5-Phenyl-1,2,5-dithiazepane

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In the title compound, $C_{10}H_{13}NS_2$, the seven-membered ring adopts a chair conformation. The S—S bond length is 2.0406 (5) Å and the C—S—S—C torsion angle is −83.89 (7)°. The amine group is sp^2-hybridized. In the crystal, molecules are linked into chains along [001] by weak intermolecular S···S contacts of 3.5246 (5) Å.

Related literature

For properties of disulfide compounds, see: Pazderlová *et al.* (2012). For similar compounds, see: Roze *et al.* (2006); Bulavin (1971). For related structures, see: Pickardt *et al.* (2006); Capasso *et al.* (1977). For standard bond lengths, see: Allen *et al.* (1987). For previous reports of S···S interactions, see: Chen *et al.* (2009); Reinheimer *et al.* (2009). For the calculation of the functionality of the amine group in terms of hybridization, see: Allen *et al.* (1995). For the synthesis, see: Elderfield *et al.* (1958).
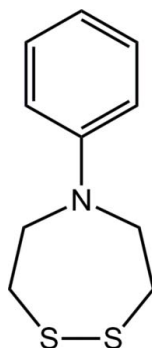
Experimental

Crystal data

$C_{10}H_{13}NS_2$	Monoclinic, $P2_1/c$
$M_r = 211.33$	$a = 9.5760$ (2) Å
$b = 12.2310$ (3) Å	Mo $K\alpha$ radiation
$c = 9.9811$ (2) Å	$\mu = 0.48$ mm^{-1}
$\beta = 120.392$ (2)°	$T = 153$ K
$V = 1008.38$ (4) Å^3	$0.50 \times 0.30 \times 0.20$ mm
$Z = 4$	

Data collection

Nonius Kappa CCD diffractometer	3055 measured reflections
Absorption correction: multi-scan	1763 independent reflections
(*DENZO* and *SCALEPACK*;	1675 reflections with $I > 2\sigma(I)$
Otwinowski & Minor, 1997)	$R_{int} = 0.012$
$T_{min} = 0.856$, $T_{max} = 1$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	118 parameters
$wR(F^2) = 0.064$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{max} = 0.25$ e Å^{-3}
1763 reflections	$\Delta\rho_{min} = -0.21$ e Å^{-3}

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *COLLECT*; data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999) within *WinGX* (Farrugia, 2012); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2010).

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S1. Comment

Cyclic disulfides are of special interest because they are often a key component in many biologically relevant peptides (Pazderlová *et al.*, 2012). Because of this disulfide compounds are regularly found to have pharmacological activities. Herein is described the crystallographic properties of a 7-membered cyclic disulfide compound. The molecular structure of the title compound can be seen in Fig. 1.

The S—S bond distance is 2.0406 (5) Å. This value is comparable to other disulfide compounds. The mean average bond length for C—S—S—C bonds from 99 samples, reported by (Allen *et al.*, 1987) is 2.048 Å. The torsion in the C—S—S—C bonds is -83.89 (7)°, this compares similarly to the C—S—S—C torsion in the 7-membered ring disulfide 1,2,4,6-tetrathiacycloheptane reported in (Pickardt *et al.*, 2006), which has a C—S—S—C torsion of -89.4 (2)°.

The seven-membered ring adopts a chair conformation, as it does in the cyclic disulfide compound reported by Pickardt *et al.* (2006). The dominant intermolecular interactions are between S1···S2 of symmetry-related molecules. The contacts have a distance of 3.5246 (5) Å, this compares similarly to S···S interactions observed perviously by Chen *et al.* (2009) and Reinheimer *et al.* (2009) which are 3.396 (1) - 3.470 (1) Å and 3.580 (4) Å respectively.

The pyramidality of the amine functionality, measured by χ_n, the angle between the C1—N1 vector and the N1/C7/C9 plane, described by Allen *et al.* (1995), is 7.26 (15)°, indicating that the hybridization of the nitrogen atoms is mainly sp^2 (sp^2 $\chi_n \simeq 0°$, sp^3 $\chi_n \simeq 60°$).

