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6-Aminopyridine-3-thiol

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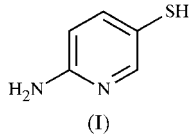
The title compound, $C_5H_6N_2S$, is a simple but novel pyridinethiol of pharmacological interest. The molecule is planar. The crystal packing is dominated by hydrophobic contacts and a pair of hydrogen-bond interactions between the amino group of one pyridine molecule and the ring N atom of a neighbouring base, stabilizing the structure.

Comment

During research on reproduction suppressors of *Schistosoma mansoni* and *Trypanosoma cruzi*, a number of compounds containing sulfur have been prepared (Van den Hoek *et al.*, 1998). Enzyme assays have shown that some dithiocarbamates are capable of inhibiting superoxide dismutase activity (da Silva, 2000). Such enzymes have been found in *S. mansoni* and *T. cruzi* and may play an important role in the parasite's defence against the host's immune response (Hong *et al.*, 1992; Temperton *et al.*, 1996). The preparation of such dithiocarbamates, derived from amines, generates secondary products of reaction, such as pyridinethiols, which are also active against schistosomes (da Silva, 2000; Fathala *et al.*, 2000). In the light of this work, the structure of the title compound, (I), has been determined and the results are presented here.



(I)

The structure of (I) is essentially planar, with an angle of 9 (2)° between the plane of the ring and that of the amino group, with the following atomic displacements: N2 −0.017 (3), H2*A* −0.02 (3) and H2*B* 0.11 (3) Å. The three angles around atom C5 are slightly deformed by the amino group, as is also seen in other aminopyridines (Chao *et al.*, 1975; Kvick *et al.*, 1976). This behaviour characterizes the resonance of the N2 lone pair with the aromatic ring. The effect can also be verified by the shortening of the C5—N2 bond [1.367 (3) Å] relative to a normal single C—N bond [*e.g.* 1.483 Å for C—N in methaneamine, as reported by Atoji & Lipscomb (1953)].

The thiol group at the C2 position (*para* to the amino group) does not cause much distortion of the angles around C2 from 120°, as was also seen when the substituent was a chloro group (Kvick *et al.*, 1976). However, the angles around this same carbon position in unsubstituted 2-aminopyridine (Chao *et al.*, 1975) are significantly distorted from 120°.

The crystal packing in (I) is dominated by hydrophobic contacts and a pair of hydrogen-bond interactions between the N2 amino group of one pyridine molecule and the ring N1 atom of another molecule related by a centre of symmetry, with $N2\cdots N1^{i}$ = 3.028 (2) Å and $N2-H\cdots N1^{i}$ = 179 (3)° [Fig. 2; symmetry code: (i) $-x$, $-y$, $-z$]. As in other 2-aminopyridines (Chao *et al.*, 1975; Kvick *et al.*, 1976), base–base stacking interactions do not appear to be an additional factor stabilizing the crystal structure, such as has been reported for aminopyrimidine packing (Aoki & Yamazaki, 1989).

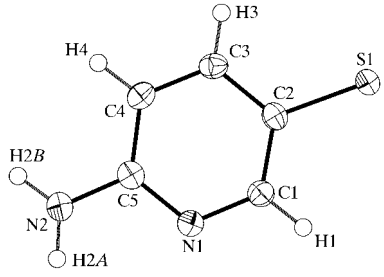


Figure 1
The molecular structure of (I) with 50% probability displacement ellipsoids. The H atom bound to the S atom has been omitted, and the remaining H atoms are shown as small spheres of arbitrary radii.

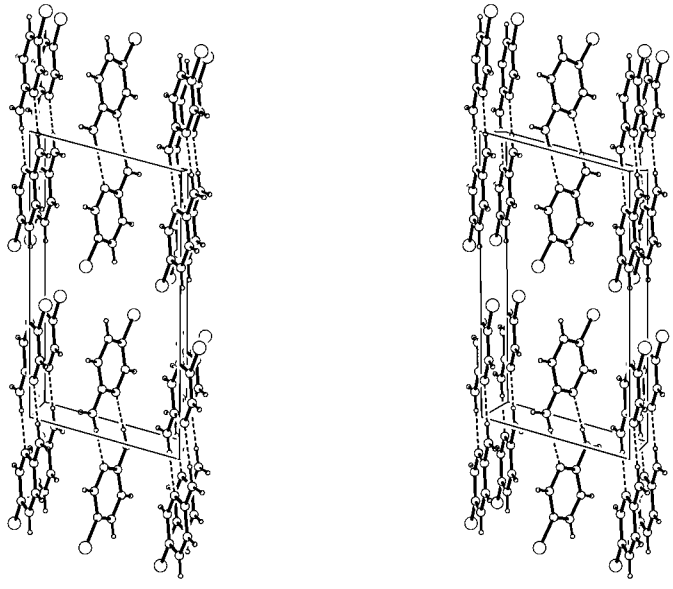


Figure 2
A stereoview of the crystal packing in (I), showing the N—H···N hydrogen bonds (broken lines) between the rings, which are related by a centre of symmetry. The *b* axis is normal to the page.

