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1-(2-Aminoethyl)-3-phenylthiourea

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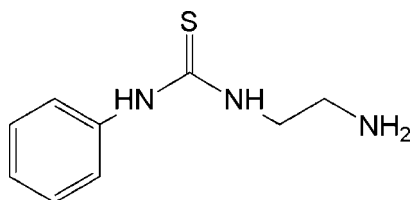
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 Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å;
 R factor = 0.033; wR factor = 0.088; data-to-parameter ratio = 17.6.

In the crystal structure of the title compound, $\text{C}_9\text{H}_{13}\text{N}_3\text{S}$, molecules are linked through $\text{N}-\text{H}\cdots\text{S}$ and $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds, forming hydrogen-bonded tapes along the b axis. The dihedral angle between the phenyl ring and the thiourea group is $44.9(2)^\circ$.

Related literature

For the synthesis of the title compound, see: Lee *et al.* (1985). For applications of thioureas, see: Tommasino *et al.* (1999, 2000); Leung *et al.* (2008). For similar structures, see: Guo (2007); Okino *et al.* (2005).



Experimental

Crystal data

 $\text{C}_9\text{H}_{13}\text{N}_3\text{S}$
 $M_r = 195.28$
 Monoclinic, $P2_1/c$
 $a = 8.5105(2)$ Å
 $b = 11.5644(3)$ Å
 $c = 9.9829(3)$ Å
 $\beta = 93.580(1)^\circ$
 $V = 980.59(5)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.29$ mm⁻¹
 $T = 173$ K
 $0.52 \times 0.51 \times 0.25$ mm

Data collection

 Bruker APEXII CCD
 diffractometer
 11919 measured reflections

 2365 independent reflections
 1893 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.042$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.088$
 $S = 1.05$
 2365 reflections
 134 parameters

 H atoms treated by a mixture of
 independent and constrained
 refinement
 $\Delta\rho_{\text{max}} = 0.25$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.31$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|--------------|--------------------|-------------|----------------------|
| $\text{N1}-\text{H1N}\cdots\text{S1}^{\text{i}}$ | 0.898 (17) | 2.445 (17) | 3.3108 (12) | 162.0 (12) |
| $\text{N2}-\text{H2N}\cdots\text{N3}^{\text{ii}}$ | 0.836 (15) | 2.232 (15) | 2.9974 (16) | 152.5 (13) |

 Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $-x + 1, -y, -z$.

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FY2013).

References

- Bruker (2006). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Guo, H.-M. (2007). *Acta Cryst.* **E63**, o2781.
- Lee, K. N., Fesus, L., Yancey, S. T., Girardg, J. E. & Chung, S. I. (1985). *J. Biol. Chem.* **260**, 14689–14694.
- Leung, A. N., Degenhardt, D. A. & Bühlmann, P. (2008). *Tetrahedron*, **64**, 2530–2536.
- Okino, T., Hoashi, Y., Furukawa, T., Xu, X. & Takemoto, Y. (2005). *J. Am. Chem. Soc.* **127**, 119–125.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Tommasino, M. L., Thomazeau, C., Touchard, F. & Lemaire, M. (1999). *Tetrahedron Asymmetry* **11**, 1813–1819.
- Tommasino, M. L., Thomazeau, C., Touchard, F. & Lemaire, M. (2000). *Tetrahedron:Asymmetry* **11**, 4835–4841.

supporting information

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1-(2-Aminoethyl)-3-phenylthiourea**Pramod Pansuriya, Holger B. Friedrich and Glenn E. M. Maguire****S1. Comment**

Thioureas have been employed as ligands for metal complexes used in asymmetric catalytic hydrogenation (Tommasino *et al.*, 1999, 2000) as well as synthetic anion hosts (Leung *et al.*, 2008). A number of single-crystal X-ray structures have been reported demonstrating a range of inter- and intra molecular hydrogen bonding motifs (Guo, 2007) and (Okino *et al.*, 2005). The title compound is commercially available, but its structure determination (Fig. 1) has not been reported previously.

In the crystal, molecules are linked through intermolecular N—H \cdots S and N—H \cdots N hydrogen bonds (Table 1), forming hydrogen-bonded tapes lying parallel to the *b* axis (Fig. 2). The closest structural analogues all demonstrate intramolecular hydrogen bonding. The hydrogen atoms of the primary amino group are not involved in any short intermolecular contact.

