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1-Ethyl-4-phenyl-1,5-benzodiazepine-2-thione

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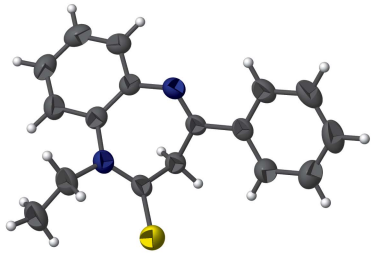
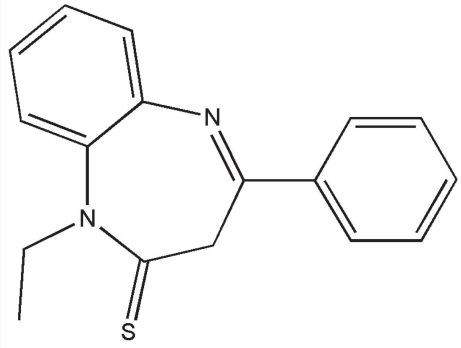
In the title compound, $C_{17}H_{16}N_2S$, the seven-membered ring adopts a boat conformation. The two aromatic rings are inclined at an angle of 34.7 (1)° to one another. The molecules pack in helical chains running along the *c*-axis direction through C—H···S hydrogen bonds. These are further linked into layers parallel to (100) by weak C—H···π(ring) interactions. The structure was refined as a two-component inversion twin.

3D view



Chemical scheme



Structure description

1,5-Benzodiazepines have attracted attention as an important class of heterocyclic molecules in medicinal chemistry as drugs and pharmaceuticals. They are widely used as anticonvulsant (Narayana *et al.*, 2006), anti-HIV-1 (Di Braccio *et al.*, 2001), antimicrobial (Kumar & Joshi, 2007) and antitumor agents (Kamal *et al.*, 2008). They are also employed as intermediates in the syntheses of several heterocyclic compounds (Minnih *et al.*, 2014; Ahabchane *et al.*, 1999).

The dihedral angle between the mean planes of the C1–C6 and C10–C15 aromatic rings is 34.7 (1) Å. Puckering analysis of the seven-membered ring (Fig. 1) gave the parameters $Q(1)$ = 0.876 (3) Å, $Q(3)$ = 0.239 (3) Å, $\varphi(2)$ = 206.8 (2)° and $\varphi(3)$ = 308.0 (7) and a total puckering amplitude of 0.908 (3) Å. This ring is in a boat conformation.

In the crystal, molecules form helical chains running along the *c*-axis direction through C13—H13···S1 hydrogen bonds (Table 1, Figs. 2 and 3). These chains are linked into layers parallel to (100) by weak C8—H8*B*···π(ring) interactions (Table 1, and Figs. 2 and 3).

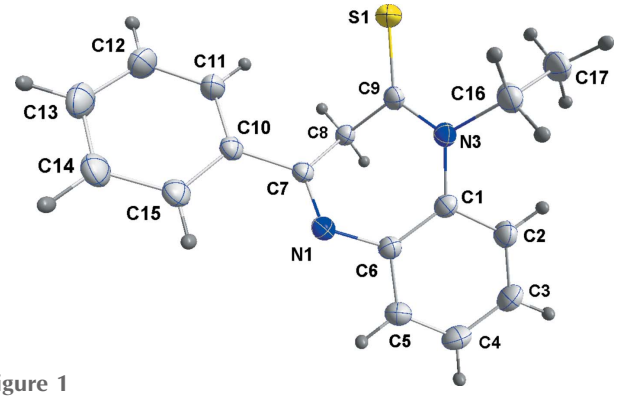


Figure 1
The title molecule with labeling scheme and 25% probability ellipsoids.

Synthesis and crystallization

To a solution of 1-ethyl-4-phenyl-1,5-benzodiazepin-2-one (0.80 g, 3.04 mmol) in 20 ml of pyridine was added phosphorus pentasulfide (0.84 g, 3.65 mmol). The mixture was refluxed for 4 h and the solvent was then evaporated under reduced pressure. The precipitate formed was washed with hot water. The residue obtained was crystallized from ethanol to afford crystals of the title compound.