S2. Experimental

The title compound was prepared from *N,N*-bis(2-chloroethyl)aniline which had been prepared following literature methods reported by Elderfield *et al.* (1958). NaSH·H_2O (1.08 g, 14.78 mmol) was stirred in ethanol (20 ml) under an argon atmosphere for 1 hr. *N,N*-bis(2-chloroethyl)aniline (0.5124 g, 2.35 mmol) was dissolved in ethanol (10 ml) under argon and then transferred into the NaSH·H_2O solution *via* cannula. The reaction mixture was then heated to reflux for 24 hrs. The solvent volume was reduced by half *in vacuo* before degassed CH_2Cl_2 and H_2O were added to the reaction flask and the product was extracted under argon. The organic phase was then transferred *via* cannula into a flask containing $MgSO_4$. The product was isolated by filtration and removal of the solvent under vacuum. The X-ray quality crystals were obtained from a saturated dichloromethane solution of the title compound upon standing at 263 K for several days. Yield = 83%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25 (m, 2H), 6.85 (m, 3H), 3.52 (m, 4H), 2.74 (m, 4H).

S3. Refinement

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93–0.97 Å and with U_{iso}(H) = 1.2U_{eq}(C).
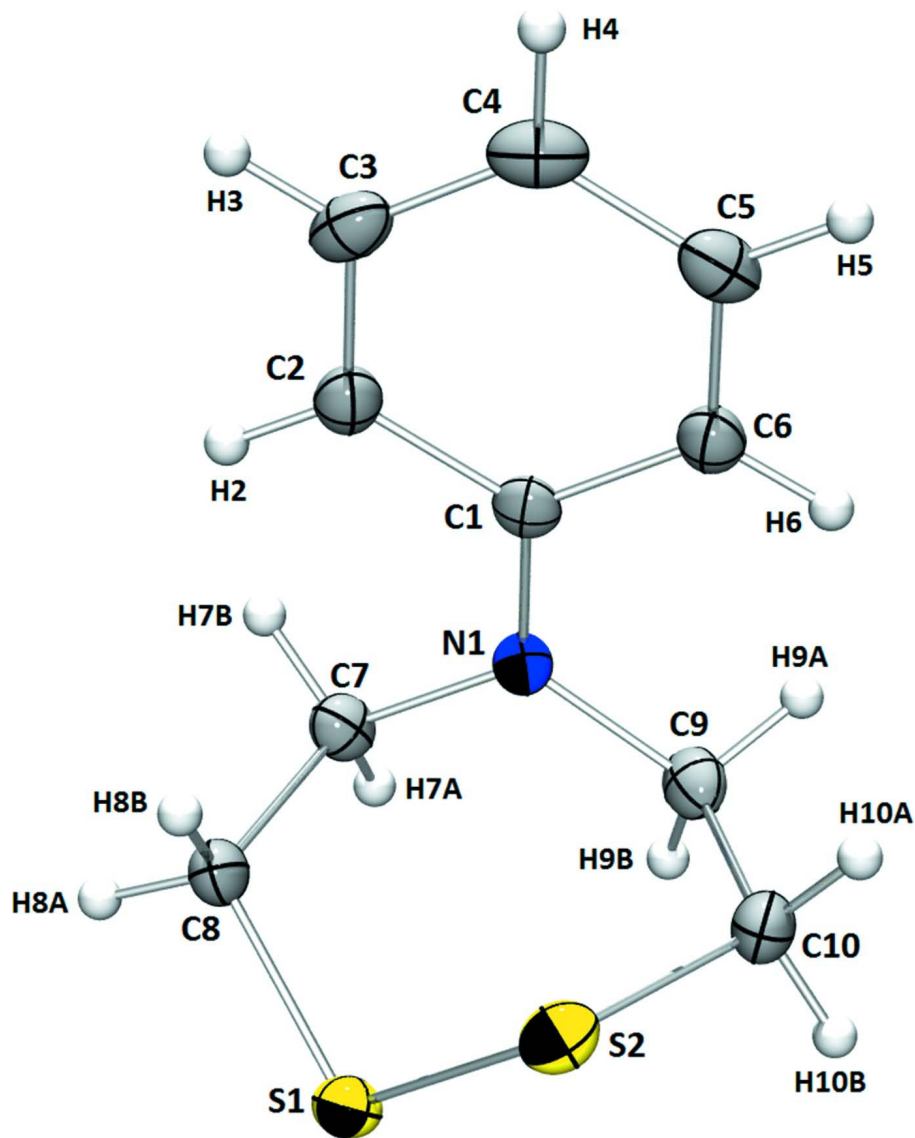
Figure 1

