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5,6-Diamino-1,3-benzodithiole-2-thione

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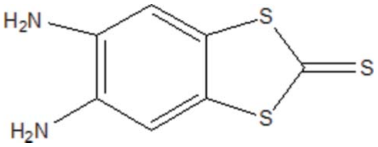
Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.003 Å; R factor = 0.032; wR factor = 0.097; data-to-parameter ratio = 12.8.

The molecule of the title compound, $C_7H_6N_2S_3$, is almost planar, the dihedral angle between the benzene plane and the 1,3-dithiole-2-thione plane being 2.21 (6)°. In the crystal, molecules are linked by intermolecular N—H⋯S and N—H⋯N hydrogen bonds into a three-dimensional network. The crystal packing also exhibits weak intermolecular S⋯S interactions [3.5681 (9) Å].

Related literature

For background to tetrathiofulvalene and its derivatives, see: Yamada & Sugimoto (2004). For the synthesis and properties of tetrathiofulvalene and its derivatives, see: Otsubo & Takimiya (2004); Krief (1986); Jia *et al.* (2007).



Experimental

Crystal data

$C_7H_6N_2S_3$
M_r = 214.35
Monoclinic, $P2_1/n$
a = 5.7695 (9) Å
b = 7.6130 (11) Å
c = 19.993 (3) Å
β = 94.265 (2)°
V = 875.7 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.79 mm^{-1}
T = 291 K
0.35 × 0.10 × 0.05 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.910, T_{max} = 0.961
4517 measured reflections
1702 independent reflections
1521 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.097
S = 1.00
1702 reflections
133 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H2A⋯S3^{i}	0.84 (4)	2.87 (4)	3.711 (3)	176 (3)
N2—H3A⋯N1^{ii}	0.83 (3)	2.45 (3)	3.226 (3)	156 (3)
N2—H4A⋯S3^{iii}	0.84 (3)	2.90 (3)	3.588 (2)	141 (3)

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2516).

References

Bruker (2000). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Jia, C., Liu, S.-X., Tanner, C., Leiggener, C., Neels, A., Sanguinet, L., Levillain, E., Leutwyler, S., Hauser, A. & Decurtins, S. (2007). *Chem. Eur. J.* **13**, 3804–3812.
Krief, A. (1986). *Tetrahedron*, **42**, 1209–1252.
Otsubo, T. & Takimiya, K. (2004). *Bull. Chem. Soc. Jpn*, **77**, 43–58.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Yamada, J. & Sugimoto, T. (2004). *TTF Chemistry. Fundamentals and applications of Tetrathiafulvalene.* Berlin: Springer.

supporting information

Acta Cryst. (2010). E**66**, o3184 [https://doi.org/10.1107/S1600536810046532]

5,6-Diamino-1,3-benzodithiole-2-thione

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S1. Comment

Tetrathiofulvalene (TTF) and its derivatives are successfully used as versatile building blocks for charge-transfer salts, giving rise to organic conductors and superconductors because of their unique π-donor properties (Yamada & Sugimoto, 2004). Extensive reviews on the synthesis and properties of TTF and its derivatives have been published (Otsubo & Takimiya, 2004; Krief, 1986). 1,3-Dithiole-2-thiones are a key intermediates in TTF synthesis routes (Jia *et al.*, 2007). The synthesis and crystal structure of the title compound is reported herein.

The molecular structure of the title compound is shown in Fig. 1. The dihedral angle between the benzene plane and the 1,3-dithiole-2-thione plane is 2.21 (6)°. The moleculess are linked by the intermolecular N–H···S and N–H···N hydrogen bonds (Table 1) and S···S weak interactions (3.5681 (9) Å) into a three-dimensional network (Fig. 2).