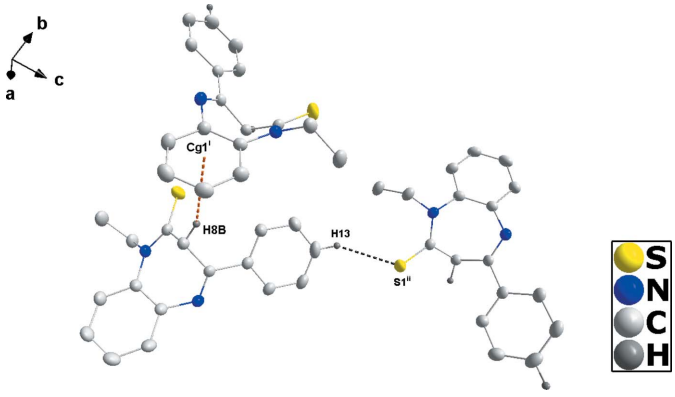


Figure 2
Detail of the intermolecular interactions [symmetry codes: (i) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $\frac{3}{2}-x, 2-y, \frac{1}{2}+z$], with the C—H···S and C—H···π(ring) interactions shown, respectively, as black and orange dashed lines.

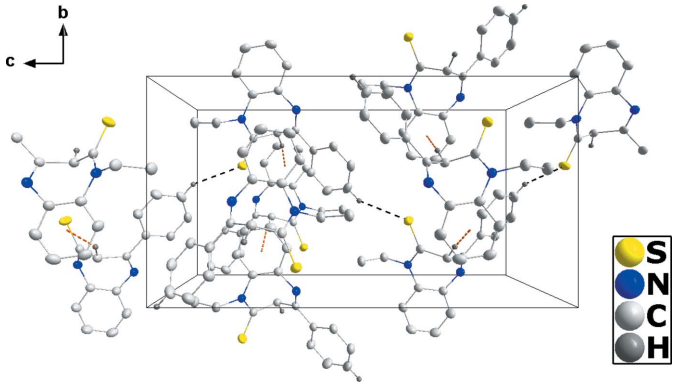


Figure 3
Packing viewed along the *a* axis. The depiction of the intermolecular interactions is the same as in Fig. 2.

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

*Cg*1 is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8*B*···*Cg*1^{i}	0.97	2.92	3.810 (3)	154
C13—H13···S1^{ii}	0.97	2.86	3.706 (4)	152

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{17}H_{16}N_2S$
M_r	280.38
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	296
a, *b*, *c* (Å)	8.4001 (8), 9.6239 (9), 18.0037 (18)
V (Å^3)	1455.5 (2)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.21
Crystal size (mm)	0.32 × 0.14 × 0.05
Data collection	
Diffractometer	Bruker SMART APEX CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.83, 0.99
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13778, 3544, 2226
R_{int}	0.050
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.045, 0.117, 1.02
No. of reflections	3544
No. of parameters	183
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.14
Absolute structure	Refined as an inversion twin
Absolute structure parameter	0.44 (13)

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The structure was refined as a two-component inversion twin.

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x161998 [https://doi.org/10.1107/S2414314616019982]

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1-Ethyl-4-phenyl-1,5-benzodiazepine-2-thione

Crystal data

$C_{17}H_{16}N_2S$
M_r = 280.38
Orthorhombic, $P2_12_12_1$
a = 8.4001 (8) Å
b = 9.6239 (9) Å
c = 18.0037 (18) Å
V = 1455.5 (2) Å^3
Z = 4
F(000) = 592
D_x = 1.280 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2911 reflections
θ = 2.3–21.0°
μ = 0.21 mm^{-1}
T = 296 K
Plate, colourless
0.32 × 0.14 × 0.05 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
T_{min} = 0.83, T_{max} = 0.99
13778 measured reflections
3544 independent reflections
2226 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
θ_{max} = 28.3°, θ_{min} = 2.3°
h = −11→11
k = −12→12
l = −23→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.117
S = 1.02
3544 reflections
183 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
$w = 1/[\sigma^2(F_o^2) + (0.0489P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Absolute structure: Refined as an inversion twin
Absolute structure parameter: 0.44 (13)

Special details

Experimental. The diffraction data were collected in three sets of 363 frames (0.5° width in ω) at φ = 0, 120 and 240°. A scan time of 40 sec/frame was used.

