

4,5,6,7-Tetrahydrobenzo[*d*]thiazol-2-amine

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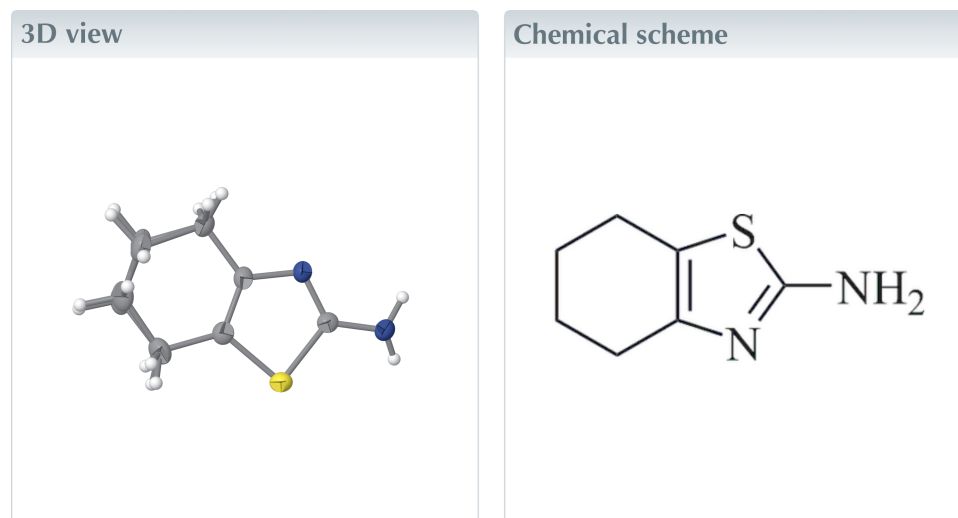
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Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, C₇H₁₀N₂S, the six-membered ring is disordered over two half-chair orientations. In the crystal, infinite [001] chains linked by N—H···N hydrogen bonds occur.



Structure description

Because of its many pharmacological uses, thiazole makes an excellent pharmacophore nucleus. Various biological properties such as antioxidant (Petrou *et al.*, 2021) and analgesic (Ye *et al.*, 2013) activities are exhibited by its derivatives. As part of our studies in this area we now report the synthesis and structure of the title compound, C₇H₁₀N₂S (Fig. 1).

As expected, the N atom of thiazole ring demonstrates noticeable inequality of C—N bond distances [1.391 (2) for C3—N1 *versus* 1.303 (2) Å for C1=N1] corresponding to the presence of single and double bonds. The C2=C3 double bond is clearly shorter [1.344 (3) Å] than the other bonds in six-membered ring. The cyclohexene ring is partially disordered (C5 and C6 and their attached H atoms) over two half-chair orientations with very unequal [0.919 (4) *versus* 0.081 (4)] occupancies.

In the extended structure, the molecules are linked by strong N2—H2B···N1 hydrogen bonds (Table 1, Fig. 2) between the amino group of one molecule and the thiazole N atom of another molecule to generate infinite chains running along the crystallographic *c*-axis direction. Weaker N2—H2A···N1 bonds reinforce the chains.

A total of 40 structures containing a 4,5,6,7-tetrahydrobenzo[*d*]thiazol-2-amine core were found in a search of the Cambridge Structural Database (CSD, Version 5.45, update of March 2024; Groom *et al.*, 2016). Excluding compounds with conjugated fragments and protonated salts one may find only five derivatives, namely: 6-nitro-5-phenyl-*N,N*-bis-

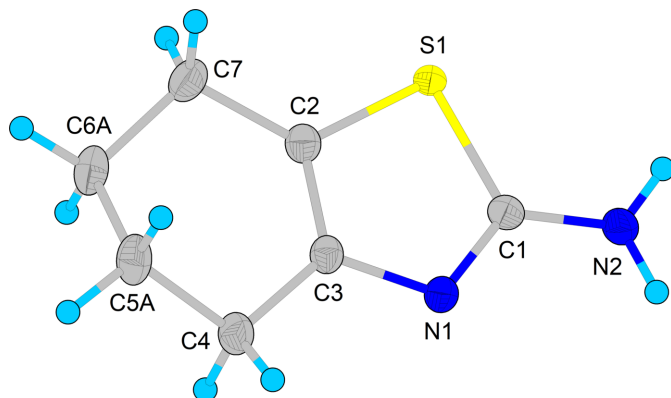


Figure 1
The molecular structure of **I** with displacement ellipsoids drawn at 50% probability. Only the major disorder component for the C5 and C6 methylene groups is shown.