S2. Experimental

1,2-Diaminobenzene-4,5-bis(thiocyanate) (10 mmol) was added to a degassed solution of $Na_2S.9H_2O$ (33 mmol) in water (100 mL), and the mixture was heated to 70 °C for an hour to produce a clear brownish solution. The mixture was cooled to 50 °C, and CS_2 (1.4 ml, 23.2 mmol) was slowly added dropwise. The mixture was stirred for two hours at 50 °C and for further three hours at room temperature. The precipitate was filtered off, washed with water, and air-dried. The crude product was purified by flash column chromatography to give the title compound as a yellow powder (yield 50%). Single crystals of the title compound suitable for X-ray analysis were obtained by slow evaporation of an ethyl acetate solution at room temperature for two weeks.

S3. Refinement

All H atoms were located in a difference Fourier map and refined freely.

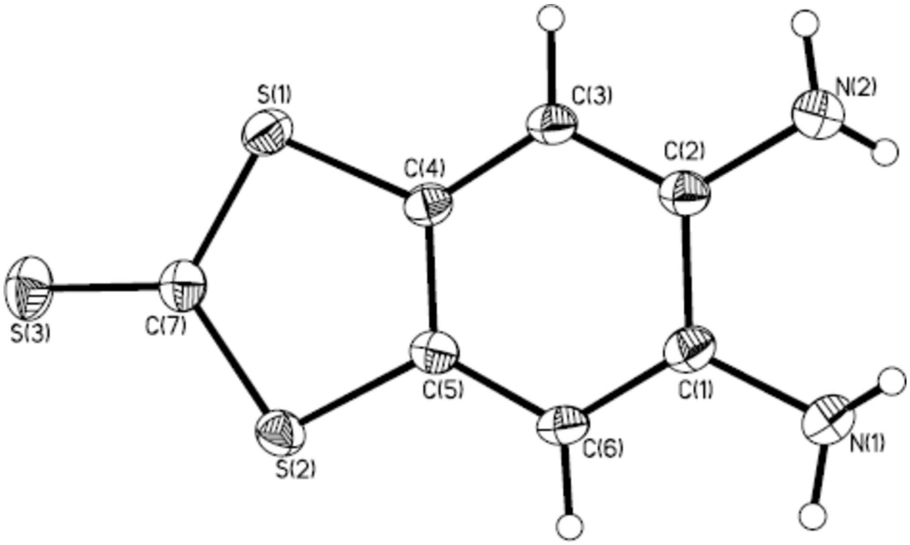

Figure 1

The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

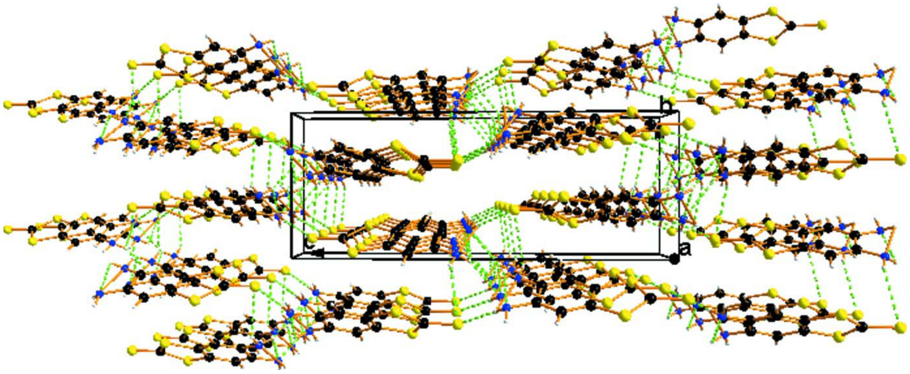

Figure 2

Crystal packing of the title compound viewed along the *a* axis. Intermolecular hydrogen bonds are shown as dashed lines.

