2-Amino-4,5,6,7-tetrahydrobenzo[b]thio-phene-3-carbonitrile

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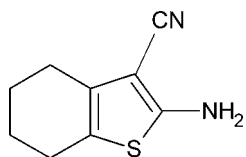Correspondence e-mail: casimone@ifsc.usp.br

The title compound, $C_9H_{10}N_2S$, was synthesized according to Gewald procedures by the reaction of cyclohexanone with malonitrile and sulfur in the presence morpholine. The cyclohexane ring adopts a half-chair conformation and the thiophene ring is essentially planar (r.m.s. deviation = 0.05 Å). The crystal packing is stabilized by two intermolecular N—H⋯N hydrogen bonds, which link the molecules into centrosymmetric rings with graph-set motif $R_2^2(12)$.

Related literature

For background to 2-amino thiophenes, see: Puterová *et al.* (2009). For antiarrhythmic and serotonin antagonist properties of 2-substituted thiophene derivatives, see: Amr *et al.* (2010). For their analgesic or anti-inflammatory activity, see: Hafez & El-Gazzar (2008). For the synthesis of 2-amino thiophenes, see: Gewald *et al.* (1966); Wang *et al.* (2010). For similar structures, see: Larson & Simonsen (1988); Mendonça Junior *et al.* (2010). For puckering parameters, see: Cremer & Pople (1975). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).

Experimental

Crystal data

$C_9H_{10}N_2S$ $M_r = 178.25$

Monoclinic, $P2_1/c$
$a = 10.4274$ (3) Å
$b = 8.1487$ (3) Å
$c = 13.2342$ (4) Å
$\beta = 126.937$ (2)°
$V = 898.81$ (5) Å^3

$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.30$ mm^{-1}
$T = 295$ K
$0.22 \times 0.22 \times 0.20$ mm

Data collection

Nonius KappaCCD diffractometer
12462 measured reflections
2058 independent reflections

1630 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.137$
$S = 1.04$
2058 reflections

109 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H2A⋯N1^i	0.86	2.28	3.121 (2)	166
N2—H2B⋯N1^{ii}	0.86	2.42	3.225 (3)	155

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

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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supporting information

2-Amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile

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S1. Comment

Thiophenes and their fused heterocyclic ring systems possess a wide spectrum of biological activities, as antiarrhythmic and serotonin antagonist (Amr *et al.*, 2010) and analgesic or anti-inflammatory activities (Hafez & El-Gazzar, 2008). In this work, the title compound was obtained according Gewald procedures, by the reaction of cyclohexanone with malonitrile and sulfur in the presence morpholine (Gewald *et al.*, 1966; Wang *et al.*, 2010). In the title compound, the cyclohexane ring adopts a half-chair conformation with calculated puckering parameters of: $Q_T = 0.487$ (1) Å, $\theta = 50.6$ (1)°, $\varphi = 148.6$ (2)° (Cremer & Pople, 1975). The crystal packing is stabilized by two intermolecular N—H···N hydrogen bonds, which links the molecules into rings with graph-set notation $R_2^2(12)$, Table 1 & Fig.2.

S2. Experimental

Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation at room temperature of a solution from ethanol/water.