(propan-2-yl)-4,5,6,7-tetrahydro-1,3-benzothiazol-2-amine (Richter *et al.*, 2018), *N*-(6-hydroxy-4,5,6,7-tetrahydro-1,3-benzothiazol-2-yl)acetamide monohydrate and *N*-(6-hydroxy-4,5,6,7-tetrahydro-1,3-benzothiazol-2-yl)acetamide (Ciceri *et al.*, 2020), 2-amino-4,4,7,7-tetramethyl-4,5,6,7-tetrahydro-1,3-benzothiazol-3-ium 4,4,7,7-tetramethyl-4,5,6,7-tetrahydro-1,3-benzothiazol-2-amine 3-carboxypropanoate (Shaibah *et al.*, 2019) and 3-(4-methoxyphenyl)-2-(4,5,6,7-tetrahydro-1,3-benzothiazol-2-yl)prop-2-enitrile (Dyachenko *et al.*, 2021).

Synthesis and crystallization

61.13 mmol of thiourea (4.65 g) and 30.57 mmol (7.76 g) of iodine were mixed in a round-bottom flask. Then, 30.57 mmol (3 g) of cyclohexanone was added and the mixture was refluxed for 24 h at 100 °C. After 24 h, the system was taken out of the oil bath and left to cool to room temperature, meanwhile 350 ml of distilled water was heated to boiling and used in portions to dissolve the reaction mass, and everything

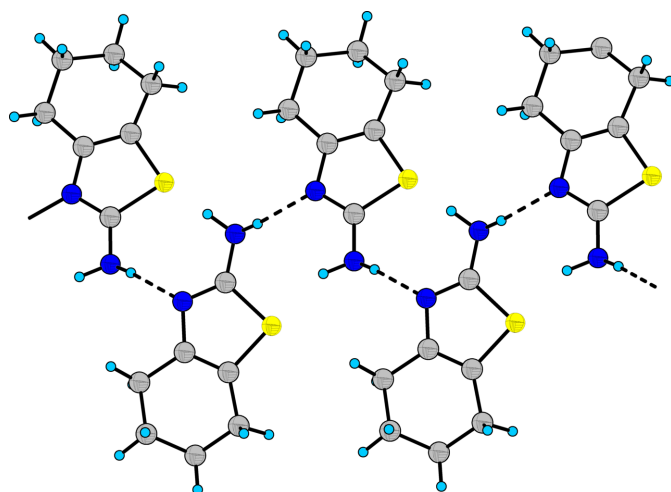


Figure 2
Fragment of a [001] chain of molecules linked by N–H...N hydrogen bonds in the crystal structure of **I**.

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

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N2–H2 <i>A</i> ...N1 ⁱ	0.93 (2)	2.56 (2)	3.392 (2)	149 (2)
N2–H2 <i>B</i> ...N1 ⁱⁱ	0.81 (2)	2.13 (2)	2.941 (2)	175 (2)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₇ H ₁₀ N ₂ S
<i>M</i> _r	154.23
Crystal system, space group	Orthorhombic, <i>Pccn</i>
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.4368 (6), 13.3928 (6), 8.0734 (4)
<i>V</i> (Å ³)	1560.99 (12)
<i>Z</i>	8
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	3.05
Crystal size (mm)	0.42 × 0.13 × 0.09
Data collection	
Diffractometer	New Gemini, Dual, Cu at home/ near, Atlas
Absorption correction	Analytical (<i>CrysAlis PRO</i> ; Rigaku OD, 2024)
<i>T</i> _{min} , <i>T</i> _{max}	0.484, 0.782
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	4399, 1606, 1284
<i>R</i> _{int}	0.037
(sin θ/ <i>λ</i>) _{max} (Å ⁻¹)	0.630
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.036, 0.101, 1.00
No. of reflections	1606
No. of parameters	106
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.28, -0.23

Computer programs: *CrysAlis PRO* (Rigaku OD, 2024), *SHELXT2014/4* (Sheldrick, 2015a), *SHELXL2016/6* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

was transferred to a crystallizing dish and left to cool to room temperature. Then, three extractions were made with 55 ml of diethyl ether to remove the unreacted ketone, I₂ and sulfur. Next, 50 ml of NH₄OH (25%) solution was added to the aqueous solution, and three extractions were made with diethyl ether (55 ml): the ethereal layers were combined, and dried over MgSO₄. After drying the organic layer was evaporated on a rotavapor. The product was obtained as a light-yellow precipitate. Colourless prisms were recrystallized from *n*-hexane solution. The reaction scheme is shown in Fig. 3.

