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# Crystal structure of 1-(4-formylbenzylidene)thiosemicarbazone

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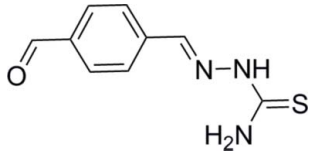
The asymmetric unit of the title compound, $C_9H_9N_3OS$, contains two approximately planar molecules (r.m.s. deviations for 14 non-H atoms = 0.094 and 0.045 Å), with different conformations. In one of them, the C=O group is *syn* to the S atom and in the other it is *anti*. Each molecule features an intramolecular N—H···N hydrogen bond, which generates an *S*(5) ring. In the crystal, molecules are linked by N—H···O and N—H···S hydrogen bonds, generating discrete networks; the *syn* molecules form [010] chains and the *anti* molecules form (100) sheets.

**Keywords:** crystal structure; thiosemicarbazone; hydrogen bonds.

**CCDC reference**: 1016158

## 1. Related literature

For further synthetic details, see: Jagst *et al.* (2005). For structure–biological activity relationships in thiosemicarbazones, see: Lukmantara *et al.* (2013). For their biological properties, see: Serda *et al.* (2012).




## 2. Experimental

### 2.1. Crystal data

$C_9H_9N_3OS$
$M_r$ = 207.25
Monoclinic, $P2_1/c$
$a$ = 12.3888 (9) Å
$b$ = 11.7972 (8) Å
$c$ = 14.9428 (11) Å
$\beta$ = 110.286 (1)°
$V$ = 2048.5 (3) Å$^3$
$Z$ = 8
Mo $K\alpha$ radiation
$\mu$ = 0.29 mm$^{-1}$
$T$ = 293 K
0.51 × 0.44 × 0.33 mm

### 2.2. Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.693, $T_{max}$ = 0.746
19018 measured reflections
4920 independent reflections
3344 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.022

### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.119
$S$ = 1.03
4920 reflections
277 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.36 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.35 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1$A$—H1$NA$···N3$A$ | 0.84 (3) | 2.32 (2) | 2.630 (2) | 102.0 (19) |
| N1$A$—H1$NA$···O1$A^{i}$ | 0.84 (3) | 2.41 (3) | 3.190 (3) | 154 (2) |
| N1$A$—H2$NA$···S1$A^{ii}$ | 0.87 (3) | 2.52 (3) | 3.391 (2) | 172 (2) |
| N2$A$—H3$NA$···S1$B^{iii}$ | 0.84 (2) | 2.50 (2) | 3.3270 (19) | 166.1 (19) |
| N1$B$—H1$NB$···N3$B$ | 0.91 (3) | 2.21 (3) | 2.619 (3) | 106 (3) |
| N1$B$—H2$NB$···O1$B^{iv}$ | 0.88 (3) | 2.01 (3) | 2.857 (3) | 161 (3) |
| N2$B$—H3$NB$···S1$A^{v}$ | 0.84 (2) | 2.58 (2) | 3.409 (2) | 171 (2) |

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

Data collection: *SMART* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

## Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7254).

## References

Bruker (2008). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Jagst, A., Sánchez, A., Vázquez-López, E. M. & Abram, U. (2005). *Inorg. Chem.* **44**, 5738–5744.
Lukmantara, A. Y., Kalinowski, D. S., Kumar, N. & Richardson, D. R. (2013). *Bioorg. Med. Chem. Lett.* **23**, 967–974.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Serda, M., Mrozek-Wilczkiewicz, A., Jampilek, J., Pesko, M., Kralova, K., Vejsova, M., Musiol, R., Ratuszna, A. & Polanski, J. (2012). *Molecules*, **17**, 13483–13502.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

# supporting information

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## Crystal structure of 1-(4-formylbenzylidene)thiosemicarbazone

**Rosa Carballo, Arantxa Pino-Cuevas and Ezequiel M. Vázquez-López**

### S1. Chemical context

The study of the thiosemicarbazones is interesting because they are compounds which show diverse biological properties (Serda *et al.*, 2012) and pharmacological activities (Lukmantara *et al.*, 2013). Also the thiosemicarbazones are of interest from a supramolecular point of view since they can be functionalized to give different supramolecular arrays by hydrogen bonds.