5,6-Diamino-1,3-benzodithiole-2-thione

Crystal data

$C_7H_6N_2S_3$

$M_r = 214.35$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 5.7695$ (9) Å

$b = 7.6130$ (11) Å

$c = 19.993$ (3) Å

$\beta = 94.265$ (2)°

$V = 875.7$ (2) Å^3

$Z = 4$

$F(000) = 440$

$D_x = 1.626$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2863 reflections

$\theta = 3.1$–$27.3°$

$\mu = 0.79$ mm^{-1}

$T = 291$ K

Block, yellow

0.35 × 0.10 × 0.05 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min} = 0.910$, $T_{\max} = 0.961$

4517 measured reflections
1702 independent reflections
1521 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.029$
$\theta_{\max} = 26.0°$, $\theta_{\min} = 2.9°$
$h = -6 \rightarrow 7$
$k = -9 \rightarrow 9$
$l = -20 \rightarrow 24$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.097$
$S = 1.00$
1702 reflections
133 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 atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0558P)^2 + 0.4807P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.5326 (4)	0.8170 (3)	0.39432 (11)	0.0350 (5)
C2	0.3149 (4)	0.8999 (3)	0.37772 (11)	0.0334 (4)
C3	0.2459 (4)	0.9342 (3)	0.31133 (11)	0.0316 (4)
C4	0.3887 (3)	0.8872 (3)	0.26093 (10)	0.0305 (4)
C5	0.6025 (4)	0.8080 (3)	0.27734 (10)	0.0312 (4)
C6	0.6739 (4)	0.7722 (3)	0.34410 (11)	0.0332 (4)
C7	0.5787 (4)	0.8467 (3)	0.14729 (11)	0.0369 (5)
H3	0.097 (5)	0.992 (3)	0.3011 (12)	0.038 (6)*
H6	0.820 (4)	0.719 (3)	0.3564 (12)	0.040 (6)*
H1A	0.724 (6)	0.720 (4)	0.4636 (16)	0.073 (10)*
H2A	0.490 (7)	0.760 (4)	0.4841 (17)	0.066 (10)*
H3A	0.250 (5)	0.978 (4)	0.4623 (15)	0.058 (9)*
H4A	0.060 (6)	0.999 (4)	0.4153 (15)	0.057 (8)*
N1	0.6017 (4)	0.7889 (3)	0.46186 (11)	0.0482 (5)
N2	0.1723 (4)	0.9361 (3)	0.42920 (11)	0.0465 (5)

S1	0.32535 (10)	0.93005 (7)	0.17590 (3)	0.03893 (19)
S2	0.76856 (9)	0.76272 (7)	0.20996 (3)	0.03781 (19)
S3	0.63040 (13)	0.84730 (10)	0.06737 (3)	0.0540 (2)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0329 (11)	0.0347 (10)	0.0364 (11)	0.0004 (8)	−0.0046 (8)	0.0003 (8)
C2	0.0290 (10)	0.0325 (10)	0.0383 (11)	0.0010 (8)	0.0003 (8)	−0.0026 (8)
C3	0.0246 (10)	0.0318 (10)	0.0380 (11)	0.0016 (8)	−0.0013 (8)	−0.0015 (8)
C4	0.0274 (10)	0.0288 (9)	0.0347 (10)	−0.0011 (8)	−0.0011 (8)	0.0014 (8)
C5	0.0274 (10)	0.0276 (9)	0.0385 (11)	−0.0005 (8)	0.0006 (8)	−0.0028 (8)
C6	0.0261 (10)	0.0326 (10)	0.0399 (11)	0.0047 (8)	−0.0037 (8)	0.0011 (8)
C7	0.0378 (12)	0.0344 (11)	0.0382 (12)	−0.0078 (9)	0.0023 (9)	−0.0027 (8)
N1	0.0430 (13)	0.0641 (13)	0.0362 (11)	0.0132 (11)	−0.0044 (9)	0.0018 (10)
N2	0.0384 (11)	0.0626 (14)	0.0382 (11)	0.0120 (10)	0.0008 (9)	−0.0053 (10)
S1	0.0351 (3)	0.0450 (3)	0.0360 (3)	0.0018 (2)	−0.0018 (2)	0.0058 (2)
S2	0.0304 (3)	0.0421 (3)	0.0412 (3)	0.0014 (2)	0.0044 (2)	−0.0036 (2)
S3	0.0592 (4)	0.0666 (4)	0.0368 (4)	−0.0103 (3)	0.0088 (3)	−0.0028 (3)