FTIR (ATR/cm⁻¹): 3430–3250 (NH₂, stretching), 2850–2950 (CH₂, asymmetric stretching). 3430 (NH₂, asymmetric stretching), 3250 (NH₂, symmetric stretching), 3150, 3100,



Figure 3
Reaction scheme.

3050 (CH, aromatic stretching), 1650 (NH₂, bending deformations). ¹³C-NMR(δ/p.p.m.): 165.86, 145.35, 114.96, 26.75, 23.72, 23.17, 23.04. ¹H-NMR (DMSO-*d*₆, δ/p.p.m.): 6.58 (2*H*, *s*), 2.51 (2*H*, *t*), 2.50 (2*H*, *t*), 2.48 (4*H*, *m*). Elemental analysis: calculated C 54.51; H 6.54; N,18.16. Found: C 54.75; H 7.04; N 18.32. TOF MS ES+(*m/e*): 155 [*M* + H]⁺, 177 [*M* + Na]⁺.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

IUCrData (2025). **10**, x250913 [<https://doi.org/10.1107/S2414314625009137>]

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Crystal data

$C_7H_{10}N_2S$

$M_r = 154.23$

Orthorhombic, *Pccn*

$a = 14.4368$ (6) Å

$b = 13.3928$ (6) Å

$c = 8.0734$ (4) Å

$V = 1560.99$ (12) Å³

$Z = 8$

$F(000) = 656$

$D_x = 1.313$ Mg m⁻³

Cu *Kα* radiation, $\lambda = 1.54184$ Å

Cell parameters from 2022 reflections

$\theta = 4.5$ – 75.3°

$\mu = 3.05$ mm⁻¹

$T = 150$ K

Prism, colourless

$0.42 \times 0.13 \times 0.09$ mm

Data collection

New Gemini, Dual, Cu at home/near, Atlas diffractometer

Radiation source: fine-focus sealed X-ray tube,

Enhance (Cu) X-ray Source

Graphite monochromator

Detector resolution: 10.6426 pixels mm⁻¹

ω scans

Absorption correction: analytical

(CrysAlisPro; Rigaku OD, 2024)

$T_{\min} = 0.484$, $T_{\max} = 0.782$

4399 measured reflections

1606 independent reflections

1284 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$

$\theta_{\max} = 76.2^\circ$, $\theta_{\min} = 4.5^\circ$

$h = -17 \rightarrow 18$

$k = -14 \rightarrow 16$

$l = -9 \rightarrow 7$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.101$

$S = 1.00$

1606 reflections

106 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2 + 0.0974P]$

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

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

$\Delta\rho_{\max} = 0.28$ e Å⁻³

$\Delta\rho_{\min} = -0.23$ e Å⁻³

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. 1. Fixed Uiso At 1.2 times of: All C(H,H) groups, All C(H,H,H,H) groups 2. Uiso/Uanis restraints and constraints Uanis(C5B) = Uanis(C5A) Uanis(C6B) = Uanis(C6A) 3. Others

Sof(H4BC)=Sof(H4BD)=Sof(C5B)=Sof(H5BA)=Sof(H5BB)=Sof(C6B)=Sof(H6BA)=Sof(H6BB)=
Sof(H7BC)=Sof(H7BD)=1-FVAR(1)

Sof(H4AA)=Sof(H4AB)=Sof(C5A)=Sof(H5AA)=Sof(H5AB)=Sof(C6A)=Sof(H6AA)=Sof(H6AB)=

Sof(H7AA)=Sof(H7AB)=FVAR(1) 4.a Secondary CH2 refined with riding coordinates: C4(H4AA,H4AB),
C4(H4BC,H4BD), C5A(H5AA,H5AB), C5B(H5BA,H5BB), C6A(H6AA,H6AB), C6B(H6BA,H6BB),
C7(H7AA,H7AB), C7(H7BC,H7BD)