### S2. Structural commentary

We report here the synthesis and structural characterization of (4-formylbenzylidine)-thiosemicarbazone (Fig.1). The two molecules in the asymmetric unit are structurally different due to the different orientation of the carbonyl group respect to the thiosemicarbazone chain. The thiosemicarbazone moiety in both molecules shows an E conformation with the sulfur atom trans to the iminic nitrogen N3 atom. The molecules labeled as B are linked into lineal chains by N—H···O hydrogen bonds with a d(N···O) of 2.857 (3) Å but the molecules labeled as A use the same kind of hydrogen bond with a longer d(N···O) of 3.190 (3) Å to form helical chains (Fig. 2). The two types of chains are packed by N—H···S hydrogen bonds with d(N—S) in the range 3.32-3.41 Å and (NHS) angles close to linearity (between 166 and 172°).

### S3. Synthesis and crystallization

A solution of thiosemicarbazide (342mg, 3.72 mmol) in 50 ml of water was slowly added at 50°C to a solution of terephthaldicarboxaldehyde (500 mg, 3.73 mmol) in 100 ml water. Then the mixture was stirred at 50°C for 30 mins. Once cooled to room temperature, the yellow solid was filtered off and vacuum dried. Yellow prisms were obtained by recrystallization from EtOH/$H_2O$ (1:1) solution. Yield: 78%. M.pt: 212–214°C. IR data (KBr, $cm^{-1}$): 3452w, 3328m, 3152m *ν*(NH); 2974w, 2863w *ν*(C—H aldehyde); 1686s *ν*(C=O); 1533s, 1281m *ν*(C=N), 830m, 793m *ν*(C=S). $^1$H NMR data (DMSO-$d_6$, ppm): 10.60 (s, 1H, N(2)—H); 10.01 (s, 1H, C(1)—H); 8.32 (s, 1H, N(2)—H); 8.15 (s, 1H, N(2)—H); 8.09 (s, 1H, C(8)—H); 8.02 (d, 2H, J = 8.2 Hz, C(3,7)-H); 7.91 (d, 2H, J = 8.2 Hz, C(4,6)-H).

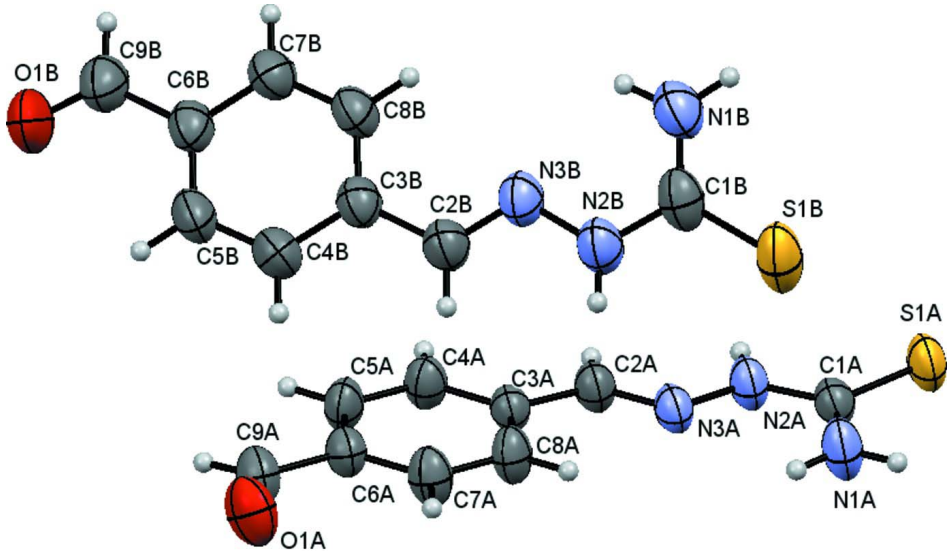


**Figure 1**

*ORTEP* view of the two molecules of the title compound. Displacement ellipsoids shown at the 50% probability level.