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Experimental

Dithiocarbamates were prepared as previously described by Bereman & Nalewajek (1978). The compound used in the present experiment was obtained by adding *n*-butyllithium (4.20 ml, 2.4 *M*) to 2-amino-5-chloropyridine (1.31 g, 10 mmol) dissolved in dry tetrahydrofuran (20 ml) and allowing the reaction to proceed for 1 h. Carbon disulfide (0.62 ml, 12 mmol) was added dropwise to the mixture at 195 K over a period of 30 min. The resulting red–yellow solution was stirred for 1 h. Precipitation was achieved by adding degassed hexane at 253 K and the precipitate was collected by filtration. The crystalline powder, (I), was recrystallized from acetone at room temperature.

Crystal data

$C_5H_6N_2S$
M_r = 126.18
Monoclinic, $P2_1/c$
a = 13.3430 (3) Å
b = 5.7560 (3) Å
c = 7.2730 (6) Å
β = 104.753 (3)°
V = 540.17 (5) Å^3
Z = 4
D_x = 1.539 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2311 reflections
θ = 3.2–27.5°
μ = 0.47 mm^{-1}
T = 100 K
Prismatic, light orange
0.07 × 0.05 × 0.03 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Oscillation scans
2311 measured reflections
1240 independent reflections
1001 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 27.5°
$h = 0 \rightarrow 17$
$k = -7 \rightarrow 7$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.100
S = 1.05
1240 reflections
86 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0563P)^2 + 0.08P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.031 (6)

At room temperature, rapid intensity decay occurred after short exposure to the X-ray beam and the crystals became completely black. The sample was immersed in synthetic oil, attached to a glass fibre by surface tension and quenched under a nitrogen stream at 100 K, which eliminated the crystal decay. Cell parameters were determined with all data. The data were corrected for polarization and Lorentz factors but not for absorption. Atoms H1, H3 and H4 were placed in calculated positions, with C—H distances of 0.95 Å, while atoms H2*A* and H2*B* were located in difference Fourier maps and constrained to be 0.92 Å from atom N2 (Fig. 1). Atoms H1, H3 and H4 were refined with riding-model constraints, with $U_{iso}(H) = 1.2U_{eq}(C)$, while atoms H2*A* and H2*B* were refined isotropically. The H atom bound to the S atom was omitted from the refinement; a previous attempt to refine the thiol H atom with an S—H distance restraint was unsuccessful, and another refinement with free structural parameters resulted in an inappropriate S—H bond length.

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *COLLECT*; data reduction: *HKL*2000 (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL*97.

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.344 (2)	C3—C4	1.373 (3)
C1—C2	1.382 (2)	C4—C5	1.408 (3)
C2—C3	1.394 (3)	C5—N1	1.346 (3)
C2—S1	1.7406 (18)	C5—N2	1.367 (3)
C1—C2—C3	119.28 (17)	N2—C5—C4	121.23 (18)
C1—C2—S1	120.31 (15)	C5—N2—H2*A*	117.0 (17)
C3—C2—S1	120.39 (14)	C5—N2—H2*B*	119.5 (17)
N1—C5—N2	117.01 (17)	H2*A*—N2—H2*B*	123 (2)
N1—C5—C4	121.72 (17)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···N1^{i}	0.92 (2)	2.11 (2)	3.028 (2)	178.11 (11)

Symmetry code: (i) $-x, -y, -z$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1211). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Aoki, K. & Yamazaki, H. (1989). *Acta Cryst.* C**45**, 730–734.
Atoji, M. & Lipscomb, W. N. (1953). *Acta Cryst.* **6**, 770.
Bereman, R. D. & Nalewajek, D. (1978). *Inorg. Chem.* **17**, 1085–1087.
Chao, M., Schempp, E. & Rosenstein, R. D. (1975). *Acta Cryst.* B**31**, 2924–2926.
Fathala, O. A., Gad, H. S. M. & Maghaby, A. S. (2000). *Arch. Pharmacol. Res.* **23**, 128–138.
Hong, Z., Lo Verde, P. T., Hamarskjold, M. L. & Rekosh, D. (1992). *Exp. Parasitol.* **75**, 308–322.
Kvick, A., Thomas, R. & Koetzle, T. F. (1976). *Acta Cryst.* B**32**, 224–231.
Nonius (1997–2000). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter & R. M. Sweet, pp. 307–326. London: Academic Press.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Silva, C. H. T. P. da (2000). Personal communication.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Temperton, N. J., Wilkinson, S. R. & Kelly, J. M. (1996). *Mol. Biochem. Parasitol.* **76**, 339–343.
Van den Hoek, T. L., Becker, L. B., Shao, Z., Li, C. & Schumaker, P. T. (1998). *J. Biol. Chem.* **273**, 18092–18098.