The hydrogen atoms of the amino group were localized in difference Fourier maps and refined freely. Other H-atoms were placed at calculated positions and refined as riding atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
S1	0.58597 (3)	0.40079 (3)	0.15755 (6)	0.02956 (17)	
N1	0.65849 (10)	0.36334 (11)	0.44247 (18)	0.0258 (3)	
N2	0.63974 (11)	0.22015 (11)	0.2777 (2)	0.0287 (3)	
H2A	0.6776 (17)	0.1863 (19)	0.352 (3)	0.038 (6)*	
H2B	0.6455 (17)	0.2007 (18)	0.183 (3)	0.035 (6)*	
C1	0.63374 (11)	0.31960 (13)	0.3052 (2)	0.0240 (3)	
C2	0.60279 (12)	0.49990 (13)	0.2947 (2)	0.0268 (4)	
C3	0.64083 (11)	0.46534 (12)	0.4353 (2)	0.0244 (3)	
C4	0.66431 (13)	0.53193 (13)	0.5791 (2)	0.0319 (4)	
H4AA	0.724328	0.511269	0.627540	0.038*	0.919 (4)
H4AB	0.616144	0.525577	0.665786	0.038*	0.919 (4)
H4BC	0.732233	0.540469	0.588221	0.038*	0.081 (4)
H4BD	0.640952	0.502830	0.683839	0.038*	0.081 (4)
C5A	0.67030 (17)	0.64067 (15)	0.5214 (3)	0.0369 (5)	0.919 (4)
H5AA	0.673707	0.685204	0.619040	0.044*	0.919 (4)
H5AB	0.727418	0.650166	0.455371	0.044*	0.919 (4)
C5B	0.615 (2)	0.6383 (18)	0.543 (4)	0.0369 (5)	0.081 (4)
H5BA	0.546954	0.631106	0.557296	0.044*	0.081 (4)
H5BB	0.636943	0.688128	0.624377	0.044*	0.081 (4)
C6A	0.58632 (17)	0.66856 (16)	0.4168 (3)	0.0375 (6)	0.919 (4)
H6AA	0.589342	0.740445	0.388740	0.045*	0.919 (4)
H6AB	0.529217	0.657193	0.482040	0.045*	0.919 (4)
C6B	0.635 (2)	0.6745 (18)	0.373 (4)	0.0375 (6)	0.081 (4)
H6BA	0.701811	0.671058	0.350239	0.045*	0.081 (4)
H6BB	0.613909	0.744546	0.360579	0.045*	0.081 (4)
C7	0.58170 (14)	0.60702 (14)	0.2562 (3)	0.0351 (4)	
H7AA	0.519122	0.612469	0.206832	0.042*	0.919 (4)
H7AB	0.627174	0.633060	0.175189	0.042*	0.919 (4)
H7BC	0.514371	0.619176	0.267818	0.042*	0.081 (4)
H7BD	0.599574	0.622040	0.140437	0.042*	0.081 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0339 (3)	0.0302 (3)	0.0246 (3)	0.00217 (16)	-0.00544 (16)	-0.00116 (16)

N1	0.0307 (7)	0.0205 (7)	0.0261 (7)	-0.0012 (5)	-0.0006 (6)	-0.0002 (5)
N2	0.0369 (8)	0.0238 (7)	0.0254 (8)	-0.0029 (6)	-0.0002 (6)	-0.0022 (6)
C1	0.0226 (7)	0.0263 (8)	0.0231 (8)	-0.0018 (6)	0.0015 (6)	0.0001 (6)
C2	0.0246 (7)	0.0264 (9)	0.0293 (9)	0.0007 (6)	0.0016 (6)	-0.0011 (7)
C3	0.0238 (7)	0.0212 (7)	0.0282 (8)	-0.0008 (6)	0.0031 (6)	-0.0007 (6)
C4	0.0377 (9)	0.0239 (8)	0.0340 (10)	-0.0003 (7)	-0.0045 (7)	-0.0050 (7)
C5A	0.0385 (13)	0.0227 (9)	0.0494 (13)	-0.0015 (8)	-0.0033 (10)	-0.0075 (9)
C5B	0.0385 (13)	0.0227 (9)	0.0494 (13)	-0.0015 (8)	-0.0033 (10)	-0.0075 (9)
C6A	0.0382 (12)	0.0255 (9)	0.0489 (14)	0.0074 (9)	0.0026 (10)	-0.0016 (9)
C6B	0.0382 (12)	0.0255 (9)	0.0489 (14)	0.0074 (9)	0.0026 (10)	-0.0016 (9)
C7	0.0362 (9)	0.0293 (9)	0.0398 (11)	0.0080 (7)	-0.0002 (8)	0.0061 (8)