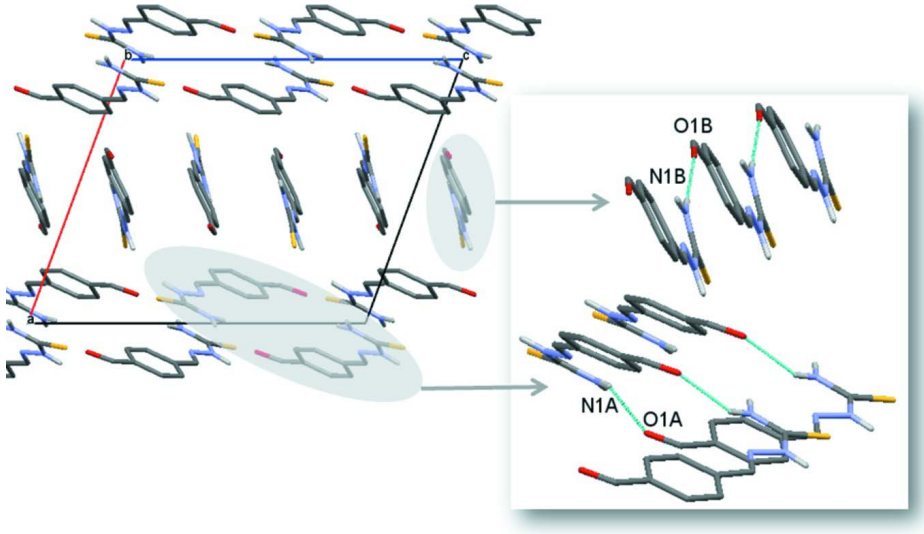


**Figure 2**

View of the crystal packing showing the two different chains.

### 1-(4-Formylbenzylidene)thiosemicarbazone

*Crystal data*

$C_9H_9N_3OS$
$M_r = 207.25$
Monoclinic, $P2_1/c$
$a = 12.3888$ (9) Å
$b = 11.7972$ (8) Å
$c = 14.9428$ (11) Å
$\beta = 110.286$ (1)°
$V = 2048.5$ (3) Å$^3$
$Z = 8$
$F(000) = 864$
$D_x = 1.344$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6097 reflections
$\theta = 2.3$–27.2°
$\mu = 0.29$ mm$^{-1}$
$T = 293$ K
Prism, yellow
0.51 × 0.44 × 0.33 mm

*Data collection*

Bruker SMART 1000 CCD diffractometer
Radiation source: sealed X-ray tube
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.693, $T_{max}$ = 0.746
19018 measured reflections
4920 independent reflections
3344 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.022
$\theta_{max}$ = 28.1°, $\theta_{min}$ = 1.8°
$h$ = −16→16
$k$ = −15→15
$l$ = −19→19