S2. Experimental

The title compound was synthesized as reported by Lee *et al.* (1985). A solution of phenyl isothiocyanate (6.75 g, 50 mmole) in diethylether (15 ml) was added dropwise at 15°C to a vigorously stirred solution of anhydrous ethylenediamine (6.01 g, 100 mmole) in isopropyl alcohol (100 ml) over a period of 30 min. The reaction mixture was stirred for 2 hrs at room temperature and quenched with water (200 ml). The reaction mixture was maintained overnight at room temperature. Then the reaction mixture was acidified with conc. HCl up to a pH of 2.6. The solvents were evaporated under vacuum and the residue was suspended in hot water for 30 min and the resulting precipitate was filtered. The filtrate was basified by the addition of caustic lye, and a precipitate formed. This in turn was filtered, washed with ice cold water and dried. The yield was 5.06 g. (75%).

Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation from ethyl acetate at room temperature. M.p. = 408–409 K.

S3. Refinement

With the exception of those involved in hydrogen bonding, all hydrogen atoms were first located in the difference map then positioned geometrically and allowed to ride on their respective parent atoms with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic and C—H = 0.99 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for CH₂ hydrogen atoms. Hydrogen atoms involved in hydrogen bonding were located in the difference map and refined freely.

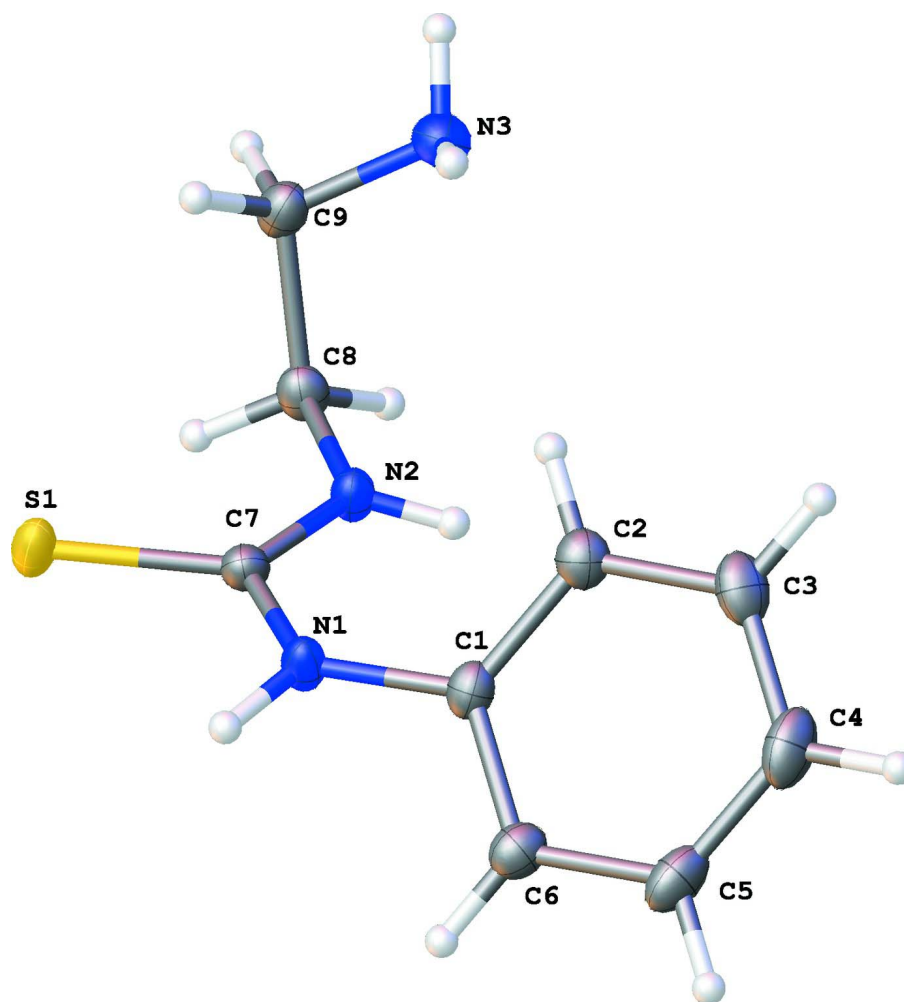


Figure 1

The molecular structure of the title compound. Displacement ellipsoids are drawn at 40% probability. Hydrogen atoms are shown as spheres of arbitrary radii.