Geometric parameters (Å, °)

S1—C1	1.7548 (17)	C5A—H5AA	0.9900
S1—C2	1.7453 (18)	C5A—H5AB	0.9900
N1—C1	1.303 (2)	C5A—C6A	1.524 (3)
N1—C3	1.391 (2)	C5B—H5BA	0.9900
N2—H2A	0.93 (3)	C5B—H5BB	0.9900
N2—H2B	0.81 (3)	C5B—C6B	1.48 (4)
N2—C1	1.353 (2)	C6A—H6AA	0.9900
C2—C3	1.344 (3)	C6A—H6AB	0.9900
C2—C7	1.499 (2)	C6A—C7	1.538 (3)
C3—C4	1.503 (2)	C6B—H6BA	0.9900
C4—H4AA	0.9900	C6B—H6BB	0.9900
C4—H4AB	0.9900	C6B—C7	1.51 (3)
C4—H4BC	0.9900	C7—H7AA	0.9900
C4—H4BD	0.9900	C7—H7AB	0.9900
C4—C5A	1.532 (3)	C7—H7BC	0.9900
C4—C5B	1.62 (3)	C7—H7BD	0.9900
C2—S1—C1	89.19 (8)	C6A—C5A—H5AB	109.5
C1—N1—C3	110.86 (15)	C4—C5B—H5BA	109.3
H2A—N2—H2B	113 (2)	C4—C5B—H5BB	109.3
C1—N2—H2A	114.4 (16)	H5BA—C5B—H5BB	108.0
C1—N2—H2B	118.6 (18)	C6B—C5B—C4	112 (2)
N1—C1—S1	114.00 (13)	C6B—C5B—H5BA	109.3
N1—C1—N2	124.38 (16)	C6B—C5B—H5BB	109.3
N2—C1—S1	121.56 (14)	C5A—C6A—H6AA	109.3
C3—C2—S1	109.32 (13)	C5A—C6A—H6AB	109.3
C3—C2—C7	126.01 (17)	C5A—C6A—C7	111.73 (18)
C7—C2—S1	124.62 (15)	H6AA—C6A—H6AB	107.9
N1—C3—C4	120.63 (16)	C7—C6A—H6AA	109.3
C2—C3—N1	116.63 (16)	C7—C6A—H6AB	109.3
C2—C3—C4	122.73 (16)	C5B—C6B—H6BA	110.4
C3—C4—H4AA	109.7	C5B—C6B—H6BB	110.4
C3—C4—H4AB	109.7	C5B—C6B—C7	107 (2)
C3—C4—H4BC	110.4	H6BA—C6B—H6BB	108.6

C3—C4—H4BD	110.4	C7—C6B—H6BA	110.4
C3—C4—C5A	109.98 (16)	C7—C6B—H6BB	110.4
C3—C4—C5B	106.4 (10)	C2—C7—C6A	109.22 (17)
H4AA—C4—H4AB	108.2	C2—C7—C6B	109.8 (10)
H4BC—C4—H4BD	108.6	C2—C7—H7AA	109.8
C5A—C4—H4AA	109.7	C2—C7—H7AB	109.8
C5A—C4—H4AB	109.7	C2—C7—H7BC	109.7
C5B—C4—H4BC	110.4	C2—C7—H7BD	109.7
C5B—C4—H4BD	110.4	C6A—C7—H7AA	109.8
C4—C5A—H5AA	109.5	C6A—C7—H7AB	109.8
C4—C5A—H5AB	109.5	C6B—C7—H7BC	109.7
H5AA—C5A—H5AB	108.0	C6B—C7—H7BD	109.7
C6A—C5A—C4	110.91 (18)	H7AA—C7—H7AB	108.3
C6A—C5A—H5AA	109.5	H7BC—C7—H7BD	108.2

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

<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	0.93 (2)	2.56 (2)	3.392 (2)	149 (2)
N2—H2 <i>B</i> \cdots N1 ⁱⁱ	0.81 (2)	2.13 (2)	2.941 (2)	175 (2)

Symmetry codes: (i) $-x+3/2, -y+1/2, z$; (ii) $x, -y+1/2, z-1/2$.