5)	-0.0028 (5)
C2	0.0178 (6)	0.0215 (6)	0.0180 (6)	0.0010 (5)	-0.0013 (5)	-0.0027 (5)
C3	0.0230 (6)	0.0224 (6)	0.0223 (6)	0.0058 (5)	0.0005 (5)	-0.0014 (5)
C4	0.0220 (6)	0.0220 (6)	0.0220 (7)	0.0020 (5)	-0.0016 (5)	0.0017 (5)
C5	0.0177 (6)	0.0222 (6)	0.0181 (6)	-0.0034 (5)	0.0012 (5)	-0.0020 (5)
C6	0.0182 (6)	0.0217 (6)	0.0229 (7)	0.0026 (5)	0.0010 (5)	-0.0027 (5)
C7	0.0182 (6)	0.0196 (6)	0.0202 (6)	0.0018 (5)	-0.0027 (5)	-0.0012 (5)
C8	0.0339 (8)	0.0290 (8)	0.0213 (7)	-0.0006 (6)	0.0037 (6)	0.0052 (6)

Geometric parameters (Å, °)

S1—C7	1.7443 (13)	C3—C4	1.3920 (19)
S1—C1	1.7705 (14)	C3—H3A	0.9500
O1—C5	1.3832 (16)	C4—C5	1.3962 (18)
O1—C8	1.4342 (17)	C4—H4A	0.9500
N1—C1	1.3028 (18)	C5—C6	1.3908 (18)
N1—C2	1.3956 (17)	C6—C7	1.3864 (18)
N2—C1	1.3417 (18)	C6—H6A	0.9500
N2—H2A	0.8800	C8—H8A	0.9800
N2—H2B	0.8800	C8—H8B	0.9800
C2—C3	1.3864 (18)	C8—H8C	0.9800
C2—C7	1.4083 (18)		
C7—S1—C1	88.73 (6)	C5—C4—H4A	120.1
C5—O1—C8	117.23 (10)	O1—C5—C6	114.99 (11)
C1—N1—C2	110.55 (11)	O1—C5—C4	123.59 (12)
C1—N2—H2A	120.0	C6—C5—C4	121.42 (12)
C1—N2—H2B	120.0	C7—C6—C5	117.76 (12)
H2A—N2—H2B	120.0	C7—C6—H6A	121.1
N1—C1—N2	123.98 (13)	C5—C6—H6A	121.1
N1—C1—S1	115.86 (10)	C6—C7—C2	121.99 (12)
N2—C1—S1	120.15 (11)	C6—C7—S1	128.57 (10)
C3—C2—N1	125.63 (12)	C2—C7—S1	109.44 (10)
C3—C2—C7	118.96 (12)	O1—C8—H8A	109.5
N1—C2—C7	115.41 (11)	O1—C8—H8B	109.5
C2—C3—C4	120.01 (12)	H8A—C8—H8B	109.5

C2—C3—H3A	120.0	O1—C8—H8C	109.5
C4—C3—H3A	120.0	H8A—C8—H8C	109.5
C3—C4—C5	119.86 (12)	H8B—C8—H8C	109.5
C3—C4—H4A	120.1		
C2—N1—C1—N2	179.99 (13)	C3—C4—C5—C6	-0.3 (2)
C2—N1—C1—S1	-0.87 (15)	O1—C5—C6—C7	179.48 (11)
C7—S1—C1—N1	0.50 (11)	C4—C5—C6—C7	0.19 (19)
C7—S1—C1—N2	179.67 (12)	C5—C6—C7—C2	0.6 (2)
C1—N1—C2—C3	-178.88 (13)	C5—C6—C7—S1	-179.95 (10)
C1—N1—C2—C7	0.90 (17)	C3—C2—C7—C6	-1.2 (2)
N1—C2—C3—C4	-179.23 (12)	N1—C2—C7—C6	179.05 (12)
C7—C2—C3—C4	1.0 (2)	C3—C2—C7—S1	179.27 (10)
C2—C3—C4—C5	-0.3 (2)	N1—C2—C7—S1	-0.53 (15)
C8—O1—C5—C6	180.00 (11)	C1—S1—C7—C6	-179.51 (13)
C8—O1—C5—C4	-0.72 (18)	C1—S1—C7—C2	0.04 (10)
C3—C4—C5—O1	-179.55 (12)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N2—H2 <i>A</i> \cdots N1 ⁱ	0.88	2.13	2.9774 (16)	163
N2—H2 <i>B</i> \cdots O1 ⁱⁱ	0.88	2.10	2.9655 (16)	170

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