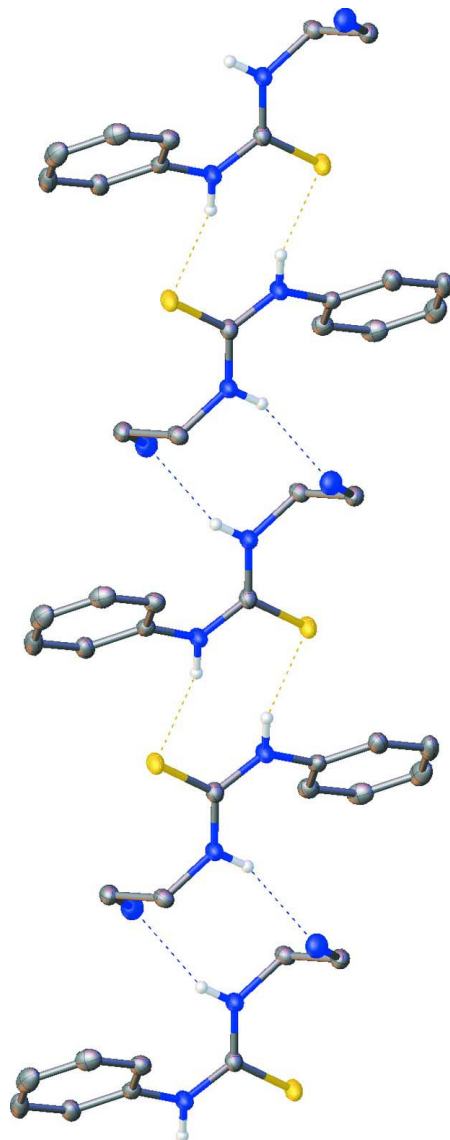


Figure 2

Hydrogen bonding interactions viewed on the *ab* plane. All hydrogens except those involved in bonding have been omitted for clarity.

1-(2-Aminoethyl)-3-phenylthiourea

Crystal data

$C_9H_{13}N_3S$

$M_r = 195.28$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 8.5105\ (2)\ \text{\AA}$

$b = 11.5644\ (3)\ \text{\AA}$

$c = 9.9829\ (3)\ \text{\AA}$

$\beta = 93.580\ (1)^\circ$

$V = 980.59\ (5)\ \text{\AA}^3$

$Z = 4$

$F(000) = 416$

$D_x = 1.323\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 4309 reflections

$\theta = 2.4\text{--}28.3^\circ$

$\mu = 0.29\ \text{mm}^{-1}$

$T = 173\ \text{K}$

Plate, colourless

$0.52 \times 0.51 \times 0.25\ \text{mm}$

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

11919 measured reflections

2365 independent reflections

1893 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.042$

$\theta_{\text{max}} = 28.0^\circ$, $\theta_{\text{min}} = 2.4^\circ$

$h = -11 \rightarrow 11$

$k = -15 \rightarrow 15$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.088$

$S = 1.05$

2365 reflections

134 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

$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 0.1114P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.25 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.31 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|---------------|----------------------------------|
| C1 | 0.70454 (14) | 0.28612 (11) | -0.12947 (13) | 0.0231 (3) |
| C2 | 0.67903 (16) | 0.18764 (12) | -0.20730 (13) | 0.0276 (3) |
| H2 | 0.5781 | 0.1523 | -0.2139 | 0.033* |
| C3 | 0.80133 (18) | 0.14084 (13) | -0.27550 (14) | 0.0337 (3) |
| H3 | 0.7842 | 0.0726 | -0.3273 | 0.040* |
| C4 | 0.94801 (17) | 0.19291 (15) | -0.26863 (15) | 0.0384 (4) |
| H4 | 1.0311 | 0.1611 | -0.3162 | 0.046* |
| C5 | 0.97292 (15) | 0.29189 (15) | -0.19184 (15) | 0.0349 (4) |
| H5 | 1.0734 | 0.3280 | -0.1872 | 0.042* |
| C6 | 0.85235 (14) | 0.33857 (13) | -0.12171 (14) | 0.0279 (3) |
| H6 | 0.8704 | 0.4060 | -0.0686 | 0.033* |
| C7 | 0.46708 (13) | 0.29317 (11) | 0.00584 (13) | 0.0232 (3) |
| C8 | 0.35806 (15) | 0.12066 (11) | 0.11161 (14) | 0.0258 (3) |
| H8A | 0.3210 | 0.1745 | 0.1800 | 0.031* |
| H8B | 0.4109 | 0.0549 | 0.1593 | 0.031* |
| C9 | 0.21718 (15) | 0.07587 (12) | 0.02639 (14) | 0.0283 (3) |