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.119
$S$ = 1.03
4920 reflections
277 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0442P)^2 + 0.8755P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.36 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.35 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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| N3A | 0.89210 (14) | 0.63007 (12) | −0.01356 (11) | 0.0479 (4) |
| S1A | 0.90693 (5) | 0.91696 (4) | −0.13892 (4) | 0.06120 (17) |
| O1A | 0.89088 (17) | 0.16790 (14) | 0.29083 (12) | 0.0778 (5) |
| N1A | 0.97843 (19) | 0.83357 (16) | 0.03697 (14) | 0.0646 (5) |
| C1A | 0.92577 (17) | 0.81529 (15) | −0.05446 (14) | 0.0488 (4) |
| N2A | 0.88481 (15) | 0.71091 (13) | −0.08158 (13) | 0.0519 (4) |
| C2A | 0.84890 (17) | 0.53375 (15) | −0.04474 (14) | 0.0499 (4) |
| H2A | 0.8172 | 0.5214 | −0.1102 | 0.060* |
| C3A | 0.84875 (16) | 0.44243 (14) | 0.02136 (13) | 0.0446 (4) |
| C4A | 0.80002 (18) | 0.33905 (16) | −0.01569 (14) | 0.0536 (5) |
| H4A | 0.7659 | 0.3300 | −0.0813 | 0.064* |
| C5A | 0.80199 (18) | 0.24931 (15) | 0.04467 (14) | 0.0549 (5) |
| H5A | 0.7691 | 0.1803 | 0.0195 | 0.066* |
| C6A | 0.85265 (17) | 0.26217 (15) | 0.14207 (14) | 0.0487 (4) |
| C7A | 0.9008 (2) | 0.36573 (16) | 0.17931 (14) | 0.0576 (5) |
| H7A | 0.9348 | 0.3746 | 0.2450 | 0.069* |
| C8A | 0.89848 (19) | 0.45524 (16) | 0.11987 (14) | 0.0550 (5) |
| H8A | 0.9302 | 0.5245 | 0.1455 | 0.066* |
| C9A | 0.8559 (2) | 0.16499 (18) | 0.20519 (17) | 0.0615 (5) |
| H9A | 0.8286 | 0.0959 | 0.1763 | 0.074* |
| H1NA | 0.990 (2) | 0.782 (2) | 0.0779 (17) | 0.069 (7)* |
| H2NA | 1.007 (2) | 0.900 (2) | 0.0570 (17) | 0.075 (7)* |