S3. Refinement

All H atoms attached were fixed geometrically and treated as riding with C—H = 0.97 Å (methylene) and N—H = 0.86 Å and with $U_{iso}(H) = 1.2U_{eq}(C \text{ or } N)$.
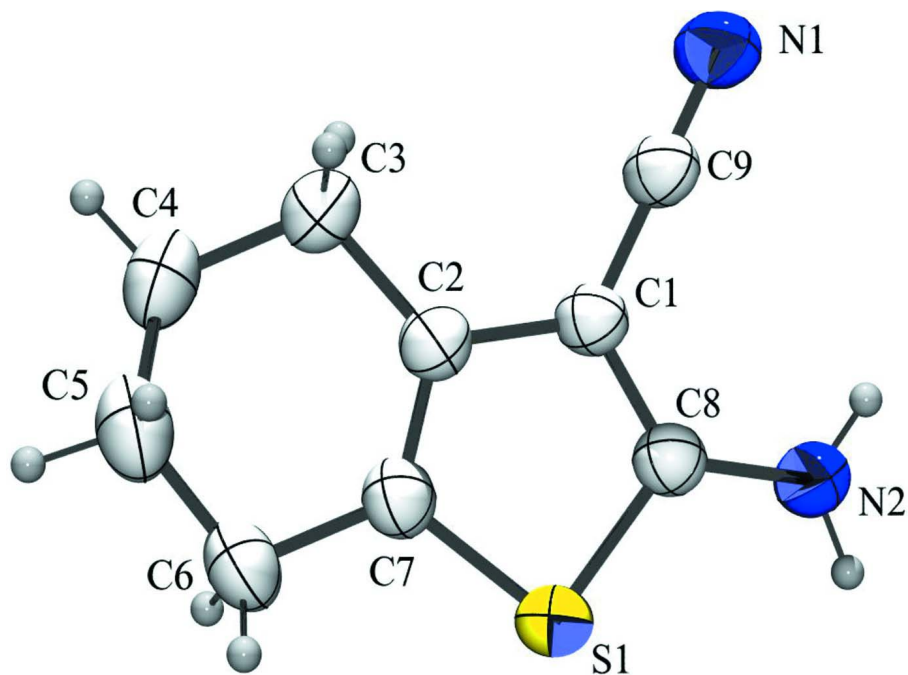
Figure 1

The structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level.
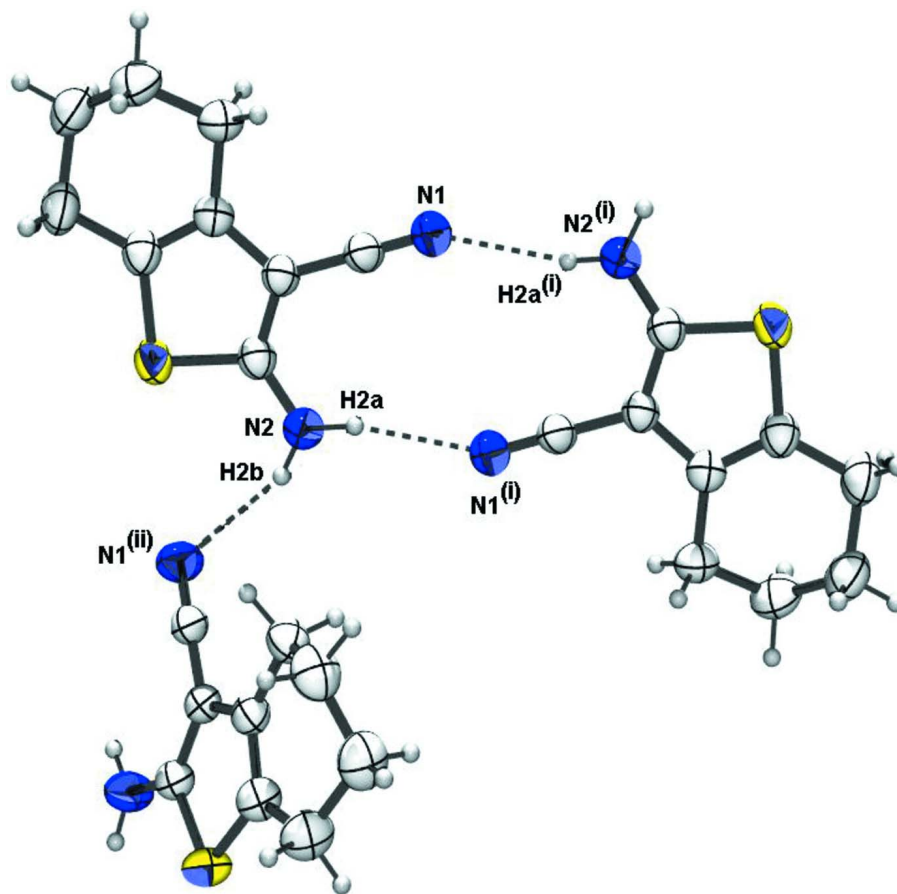
Figure 2

Part of the crystal structure showing the formation of centrosymmetric dimers $R^2_2(12)$ rings. [Symmetry codes: (i) -x, -y-1, -z; (ii) x, -y-1/2, z+1/2.]