| | | | | |
|------|--------------|---------------|---------------|--------------|
| H9A | 0.1427 | 0.0379 | 0.0848 | 0.034* |
| H9B | 0.1620 | 0.1415 | -0.0196 | 0.034* |
| N1 | 0.58075 (12) | 0.34090 (10) | -0.06492 (12) | 0.0252 (3) |
| N2 | 0.47210 (12) | 0.18047 (9) | 0.03209 (11) | 0.0235 (2) |
| S1 | 0.32346 (4) | 0.38159 (3) | 0.06009 (4) | 0.02980 (13) |
| N3 | 0.26714 (14) | -0.00755 (11) | -0.07427 (13) | 0.0323 (3) |
| H1N | 0.5828 (17) | 0.4185 (15) | -0.0621 (15) | 0.031 (4)* |
| H2N | 0.5532 (17) | 0.1426 (13) | 0.0186 (15) | 0.027 (4)* |
| H3NA | 0.298 (2) | 0.0311 (17) | -0.147 (2) | 0.056 (6)* |
| H3NB | 0.186 (2) | -0.0499 (16) | -0.1047 (18) | 0.049 (5)* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|--------------|-------------|------------|--------------|--------------|---------------|
| C1 | 0.0229 (6) | 0.0241 (7) | 0.0226 (6) | 0.0037 (5) | 0.0050 (5) | 0.0048 (5) |
| C2 | 0.0300 (7) | 0.0281 (7) | 0.0253 (7) | 0.0017 (5) | 0.0051 (5) | 0.0027 (6) |
| C3 | 0.0454 (8) | 0.0328 (8) | 0.0237 (7) | 0.0089 (6) | 0.0090 (6) | 0.0002 (6) |
| C4 | 0.0348 (8) | 0.0516 (10) | 0.0301 (8) | 0.0151 (7) | 0.0128 (6) | 0.0063 (7) |
| C5 | 0.0222 (6) | 0.0520 (10) | 0.0310 (8) | 0.0032 (6) | 0.0065 (5) | 0.0080 (7) |
| C6 | 0.0246 (6) | 0.0333 (8) | 0.0260 (7) | -0.0006 (5) | 0.0036 (5) | 0.0032 (6) |
| C7 | 0.0203 (6) | 0.0219 (7) | 0.0275 (7) | -0.0019 (5) | 0.0028 (5) | -0.0025 (5) |
| C8 | 0.0274 (6) | 0.0219 (7) | 0.0287 (7) | -0.0015 (5) | 0.0075 (5) | 0.0018 (5) |
| C9 | 0.0235 (6) | 0.0244 (7) | 0.0373 (8) | 0.0010 (5) | 0.0047 (5) | 0.0031 (6) |
| N1 | 0.0227 (5) | 0.0176 (6) | 0.0362 (7) | 0.0001 (4) | 0.0095 (5) | -0.0001 (5) |
| N2 | 0.0215 (5) | 0.0192 (6) | 0.0307 (6) | 0.0012 (4) | 0.0073 (4) | 0.0000 (5) |
| S1 | 0.02171 (17) | 0.0211 (2) | 0.0478 (2) | 0.00148 (12) | 0.01190 (14) | -0.00020 (15) |
| N3 | 0.0303 (6) | 0.0302 (7) | 0.0362 (7) | -0.0015 (5) | -0.0006 (5) | -0.0048 (6) |