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. H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 - 0.98 Å). All were included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms. Refined as a 2-component inversion twin.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.64858 (14)	0.84588 (9)	0.15748 (5)	0.0727 (3)
N1	0.8093 (3)	0.5444 (3)	0.32883 (13)	0.0490 (6)
N3	0.7707 (3)	0.5908 (2)	0.16493 (13)	0.0463 (6)
C1	0.7918 (3)	0.4569 (3)	0.19853 (16)	0.0458 (7)
C2	0.8075 (4)	0.3419 (3)	0.15237 (17)	0.0557 (8)
H2	0.8015	0.3544	0.1012	0.067*
C3	0.8313 (4)	0.2110 (3)	0.17968 (19)	0.0595 (9)
H3	0.8395	0.1358	0.1474	0.071*
C4	0.8432 (4)	0.1910 (4)	0.2555 (2)	0.0634 (9)
H4	0.8578	0.1024	0.2749	0.076*
C5	0.8330 (4)	0.3037 (3)	0.30166 (18)	0.0583 (9)
H5	0.8445	0.2902	0.3525	0.070*
C6	0.8063 (3)	0.4371 (3)	0.27555 (16)	0.0459 (7)
C7	0.7116 (3)	0.6452 (3)	0.32402 (14)	0.0419 (7)
C8	0.5878 (3)	0.6491 (3)	0.26317 (14)	0.0444 (7)
H8A	0.5381	0.5587	0.2577	0.053*
H8B	0.5060	0.7168	0.2748	0.053*
C9	0.6724 (4)	0.6887 (3)	0.19329 (15)	0.0463 (7)
C10	0.7243 (3)	0.7615 (3)	0.37858 (15)	0.0444 (7)
C11	0.6384 (4)	0.8824 (3)	0.37030 (17)	0.0600 (9)
H11	0.5703	0.8926	0.3299	0.072*
C12	0.6525 (5)	0.9886 (4)	0.4214 (2)	0.0727 (10)
H12	0.5944	1.0700	0.4150	0.087*
C13	0.7510 (5)	0.9753 (4)	0.4813 (2)	0.0733 (11)
H13	0.7582	1.0461	0.5162	0.088*
C14	0.8403 (5)	0.8549 (4)	0.48946 (16)	0.0657 (9)
H14	0.9092	0.8459	0.5296	0.079*
C15	0.8274 (4)	0.7485 (3)	0.43846 (15)	0.0551 (8)
H15	0.8878	0.6682	0.4442	0.066*
C16	0.8645 (4)	0.6230 (3)	0.09777 (15)	0.0586 (9)
H16A	0.9555	0.5611	0.0961	0.070*