| | | | | |
|---|---|---|---|---|
| H3NA | 0.8488 (18) | 0.6956 (18) | −0.1392 (16) | 0.054 (6)* |
| S1B | 0.70719 (7) | 0.87078 (5) | 0.20508 (5) | 0.0836 (2) |
| O1B | 0.36864 (17) | −0.02352 (14) | 0.06781 (17) | 0.1027 (7) |
| N1B | 0.5055 (2) | 0.77556 (19) | 0.11523 (17) | 0.0728 (6) |
| C1B | 0.6141 (2) | 0.76241 (17) | 0.16872 (15) | 0.0633 (6) |
| N2B | 0.6506 (2) | 0.65472 (15) | 0.19199 (15) | 0.0659 (5) |
| C2B | 0.61285 (19) | 0.46749 (17) | 0.18659 (16) | 0.0596 (5) |
| H2B | 0.6866 | 0.4587 | 0.2310 | 0.072* |
| N3B | 0.57577 (16) | 0.56654 (14) | 0.15795 (13) | 0.0591 (4) |
| C3B | 0.54146 (18) | 0.36782 (16) | 0.15082 (15) | 0.0539 (5) |
| C4B | 0.5824 (2) | 0.26093 (18) | 0.18761 (17) | 0.0636 (6) |
| H4B | 0.6538 | 0.2549 | 0.2358 | 0.076* |
| C5B | 0.5189 (2) | 0.16464 (18) | 0.15366 (18) | 0.0663 (6) |
| H5B | 0.5477 | 0.0941 | 0.1784 | 0.080* |
| C6B | 0.41212 (19) | 0.17280 (17) | 0.08275 (16) | 0.0574 (5) |
| C7B | 0.37016 (19) | 0.27858 (17) | 0.04567 (16) | 0.0592 (5) |
| H6B | 0.2983 | 0.2843 | −0.0020 | 0.071* |
| C8B | 0.43420 (19) | 0.37484 (17) | 0.07894 (16) | 0.0583 (5) |
| H7B | 0.4056 | 0.4451 | 0.0532 | 0.070* |
| C9B | 0.3412 (2) | 0.07213 (19) | 0.0444 (2) | 0.0723 (6) |
| H9B | 0.2691 | 0.0838 | −0.0017 | 0.087* |
| H1NB | 0.463 (3) | 0.712 (3) | 0.093 (2) | 0.107 (10)* |
| H2NB | 0.478 (2) | 0.844 (2) | 0.1003 (19) | 0.085 (8)* |
| H3NB | 0.717 (2) | 0.642 (2) | 0.2304 (17) | 0.065 (7)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| N3A | 0.0572 (9) | 0.0343 (7) | 0.0505 (8) | 0.0015 (7) | 0.0167 (7) | 0.0081 (6) |
| S1A | 0.0797 (4) | 0.0362 (2) | 0.0594 (3) | −0.0022 (2) | 0.0134 (3) | 0.0123 (2) |
| O1A | 0.1133 (14) | 0.0633 (10) | 0.0600 (10) | 0.0069 (9) | 0.0341 (9) | 0.0169 (8) |
| N1A | 0.0936 (15) | 0.0363 (9) | 0.0541 (10) | −0.0053 (9) | 0.0130 (10) | 0.0050 (8) |
| C1A | 0.0554 (11) | 0.0351 (9) | 0.0545 (11) | 0.0034 (8) | 0.0174 (9) | 0.0043 (8) |
| N2A | 0.0682 (11) | 0.0343 (7) | 0.0479 (9) | −0.0020 (7) | 0.0135 (8) | 0.0067 (7) |
| C2A | 0.0602 (11) | 0.0375 (9) | 0.0477 (10) | −0.0014 (8) | 0.0131 (8) | 0.0043 (8) |
| C3A | 0.0498 (10) | 0.0347 (8) | 0.0480 (10) | 0.0006 (7) | 0.0151 (8) | 0.0032 (7) |
| C4A | 0.0647 (12) | 0.0430 (9) | 0.0447 (10) | −0.0084 (9) | 0.0082 (9) | 0.0010 (8) |
| C5A | 0.0638 (12) | 0.0367 (9) | 0.0586 (12) | −0.0116 (8) | 0.0141 (10) | −0.0017 (8) |
| C6A | 0.0576 (11) | 0.0383 (9) | 0.0507 (10) | −0.0004 (8) | 0.0193 (9) | 0.0057 (8) |
| C7A | 0.0817 (15) | 0.0445 (10) | 0.0439 (10) | −0.0040 (10) | 0.0183 (10) | −0.0002 (8) |
| C8A | 0.0774 (14) | 0.0351 (9) | 0.0498 (10) | −0.0068 (9) | 0.0187 (10) | −0.0045 (8) |
| C9A | 0.0775 (15) | 0.0449 (10) | 0.0641 (13) | −0.0005 (10) | 0.0271 (11) | 0.0082 (9) |
| S1B | 0.1164 (6) | 0.0470 (3) | 0.0657 (4) | −0.0135 (3) | 0.0042 (3) | 0.0020 (3) |
| O1B | 0.0916 (13) | 0.0436 (9) | 0.158 (2) | −0.0036 (9) | 0.0239 (13) | −0.0026 (11) |