2-Amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile

Crystal data

$C_9H_{10}N_2S$	$F(000) = 376$
$M_r = 178.25$	$D_x = 1.317$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 6505 reflections
$a = 10.4274$ (3) Å	$\theta = 2.6–27.5°$
$b = 8.1487$ (3) Å	$\mu = 0.30$ mm^{-1}
$c = 13.2342$ (4) Å	$T = 295$ K
$\beta = 126.937$ (2)°	Prism, yellow
$V = 898.81$ (5) Å^3	$0.22 \times 0.22 \times 0.20$ mm
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	CCD rotation images,thick slices scans
Radiation source: Enraf–Nonius FR590	12462 measured reflections
Horizontally mounted graphite crystal monochromator	2058 independent reflections
	1630 reflections with $I > 2\sigma(I)$
Detector resolution: 9 pixels mm^{-1}	$R_{int} = 0.052$
	$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$

$h = -13 \rightarrow 13$

$l = -17 \rightarrow 17$

$k = -10 \rightarrow 10$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.045$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.137$	
$S = 1.04$	H-atom parameters constrained
2058 reflections	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
109 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} = 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.19$ e Å^{-3}
	$\Delta\rho_{min} = -0.36$ 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 $F^2 > \sigma(F^2)$ 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 (Å²)

	x	y	z	$U_{iso}*/U_{eq}$
S1	0.22127 (5)	0.01327 (5)	0.27769 (4)	0.0543 (2)
N1	0.0577 (2)	−0.37778 (18)	−0.07760 (14)	0.0648 (4)
N2	0.07860 (18)	−0.28276 (18)	0.20995 (14)	0.0603 (4)
H2A	0.0428	−0.3698	0.1640	0.072*
H2B	0.0719	−0.2727	0.2713	0.072*
C1	0.16686 (17)	−0.15535 (17)	0.09245 (13)	0.0426 (3)
C2	0.24712 (19)	−0.00893 (18)	0.09686 (15)	0.0445 (4)
C3	0.2917 (2)	0.0288 (2)	0.01054 (17)	0.0532 (4)
H3A	0.1965	0.0603	−0.0720	0.064*
H3B	0.3365	−0.0684	0.0002	0.064*
C4	0.4146 (2)	0.1681 (2)	0.06489 (19)	0.0662 (5)
H4A	0.5188	0.1265	0.1345	0.079*
H4B	0.4235	0.2079	0.0003	0.079*
C5	0.3678 (2)	0.3083 (2)	0.1112 (2)	0.0690 (5)
H5A	0.2627	0.3485	0.0419	0.083*
H5B	0.4439	0.3974	0.1389	0.083*
C6	0.3640 (2)	0.2565 (2)	0.22012 (18)	0.0641 (5)
H6A	0.4725	0.2486	0.2975	0.077*
H6B	0.3068	0.3380	0.2325	0.077*
C7	0.28162 (17)	0.0932 (2)	0.19015 (15)	0.0499 (4)
C8	0.14543 (17)	−0.16192 (19)	0.18582 (13)	0.0451 (4)
C9	0.10751 (18)	−0.27940 (19)	−0.00076 (14)	0.0477 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0624 (3)	0.0552 (3)	0.0567 (3)	−0.01030 (17)	0.0419 (3)	−0.01544 (17)
N1	0.0984 (12)	0.0474 (8)	0.0663 (9)	−0.0081 (8)	0.0589 (9)	−0.0091 (7)
N2	0.0834 (10)	0.0550 (9)	0.0623 (8)	−0.0155 (7)	0.0543 (8)	−0.0106 (6)
C1	0.0474 (7)	0.0386 (7)	0.0442 (7)	0.0030 (6)	0.0288 (6)	−0.0003 (6)
C2	0.0430 (8)	0.0457 (8)	0.0457 (8)	0.0023 (6)	0.0271 (7)	0.0008 (6)
C3	0.0579 (10)	0.0550 (10)	0.0544 (9)	0.0025 (7)	0.0378 (8)	0.0051 (7)
C4	0.0629 (10)	0.0718 (13)	0.0748 (11)	−0.0065 (9)	0.0472 (9)	0.0060 (9)
C5	0.0694 (11)	0.0575 (11)	0.0780 (12)	−0.0141 (9)	0.0432 (10)	−0.0016 (9)
C6	0.0630 (10)	0.0561 (10)	0.0719 (11)	−0.0175 (8)	0.0398 (9)	−0.0164 (8)
C7	0.0469 (8)	0.0497 (9)	0.0539 (8)	−0.0047 (6)	0.0308 (7)	−0.0056 (7)
C8	0.0466 (7)	0.0441 (8)	0.0468 (8)	0.0014 (6)	0.0292 (7)	−0.0020 (6)
C9	0.0618 (9)	0.0409 (8)	0.0500 (8)	0.0028 (6)	0.0387 (7)	0.0026 (6)