Molecular structure of title compound. Ellipsoids are drawn at the 50% probability level.
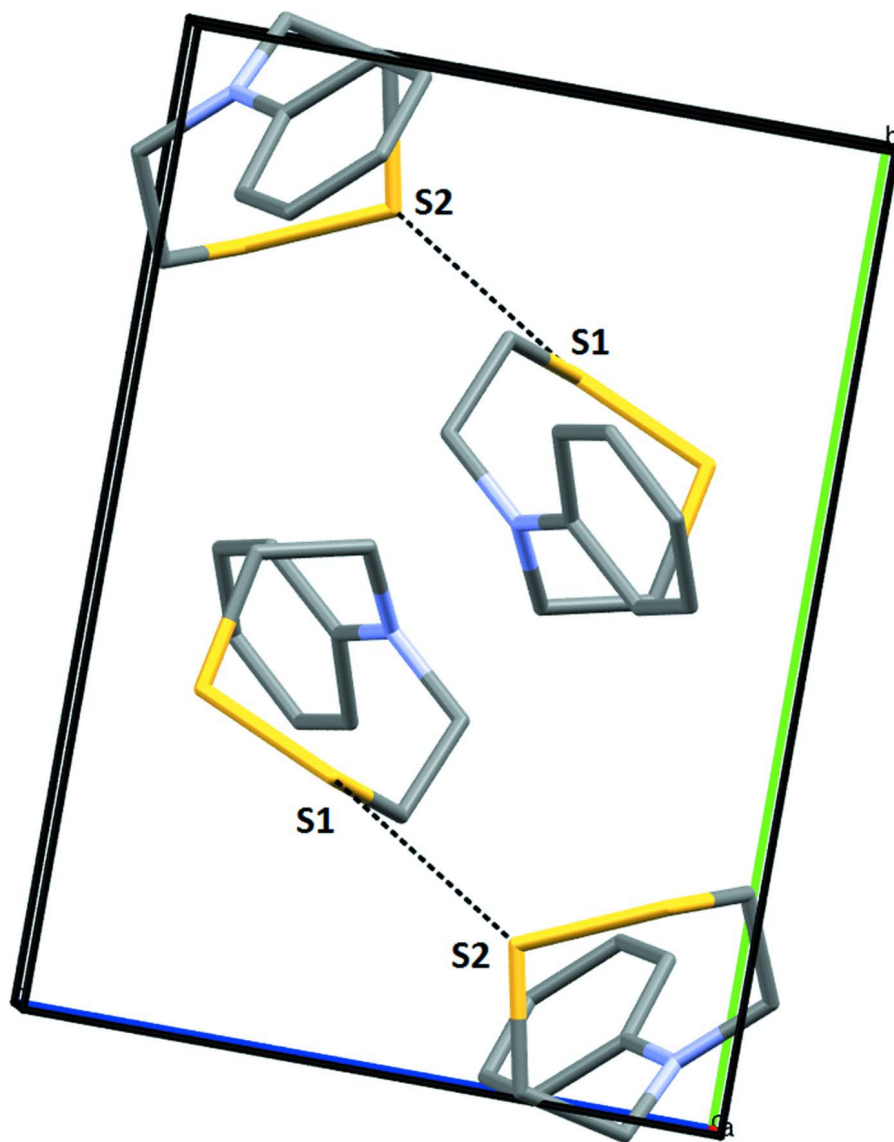
Figure 2

Part of the crystal structure viewed along the *a* axis. Interactions are shown between S1 and S2 of molecules related by the crystallographic c-glide.

5-Phenyl-1,2,5-dithiazepane

Crystal data

$C_{10}H_{13}NS_2$	$F(000) = 448$
$M_r = 211.33$	$D_x = 1.392$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71070$ Å
Hall symbol: -P 2ybc	Cell parameters from 1974 reflections
$a = 9.5760$ (2) Å	$\theta = 1.0–27.5°$
$b = 12.2310$ (3) Å	$\mu = 0.48$ mm^{-1}
$c = 9.9811$ (2) Å	$T = 153$ K
$\beta = 120.392$ (2)°	Block, white
$V = 1008.38$ (4) Å^3	$0.50 \times 0.30 \times 0.20$ mm
$Z = 4$	