H16B	0.9049	0.7171	0.1021	0.070*
C17	0.7743 (5)	0.6106 (4)	0.02465 (17)	0.0767 (12)
H17A	0.8460	0.6265	−0.0160	0.115*
H17B	0.6903	0.6782	0.0233	0.115*
H17C	0.7296	0.5191	0.0205	0.115*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.1136 (8)	0.0476 (5)	0.0567 (5)	0.0110 (5)	0.0115 (5)	0.0089 (4)
N1	0.0552 (15)	0.0485 (14)	0.0431 (13)	0.0009 (13)	−0.0045 (12)	0.0021 (11)
N3	0.0532 (14)	0.0441 (14)	0.0416 (13)	−0.0043 (11)	0.0024 (12)	−0.0025 (11)
C1	0.0447 (17)	0.0413 (15)	0.0515 (17)	−0.0010 (15)	−0.0002 (14)	−0.0027 (14)
C2	0.063 (2)	0.0537 (18)	0.0505 (16)	0.0001 (17)	0.0022 (16)	−0.0089 (16)
C3	0.0574 (19)	0.0484 (18)	0.073 (2)	0.0050 (16)	0.0027 (18)	−0.0126 (16)
C4	0.059 (2)	0.048 (2)	0.083 (2)	0.0093 (18)	0.002 (2)	0.0082 (16)
C5	0.061 (2)	0.057 (2)	0.0566 (19)	0.0122 (18)	−0.0054 (18)	0.0058 (15)
C6	0.0458 (17)	0.0451 (17)	0.0470 (17)	0.0041 (14)	−0.0011 (13)	−0.0007 (13)
C7	0.0493 (17)	0.0406 (15)	0.0357 (14)	−0.0022 (14)	0.0014 (12)	0.0042 (13)
C8	0.0477 (17)	0.0422 (16)	0.0434 (15)	−0.0016 (14)	−0.0009 (13)	−0.0019 (14)
C9	0.0539 (18)	0.0478 (17)	0.0373 (14)	−0.0023 (15)	−0.0051 (14)	−0.0025 (12)
C10	0.0495 (17)	0.0470 (17)	0.0367 (14)	−0.0047 (14)	0.0036 (14)	0.0024 (13)
C11	0.074 (2)	0.055 (2)	0.0511 (17)	0.0073 (18)	−0.0063 (16)	−0.0062 (14)
C12	0.088 (3)	0.059 (2)	0.071 (2)	0.010 (2)	0.000 (2)	−0.0149 (18)
C13	0.100 (3)	0.069 (3)	0.050 (2)	−0.017 (2)	0.008 (2)	−0.0172 (19)
C14	0.084 (2)	0.073 (2)	0.0404 (16)	−0.016 (2)	−0.0088 (17)	0.0011 (17)
C15	0.068 (2)	0.0562 (19)	0.0408 (15)	−0.0064 (18)	−0.0014 (17)	0.0056 (14)
C16	0.073 (2)	0.060 (2)	0.0430 (16)	−0.0084 (18)	0.0098 (15)	−0.0030 (15)
C17	0.116 (3)	0.071 (3)	0.0430 (18)	−0.006 (2)	0.007 (2)	−0.0023 (17)

Geometric parameters (Å, º)

S1—C9	1.657 (3)	C8—H8A	0.9700
N1—C7	1.274 (3)	C8—H8B	0.9700
N1—C6	1.409 (4)	C10—C11	1.377 (4)
N3—C9	1.353 (4)	C10—C15	1.389 (4)
N3—C1	1.434 (4)	C11—C12	1.380 (4)
N3—C16	1.476 (4)	C11—H11	0.9300
C1—C2	1.391 (4)	C12—C13	1.364 (5)
C1—C6	1.405 (4)	C12—H12	0.9300
C2—C3	1.367 (4)	C13—C14	1.388 (5)
C2—H2	0.9300	C13—H13	0.9300
C3—C4	1.383 (5)	C14—C15	1.380 (4)
C3—H3	0.9300	C14—H14	0.9300
C4—C5	1.368 (5)	C15—H15	0.9300
C4—H4	0.9300	C16—C17	1.524 (4)
C5—C6	1.386 (4)	C16—H16A	0.9700
C5—H5	0.9300	C16—H16B	0.9700