Geometric parameters (Å, º)

S1—C8	1.7280 (15)	C3—H3A	0.9700
S1—C7	1.7432 (17)	C3—H3B	0.9700
N1—C9	1.145 (2)	C4—C5	1.509 (3)
N2—C8	1.351 (2)	C4—H4A	0.9700
N2—H2A	0.8600	C4—H4B	0.9700
N2—H2B	0.8600	C5—C6	1.526 (3)
C1—C8	1.383 (2)	C5—H5A	0.9700
C1—C9	1.417 (2)	C5—H5B	0.9700
C1—C2	1.438 (2)	C6—C7	1.502 (2)
C2—C7	1.346 (2)	C6—H6A	0.9700
C2—C3	1.502 (2)	C6—H6B	0.9700
C3—C4	1.530 (2)		
C8—S1—C7	92.09 (7)	H4A—C4—H4B	108.0
C8—N2—H2A	120.0	C4—C5—C6	111.88 (16)
C8—N2—H2B	120.0	C4—C5—H5A	109.2
H2A—N2—H2B	120.0	C6—C5—H5A	109.2
C8—C1—C9	121.99 (14)	C4—C5—H5B	109.2
C8—C1—C2	113.48 (13)	C6—C5—H5B	109.2
C9—C1—C2	124.47 (13)	H5A—C5—H5B	107.9
C7—C2—C1	112.23 (14)	C7—C6—C5	109.33 (15)
C7—C2—C3	122.47 (14)	C7—C6—H6A	109.8
C1—C2—C3	125.29 (14)	C5—C6—H6A	109.8
C2—C3—C4	110.43 (14)	C7—C6—H6B	109.8
C2—C3—H3A	109.6	C5—C6—H6B	109.8
C4—C3—H3A	109.6	H6A—C6—H6B	108.3
C2—C3—H3B	109.6	C2—C7—C6	125.82 (15)
C4—C3—H3B	109.6	C2—C7—S1	111.97 (12)
H3A—C3—H3B	108.1	C6—C7—S1	122.20 (13)
C5—C4—C3	111.65 (15)	N2—C8—C1	128.53 (14)

C5—C4—H4A	109.3		N2—C8—S1	121.26 (11)
C3—C4—H4A	109.3		C1—C8—S1	110.21 (11)
C5—C4—H4B	109.3		N1—C9—C1	178.84 (18)
C3—C4—H4B	109.3			

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···N1[i]	0.86	2.28	3.121 (2)	166
N2—H2*B*···N1[ii]	0.86	2.42	3.225 (3)	155

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