| N1B | 0.0818 (15) | 0.0507 (11) | 0.0826 (14) | 0.0090 (11) | 0.0243 (12) | 0.0030 (11) |
| C1B | 0.0916 (17) | 0.0453 (11) | 0.0517 (11) | 0.0007 (11) | 0.0233 (11) | −0.0012 (9) |
| N2B | 0.0739 (13) | 0.0445 (9) | 0.0669 (12) | −0.0017 (9) | 0.0088 (10) | −0.0003 (8) |
| C2B | 0.0632 (13) | 0.0471 (11) | 0.0647 (13) | 0.0019 (10) | 0.0172 (10) | 0.0008 (9) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N3B | 0.0685 (11) | 0.0429 (9) | 0.0635 (10) | −0.0031 (8) | 0.0199 (9) | −0.0036 (8) |
| C3B | 0.0603 (12) | 0.0434 (10) | 0.0616 (12) | 0.0037 (9) | 0.0259 (10) | −0.0003 (9) |
| C4B | 0.0605 (13) | 0.0517 (11) | 0.0738 (14) | 0.0066 (10) | 0.0172 (11) | 0.0103 (10) |
| C5B | 0.0705 (15) | 0.0419 (10) | 0.0884 (16) | 0.0083 (10) | 0.0299 (13) | 0.0111 (10) |
| C6B | 0.0607 (13) | 0.0434 (10) | 0.0742 (14) | 0.0031 (9) | 0.0312 (11) | −0.0022 (9) |
| C7B | 0.0583 (12) | 0.0483 (11) | 0.0697 (13) | 0.0068 (9) | 0.0207 (10) | −0.0036 (10) |
| C8B | 0.0650 (13) | 0.0423 (10) | 0.0672 (13) | 0.0103 (9) | 0.0225 (11) | 0.0015 (9) |
| C9B | 0.0709 (15) | 0.0517 (12) | 0.0965 (18) | −0.0014 (11) | 0.0320 (13) | −0.0068 (12) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| N3A—C2A | 1.274 (2) | S1B—C1B | 1.681 (2) |
| N3A—N2A | 1.374 (2) | O1B—C9B | 1.195 (3) |
| S1A—C1A | 1.6976 (18) | N1B—C1B | 1.314 (3) |
| O1A—C9A | 1.201 (3) | N1B—H1NB | 0.91 (3) |
| N1A—C1A | 1.312 (3) | N1B—H2NB | 0.88 (3) |
| N1A—H1NA | 0.84 (3) | C1B—N2B | 1.353 (3) |
| N1A—H2NA | 0.87 (3) | N2B—N3B | 1.369 (2) |
| C1A—N2A | 1.340 (2) | N2B—H3NB | 0.84 (2) |
| N2A—H3NA | 0.84 (2) | C2B—N3B | 1.274 (3) |
| C2A—C3A | 1.462 (2) | C2B—C3B | 1.457 (3) |
| C2A—H2A | 0.9300 | C2B—H2B | 0.9300 |
| C3A—C4A | 1.388 (2) | C3B—C8B | 1.392 (3) |
| C3A—C8A | 1.393 (3) | C3B—C4B | 1.399 (3) |
| C4A—C5A | 1.386 (3) | C4B—C5B | 1.375 (3) |
| C4A—H4A | 0.9300 | C4B—H4B | 0.9300 |
| C5A—C6A | 1.379 (3) | C5B—C6B | 1.382 (3) |
| C5A—H5A | 0.9300 | C5B—H5B | 0.9300 |
| C6A—C7A | 1.388 (3) | C6B—C7B | 1.391 (3) |
| C6A—C9A | 1.476 (3) | C6B—C9B | 1.470 (3) |
| C7A—C8A | 1.374 (3) | C7B—C8B | 1.376 (3) |
| C7A—H7A | 0.9300 | C7B—H6B | 0.9300 |
| C8A—H8A | 0.9300 | C8B—H7B | 0.9300 |
| C9A—H9A | 0.9300 | C9B—H9B | 0.9300 |
| | | | |
| C2A—N3A—N2A | 115.92 (16) | C1B—N1B—H1NB | 118 (2) |
| C1A—N1A—H1NA | 122.5 (16) | C1B—N1B—H2NB | 119.2 (18) |
| C1A—N1A—H2NA | 120.1 (16) | H1NB—N1B—H2NB | 122 (3) |
| H1NA—N1A—H2NA | 117 (2) | N1B—C1B—N2B | 116.6 (2) |
| N1A—C1A—N2A | 117.74 (17) | N1B—C1B—S1B | 123.36 (18) |
| N1A—C1A—S1A | 123.28 (15) | N2B—C1B—S1B | 120.0 (2) |
| N2A—C1A—S1A | 118.98 (15) | C1B—N2B—N3B | 119.7 (2) |
| C1A—N2A—N3A | 119.56 (17) | C1B—N2B—H3NB | 120.4 (17) |
| C1A—N2A—H3NA | 121.2 (15) | N3B—N2B—H3NB | 119.7 (16) |
| N3A—N2A—H3NA | 119.0 (15) | N3B—C2B—C3B | 121.0 (2) |
| N3A—C2A—C3A | 120.60 (17) | N3B—C2B—H2B | 119.5 |
| N3A—C2A—H2A | 119.7 | C3B—C2B—H2B | 119.5 |
| C3A—C2A—H2A | 119.7 | C2B—N3B—N2B | 116.96 (19) |