C7—C10	1.493 (4)	C17—H17A	0.9600
C7—C8	1.511 (4)	C17—H17B	0.9600
C8—C9	1.494 (4)	C17—H17C	0.9600
C7—N1—C6	120.0 (2)	N3—C9—S1	124.2 (2)
C9—N3—C1	122.8 (2)	C8—C9—S1	120.2 (2)
C9—N3—C16	119.3 (2)	C11—C10—C15	119.1 (3)
C1—N3—C16	117.9 (2)	C11—C10—C7	121.7 (3)
C2—C1—C6	118.3 (3)	C15—C10—C7	119.2 (3)
C2—C1—N3	118.4 (3)	C10—C11—C12	120.6 (3)
C6—C1—N3	123.3 (2)	C10—C11—H11	119.7
C3—C2—C1	122.2 (3)	C12—C11—H11	119.7
C3—C2—H2	118.9	C13—C12—C11	120.6 (3)
C1—C2—H2	118.9	C13—C12—H12	119.7
C2—C3—C4	119.6 (3)	C11—C12—H12	119.7
C2—C3—H3	120.2	C12—C13—C14	119.4 (3)
C4—C3—H3	120.2	C12—C13—H13	120.3
C5—C4—C3	119.0 (3)	C14—C13—H13	120.3
C5—C4—H4	120.5	C15—C14—C13	120.4 (3)
C3—C4—H4	120.5	C15—C14—H14	119.8
C4—C5—C6	122.6 (3)	C13—C14—H14	119.8
C4—C5—H5	118.7	C14—C15—C10	119.9 (3)
C6—C5—H5	118.7	C14—C15—H15	120.0
C5—C6—C1	118.3 (3)	C10—C15—H15	120.0
C5—C6—N1	116.4 (3)	N3—C16—C17	115.2 (3)
C1—C6—N1	125.0 (2)	N3—C16—H16A	108.5
N1—C7—C10	118.7 (2)	C17—C16—H16A	108.5
N1—C7—C8	120.8 (2)	N3—C16—H16B	108.5
C10—C7—C8	120.5 (2)	C17—C16—H16B	108.5
C9—C8—C7	106.8 (2)	H16A—C16—H16B	107.5
C9—C8—H8A	110.4	C16—C17—H17A	109.5
C7—C8—H8A	110.4	C16—C17—H17B	109.5
C9—C8—H8B	110.4	H17A—C17—H17B	109.5
C7—C8—H8B	110.4	C16—C17—H17C	109.5
H8A—C8—H8B	108.6	H17A—C17—H17C	109.5
N3—C9—C8	115.5 (2)	H17B—C17—H17C	109.5
C9—N3—C1—C2	141.7 (3)	C1—N3—C9—C8	0.8 (4)
C16—N3—C1—C2	−40.1 (4)	C16—N3—C9—C8	−177.4 (3)
C9—N3—C1—C6	−41.9 (4)	C1—N3—C9—S1	178.2 (2)
C16—N3—C1—C6	136.3 (3)	C16—N3—C9—S1	0.0 (4)
C6—C1—C2—C3	2.0 (5)	C7—C8—C9—N3	70.5 (3)
N3—C1—C2—C3	178.6 (3)	C7—C8—C9—S1	−107.0 (3)
C1—C2—C3—C4	−1.1 (5)	N1—C7—C10—C11	170.5 (3)
C2—C3—C4—C5	−1.0 (5)	C8—C7—C10—C11	−7.9 (4)
C3—C4—C5—C6	2.1 (6)	N1—C7—C10—C15	−8.3 (4)
C4—C5—C6—C1	−1.1 (5)	C8—C7—C10—C15	173.2 (3)
C4—C5—C6—N1	−175.8 (3)	C15—C10—C11—C12	−1.0 (5)

C2—C1—C6—C5	−0.9 (4)	C7—C10—C11—C12	−179.8 (3)
N3—C1—C6—C5	−177.3 (3)	C10—C11—C12—C13	−0.4 (6)
C2—C1—C6—N1	173.3 (3)	C11—C12—C13—C14	1.6 (6)
N3—C1—C6—N1	−3.1 (5)	C12—C13—C14—C15	−1.3 (6)
C7—N1—C6—C5	−142.0 (3)	C13—C14—C15—C10	−0.2 (5)
C7—N1—C6—C1	43.7 (4)	C11—C10—C15—C14	1.3 (5)
C6—N1—C7—C10	−176.3 (2)	C7—C10—C15—C14	−179.8 (3)
C6—N1—C7—C8	2.1 (4)	C9—N3—C16—C17	−80.5 (3)
N1—C7—C8—C9	−75.7 (3)	C1—N3—C16—C17	101.3 (3)
C10—C7—C8—C9	102.7 (3)		

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8*B*···*Cg*1^{i}	0.97	2.92	3.810 (3)	154
C13—H13···S1^{ii}	0.97	2.86	3.706 (4)	152

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