Geometric parameters (Å, º)

C1—C6	1.382 (3)	C5—S2	1.745 (2)
C1—N1	1.396 (3)	C6—H6	0.95 (3)
C1—C2	1.423 (3)	C7—S3	1.647 (2)
C2—C3	1.382 (3)	C7—S2	1.725 (2)
C2—N2	1.392 (3)	C7—S1	1.730 (2)
C3—C4	1.395 (3)	N1—H1A	0.88 (4)
C3—H3	0.97 (3)	N1—H2A	0.84 (4)
C4—C5	1.390 (3)	N2—H3A	0.83 (3)
C4—S1	1.743 (2)	N2—H4A	0.84 (3)
C5—C6	1.394 (3)		

C6—C1—N1	121.6 (2)	C1—C6—C5	119.9 (2)
C6—C1—C2	119.9 (2)	C1—C6—H6	118.4 (14)
N1—C1—C2	118.5 (2)	C5—C6—H6	121.7 (15)
C3—C2—N2	121.9 (2)	S3—C7—S2	123.70 (14)
C3—C2—C1	119.6 (2)	S3—C7—S1	122.57 (14)
N2—C2—C1	118.4 (2)	S2—C7—S1	113.73 (13)
C2—C3—C4	120.15 (19)	C1—N1—H1A	108 (2)
C2—C3—H3	118.3 (14)	C1—N1—H2A	112 (2)
C4—C3—H3	121.6 (14)	H1A—N1—H2A	118 (3)
C5—C4—C3	120.12 (19)	C2—N2—H3A	110 (2)
C5—C4—S1	115.43 (16)	C2—N2—H4A	111 (2)
C3—C4—S1	124.37 (16)	H3A—N2—H4A	114 (3)
C4—C5—C6	120.3 (2)	C7—S1—C4	97.64 (10)
C4—C5—S2	115.60 (16)	C7—S2—C5	97.59 (10)
C6—C5—S2	124.07 (16)		

C6—C1—C2—C3	0.3 (3)	N1—C1—C6—C5	−177.7 (2)
N1—C1—C2—C3	178.0 (2)	C2—C1—C6—C5	−0.2 (3)
C6—C1—C2—N2	177.2 (2)	C4—C5—C6—C1	−0.6 (3)
N1—C1—C2—N2	−5.2 (3)	S2—C5—C6—C1	178.36 (16)
N2—C2—C3—C4	−176.5 (2)	S3—C7—S1—C4	180.00 (14)
C1—C2—C3—C4	0.2 (3)	S2—C7—S1—C4	0.34 (13)
C2—C3—C4—C5	−1.0 (3)	C5—C4—S1—C7	0.28 (17)
C2—C3—C4—S1	−177.76 (16)	C3—C4—S1—C7	177.22 (18)
C3—C4—C5—C6	1.1 (3)	S3—C7—S2—C5	179.66 (14)
S1—C4—C5—C6	178.20 (16)	S1—C7—S2—C5	−0.69 (13)
C3—C4—C5—S2	−177.88 (15)	C4—C5—S2—C7	0.90 (17)
S1—C4—C5—S2	−0.8 (2)	C6—C5—S2—C7	−178.06 (18)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H2*A*···S3^{i}	0.84 (4)	2.87 (4)	3.711 (3)	176 (3)
N2—H3*A*···N1^{ii}	0.83 (3)	2.45 (3)	3.226 (3)	156 (3)
N2—H4*A*···S3^{iii}	0.84 (3)	2.90 (3)	3.588 (2)	141 (3)

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