Data collection

Nonius Kappa CCD diffractometer	3055 measured reflections
Radiation source: fine-focus sealed tube	1763 independent reflections
Graphite monochromator	1675 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.012$
Absorption correction: multi-scan (*DENZO* and *SCALEPACK*; Otwinowski & Minor, 1997)	$\theta_{max} = 25.0°$, $\theta_{min} = 4.1°$
	$h = -11 \rightarrow 11$
	$k = -12 \rightarrow 14$
	$l = -11 \rightarrow 11$
$T_{min} = 0.856$, $T_{max} = 1$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.024$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.064$	
$S = 1.03$	H-atom parameters constrained
1763 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0266P)^2 + 0.5691P]$ where $P = (F_o^2 + 2F_c^2)/3$
118 parameters	
0 restraints	$(\Delta/\sigma)_{max} = 0.002$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.25$ e Å^{-3}
	$\Delta\rho_{min} = -0.21$ e Å^{-3}

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 $F^2 > 2\Sigma(F^2)$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
S1	1.04272 (4)	0.28440 (3)	0.62971 (4)	0.02268 (12)
S2	1.07376 (4)	0.34787 (3)	0.83210 (4)	0.02409 (12)
N1	0.74239 (13)	0.43703 (9)	0.57782 (13)	0.0190 (3)
C1	0.65295 (16)	0.42454 (11)	0.65031 (15)	0.0187 (3)
C2	0.66903 (17)	0.49796 (12)	0.76593 (16)	0.0218 (3)
H2	0.7434	0.5548	0.7965	0.026*
C3	0.57560 (17)	0.48654 (13)	0.83458 (16)	0.0261 (3)
H3	0.5882	0.5360	0.9107	0.031*
C4	0.46349 (18)	0.40283 (13)	0.79229 (17)	0.0282 (3)
H4	0.4006	0.3960	0.8386	0.034*
C5	0.44731 (17)	0.32959 (13)	0.67931 (17)	0.0261 (3)
H5	0.3723	0.2732	0.6495	0.031*
C6	0.54029 (17)	0.33875 (12)	0.61020 (16)	0.0223 (3)
H6	0.5285	0.2877	0.5362	0.027*
C7	0.72559 (17)	0.36111 (11)	0.45867 (16)	0.0217 (3)

H7A	0.7562	0.3982	0.3915	0.026*
H7B	0.6125	0.3407	0.3958	0.026*
C8	0.82641 (17)	0.25754 (11)	0.52070 (17)	0.0224 (3)
H8A	0.8026	0.2096	0.4342	0.027*
H8B	0.7956	0.2197	0.5873	0.027*
C9	0.87194 (17)	0.51649 (11)	0.63274 (17)	0.0231 (3)
H9A	0.8296	0.5868	0.6406	0.028*
H9B	0.9037	0.5236	0.5550	0.028*
C10	1.02434 (18)	0.49172 (12)	0.78971 (17)	0.0259 (3)
H10A	1.0103	0.5229	0.8715	0.031*
H10B	1.1157	0.5283	0.7926	0.031*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0207 (2)	0.0222 (2)	0.0268 (2)	0.00209 (13)	0.01317 (16)	0.00058 (13)
S2	0.0215 (2)	0.0287 (2)	0.0192 (2)	−0.00065 (14)	0.00822 (15)	0.00285 (13)
N1	0.0195 (6)	0.0174 (6)	0.0198 (6)	−0.0004 (4)	0.0097 (5)	−0.0012 (4)
C1	0.0171 (7)	0.0180 (7)	0.0177 (6)	0.0048 (5)	0.0062 (5)	0.0045 (5)
C2	0.0202 (7)	0.0199 (7)	0.0222 (7)	0.0019 (5)	0.0085 (6)	0.0003 (5)
C3	0.0253 (7)	0.0307 (8)	0.0217 (7)	0.0072 (6)	0.0115 (6)	0.0004 (6)
C4	0.0225 (7)	0.0376 (8)	0.0274 (7)	0.0064 (6)	0.0148 (6)	0.0083 (7)
C5	0.0178 (7)	0.0270 (8)	0.0296 (8)	0.0004 (6)	0.0090 (6)	0.0063 (6)
C6	0.0196 (7)	0.0209 (7)	0.0219 (7)	0.0010 (5)	0.0072 (6)	0.0000 (5)
C7	0.0223 (7)	0.0235 (7)	0.0180 (7)	0.0018 (6)	0.0091 (6)	−0.0007 (5)
C8	0.0215 (7)	0.0206 (7)	0.0242 (7)	−0.0005 (6)	0.0109 (6)	−0.0044 (6)
C9	0.0280 (7)	0.0183 (7)	0.0275 (7)	−0.0024 (6)	0.0173 (6)	0.0002 (6)
C10	0.0241 (7)	0.0238 (7)	0.0291 (8)	−0.0048 (6)	0.0130 (6)	−0.0069 (6)