| | | | |
|---|---|---|---|
| C4A—C3A—C8A | 119.25 (16) | C8B—C3B—C4B | 118.45 (19) |
| C4A—C3A—C2A | 118.70 (17) | C8B—C3B—C2B | 122.07 (18) |
| C8A—C3A—C2A | 122.03 (16) | C4B—C3B—C2B | 119.5 (2) |
| C5A—C4A—C3A | 120.31 (17) | C5B—C4B—C3B | 121.1 (2) |
| C5A—C4A—H4A | 119.8 | C5B—C4B—H4B | 119.5 |
| C3A—C4A—H4A | 119.8 | C3B—C4B—H4B | 119.5 |
| C6A—C5A—C4A | 120.11 (17) | C4B—C5B—C6B | 119.92 (19) |
| C6A—C5A—H5A | 119.9 | C4B—C5B—H5B | 120.0 |
| C4A—C5A—H5A | 119.9 | C6B—C5B—H5B | 120.0 |
| C5A—C6A—C7A | 119.67 (17) | C5B—C6B—C7B | 119.61 (19) |
| C5A—C6A—C9A | 119.37 (17) | C5B—C6B—C9B | 121.8 (2) |
| C7A—C6A—C9A | 120.96 (18) | C7B—C6B—C9B | 118.6 (2) |
| C8A—C7A—C6A | 120.50 (18) | C8B—C7B—C6B | 120.5 (2) |
| C8A—C7A—H7A | 119.8 | C8B—C7B—H6B | 119.7 |
| C6A—C7A—H7A | 119.8 | C6B—C7B—H6B | 119.7 |
| C7A—C8A—C3A | 120.15 (17) | C7B—C8B—C3B | 120.43 (19) |
| C7A—C8A—H8A | 119.9 | C7B—C8B—H7B | 119.8 |
| C3A—C8A—H8A | 119.9 | C3B—C8B—H7B | 119.8 |
| O1A—C9A—C6A | 125.3 (2) | O1B—C9B—C6B | 125.3 (3) |
| O1A—C9A—H9A | 117.3 | O1B—C9B—H9B | 117.4 |
| C6A—C9A—H9A | 117.3 | C6B—C9B—H9B | 117.4 |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1*A*—H1*NA*···N3*A* | 0.84 (3) | 2.32 (2) | 2.630 (2) | 102.0 (19) |
| N1*A*—H1*NA*···O1*A*$^{i}$ | 0.84 (3) | 2.41 (3) | 3.190 (3) | 154 (2) |
| N1*A*—H2*NA*···S1*A*$^{ii}$ | 0.87 (3) | 2.52 (3) | 3.391 (2) | 172 (2) |
| N2*A*—H3*NA*···S1*B*$^{iii}$ | 0.84 (2) | 2.50 (2) | 3.3270 (19) | 166.1 (19) |
| N1*B*—H1*NB*···N3*B* | 0.91 (3) | 2.21 (3) | 2.619 (3) | 106 (3) |
| N1*B*—H2*NB*···O1*B*$^{iv}$ | 0.88 (3) | 2.01 (3) | 2.857 (3) | 161 (3) |
| N2*B*—H3*NB*···S1*A*$^{v}$ | 0.84 (2) | 2.58 (2) | 3.409 (2) | 171 (2) |

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