Geometric parameters (Å, °)

| | | | |
|----------|-------------|-----------|-------------|
| C1—C2 | 1.3881 (19) | C7—N1 | 1.3509 (16) |
| C1—C6 | 1.3943 (17) | C7—S1 | 1.7074 (12) |
| C1—N1 | 1.4181 (15) | C8—N2 | 1.4651 (16) |
| C2—C3 | 1.3887 (19) | C8—C9 | 1.5173 (19) |
| C2—H2 | 0.9500 | C8—H8A | 0.9900 |
| C3—C4 | 1.384 (2) | C8—H8B | 0.9900 |
| C3—H3 | 0.9500 | C9—N3 | 1.4747 (18) |
| C4—C5 | 1.387 (2) | C9—H9A | 0.9900 |
| C4—H4 | 0.9500 | C9—H9B | 0.9900 |
| C5—C6 | 1.3871 (18) | N1—H1N | 0.898 (17) |
| C5—H5 | 0.9500 | N2—H2N | 0.836 (15) |
| C6—H6 | 0.9500 | N3—H3NA | 0.91 (2) |
| C7—N2 | 1.3296 (17) | N3—H3NB | 0.882 (19) |
| C2—C1—C6 | 119.80 (12) | N2—C8—C9 | 112.61 (11) |
| C2—C1—N1 | 121.75 (11) | N2—C8—H8A | 109.1 |
| C6—C1—N1 | 118.27 (12) | C9—C8—H8A | 109.1 |
| C1—C2—C3 | 119.89 (13) | N2—C8—H8B | 109.1 |

| | | | |
|-------------|--------------|--------------|--------------|
| C1—C2—H2 | 120.1 | C9—C8—H8B | 109.1 |
| C3—C2—H2 | 120.1 | H8A—C8—H8B | 107.8 |
| C4—C3—C2 | 120.50 (14) | N3—C9—C8 | 110.73 (10) |
| C4—C3—H3 | 119.7 | N3—C9—H9A | 109.5 |
| C2—C3—H3 | 119.7 | C8—C9—H9A | 109.5 |
| C3—C4—C5 | 119.53 (13) | N3—C9—H9B | 109.5 |
| C3—C4—H4 | 120.2 | C8—C9—H9B | 109.5 |
| C5—C4—H4 | 120.2 | H9A—C9—H9B | 108.1 |
| C4—C5—C6 | 120.53 (13) | C7—N1—C1 | 129.17 (11) |
| C4—C5—H5 | 119.7 | C7—N1—H1N | 113.9 (9) |
| C6—C5—H5 | 119.7 | C1—N1—H1N | 116.5 (9) |
| C5—C6—C1 | 119.73 (14) | C7—N2—C8 | 123.73 (11) |
| C5—C6—H6 | 120.1 | C7—N2—H2N | 119.9 (10) |
| C1—C6—H6 | 120.1 | C8—N2—H2N | 115.0 (10) |
| N2—C7—N1 | 119.23 (11) | C9—N3—H3NA | 109.6 (12) |
| N2—C7—S1 | 122.64 (9) | C9—N3—H3NB | 110.3 (11) |
| N1—C7—S1 | 118.12 (10) | H3NA—N3—H3NB | 104.6 (17) |
| | | | |
| C6—C1—C2—C3 | 0.9 (2) | N2—C8—C9—N3 | 60.48 (15) |
| N1—C1—C2—C3 | 176.02 (12) | N2—C7—N1—C1 | 6.3 (2) |
| C1—C2—C3—C4 | -1.3 (2) | S1—C7—N1—C1 | -174.59 (10) |
| C2—C3—C4—C5 | 0.7 (2) | C2—C1—N1—C7 | 44.9 (2) |
| C3—C4—C5—C6 | 0.3 (2) | C6—C1—N1—C7 | -139.94 (14) |
| C4—C5—C6—C1 | -0.6 (2) | N1—C7—N2—C8 | 177.90 (12) |
| C2—C1—C6—C5 | 0.0 (2) | S1—C7—N2—C8 | -1.17 (18) |
| N1—C1—C6—C5 | -175.28 (12) | C9—C8—N2—C7 | 89.72 (15) |

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------------------------|------------|-------------|-------------|---------------|
| N1—H1N \cdots S1 ⁱ | 0.898 (17) | 2.445 (17) | 3.3108 (12) | 162.0 (12) |
| N2—H2N \cdots N3 ⁱⁱ | 0.836 (15) | 2.232 (15) | 2.9974 (16) | 152.5 (13) |

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x+1, -y, -z$.