Geometric parameters (Å, º)

S1—C8	1.8171 (14)	C5—C6	1.379 (2)
S1—S2	2.0406 (5)	C5—H5	0.9300
S2—C10	1.8155 (15)	C6—H6	0.9300
N1—C1	1.3811 (18)	C7—C8	1.5216 (19)
N1—C7	1.4523 (18)	C7—H7A	0.9700
N1—C9	1.4478 (18)	C7—H7B	0.9700
C1—C2	1.408 (2)	C8—H8A	0.9700
C1—C6	1.410 (2)	C8—H8B	0.9700
C2—C3	1.382 (2)	C9—C10	1.537 (2)
C2—H2	0.9300	C9—H9A	0.9700
C3—C4	1.386 (2)	C9—H9B	0.9700
C3—H3	0.9300	C10—H10A	0.9700
C4—C5	1.386 (2)	C10—H10B	0.9700
C4—H4	0.9300		
C8—S1—S2	102.27 (5)	N1—C7—H7A	108.6
C10—S2—S1	104.34 (5)	C8—C7—H7A	108.6

C1—N1—C7	121.14 (11)	N1—C7—H7B	108.6
C1—N1—C9	121.04 (11)	C8—C7—H7B	108.6
C7—N1—C9	117.26 (11)	H7A—C7—H7B	107.6
N1—C1—C2	121.28 (12)	C7—C8—S1	112.92 (10)
N1—C1—C6	121.45 (12)	C7—C8—H8A	109.0
C2—C1—C6	117.26 (13)	S1—C8—H8A	109.0
C3—C2—C1	120.81 (14)	C7—C8—H8B	109.0
C3—C2—H2	119.6	S1—C8—H8B	109.0
C1—C2—H2	119.6	H8A—C8—H8B	107.8
C2—C3—C4	121.32 (14)	N1—C9—C10	116.32 (11)
C2—C3—H3	119.3	N1—C9—H9A	108.2
C4—C3—H3	119.3	C10—C9—H9A	108.2
C5—C4—C3	118.41 (14)	N1—C9—H9B	108.2
C5—C4—H4	120.8	C10—C9—H9B	108.2
C3—C4—H4	120.8	H9A—C9—H9B	107.4
C6—C5—C4	121.30 (14)	C9—C10—S2	115.45 (10)
C6—C5—H5	119.3	C9—C10—H10A	108.4
C4—C5—H5	119.3	S2—C10—H10A	108.4
C5—C6—C1	120.88 (14)	C9—C10—H10B	108.4
C5—C6—H6	119.6	S2—C10—H10B	108.4
C1—C6—H6	119.6	H10A—C10—H10B	107.5
N1—C7—C8	114.49 (11)		
C8—S1—S2—C10	−83.89 (7)	N1—C1—C6—C5	−177.53 (12)
C7—N1—C1—C2	179.96 (12)	C2—C1—C6—C5	1.6 (2)
C9—N1—C1—C2	8.78 (19)	C1—N1—C7—C8	−83.69 (15)
C7—N1—C1—C6	−0.92 (19)	C9—N1—C7—C8	87.82 (15)
C9—N1—C1—C6	−172.10 (12)	N1—C7—C8—S1	−62.44 (14)
N1—C1—C2—C3	178.13 (12)	S2—S1—C8—C7	73.74 (10)
C6—C1—C2—C3	−1.0 (2)	C1—N1—C9—C10	69.91 (16)
C1—C2—C3—C4	0.0 (2)	C7—N1—C9—C10	−101.60 (14)
C2—C3—C4—C5	0.4 (2)	N1—C9—C10—S2	32.78 (16)
C3—C4—C5—C6	0.2 (2)	S1—S2—C10—C9	44.11 (12)
C4—C5—C6—C1	−1.3 (2)		