# 2,2′-Bi-1,3,4-thiadiazole-5,5′-diamine tetrahydrate

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In the title compound, $C_4H_4N_6S_2 \cdot 4H_2O$, the complete organic molecule is generated by crystallographic twofold symmetry and the dihedral angle between the aromatic rings is 10.24 (3)°. In the crystal, intermolecular N—H⋯N, N—H⋯O, O—H⋯N and O—H⋯O hydrogen bonds and aromatic $\pi$–$\pi$ stacking interactions [centroid–centroid separations = 3.530 (3) and 3.600 (3) Å] are observed.

## Related literature

For background to the pharmacutical properties of thiadiazoles, see: Chapleo *et al.* (1986; 1987); Stillings *et al.* (1986); Clerici *et al.* (2001). For their tribological behavior, see: Zhu *et al.* (2009) and for their pesticidal activity, see: Fan *et al.* (2010).
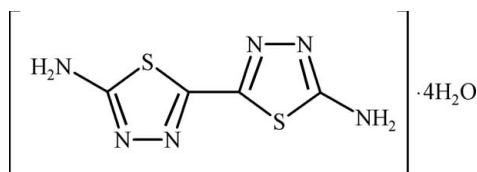


## Experimental

### Crystal data

$C_4H_4N_6S_2 \cdot 4H_2O$
$M_r$ = 272.32
Monoclinic, $C2/c$
$a$ = 19.977 (6) Å
$b$ = 6.678 (2) Å
$c$ = 9.328 (3) Å
$\beta$ = 112.514 (6)°

$V$ = 1149.7 (6) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.48 mm$^{-1}$
$T$ = 293 K
0.29 × 0.06 × 0.03 mm

### Data collection

Bruker APEX CCD diffractometer
Absorption correction: multi-scan
  (*SADABS*; Bruker, 2003)
  $T_{min}$ = 0.659, $T_{max}$ = 1.000

5047 measured reflections
1015 independent reflections
902 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.040

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.091
$S$ = 1.12
1015 reflections
91 parameters
6 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.36 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⋯$A$ |
|---|---|---|---|---|
| N3—H3$A$⋯O2$^i$ | 0.88 (2) | 2.11 (2) | 2.953 (3) | 161 (2) |
| N3—H3$B$⋯N2$^{ii}$ | 0.88 (2) | 2.12 (2) | 2.981 (3) | 170 (3) |
| O1—H1$A$⋯N1$^{iii}$ | 0.83 (2) | 2.05 (2) | 2.872 (3) | 171 (3) |
| O1—H1$B$⋯O2$^{iv}$ | 0.83 (2) | 1.96 (2) | 2.780 (3) | 168 (3) |
| O2—H2$A$⋯O1$^v$ | 0.82 (2) | 2.07 (2) | 2.867 (3) | 167 (3) |
| O2—H2$B$⋯O1$^{vi}$ | 0.83 (2) | 1.97 (2) | 2.806 (3) | 178 (3) |

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+1, y, -z+\frac{5}{2}$; (iii) $-x+1, y, -z+\frac{3}{2}$; (iv) $x, -y+1, z-\frac{1}{2}$; (v) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (vi) $-x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *Mercury*.

## References

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# supporting information

## 2,2′-Bi-1,3,4-thiadiazole-5,5′-diamine tetrahydrate

**Chaveng Pakawatchai and Saowanit Saithong**

### S1. Comment

Most of Shift bases, five membered heterocyclic thiadiazole derivatives containg N and S atoms were studied and reported due to the various applications. Different classes of thiadiazole compounds were found to be pharmacologically active using antihypertensive, anticonvulsant (Chapleo *et al.*, 1986; 1987; Stillings *et al.*, 1986), anti-depressant and anxiolytic activities (Clerici *et al.*, 2001). Recently, the friction and wear properties of 1,3,4-thiadiazole-2-thione derivatives have attracted a considerable amount of research effort. The compounds were synthesized and tested their tribological behavior as additive in rapeseed oil (ROS) to possess good thermal stabilities and anti-corrosive abilities and excellent load-carrying capacities. Moreover, they have good anti-wear and friction-reducing properties (Zhu *et al.*, 2009). In the agriculture, these compounds are widely use as pesticides activities and they have been comercialed as agrochemicals (Fan *et al.,* 2010)

In the present work, the title compound is the by-product of the reaction between copper(I) thiocyanate and 5-amino-1,3,4-thiadiazole-2-thiol ligand. Its crystal structure is reported here. The compound crystallizes in monoclinic system, space group *C*2/*c*. The asymmetric unit contains half the molecules of the title compound. The crystal structure consists of discrete molecules (Fig. 1) and 5,5′-amine-(2,2′-1,3,4-thiadiazole) molecules arrange as alternated sheets lying parallel to [010]. In addition, each set of sheets are separated by the layer of water molecules runing in same direction. The dihedral angle between mean plane of two thiadiazole rings is 10.24 (3)°. It could be indicated the effect of centroid-centroid interactions with the distances of 3.530 (3) and 3.600 (3)Å between the adjacent thidiazole rings in the same layer as depicted in Fig. 2. In the crystal lattice, amide nitrogen protons form N3—H3A···O2$^{ii}$ [N3···O2$^{ii}$ = 2.953 (3) Å] and N3—H3B···N2$^{iii}$ [N3···N2$^{iii}$ = 2.981 (3) Å] intermolecular hydrogen bonds with oxygen atoms of water molecules and one nitrogen atom of thiadiazole ring of adjacent molecules. While another thiadiazole nitrogen atom forms hydrogen bonding interaction with another water molecule in packing, O1—H1A···N1$^{i}$ [O1···N1$^{i}$ = 2.872 (3) Å]. In addition, The packing is also stabilized by the another type of hydrogen bond, O—H···O, among water molecules [O1···O2$^{iv}$ = 2.780 (3) Å, O2···O1$^{v}$ = 2.867 (3) Å, O2···O1$^{vi}$ = 2.806 (3) Å; iv, v and vi are the symmetry codes as given in Table 1]. The hydrogen bonds are shown in Fig. 3. The interactions in packings are generated the three-dimensional interaction networks and the interaction views down three axes are depicted in Fig. 4, 5 and 6.

### S2. Experimental

The 5-amino-1,3,4-thiadiazole-2-thiol (0.28 g, 2.1 mmol) was dissolved in acetronitile (40 ml) and then copper(I) thio-cyanate salt (0.16 g, 1.3 mmol) was added. After that, the reaction of mixture was performed under ultrasonic activation (338–340 K, 40 kHz) for 2 h. The light yellow filtration was kept and allowed to slowly to room temperature. Colourless blocks and rods of the title compound were recovered after a few days. Insufficient crystalline material was obtained for elemental analysis.

**S3. Refinement**

All hydrogen atoms were located in a difference Fourier map and restrained to ride on their parent atoms, N—H = 0.87–0.89 Å with $U_{iso}(H) = 1.2U_{eq}(N)$ and O—H = 0.81–0.84 Å with $U_{iso}(H) = 1.2U_{eq}(O)$, respectively.
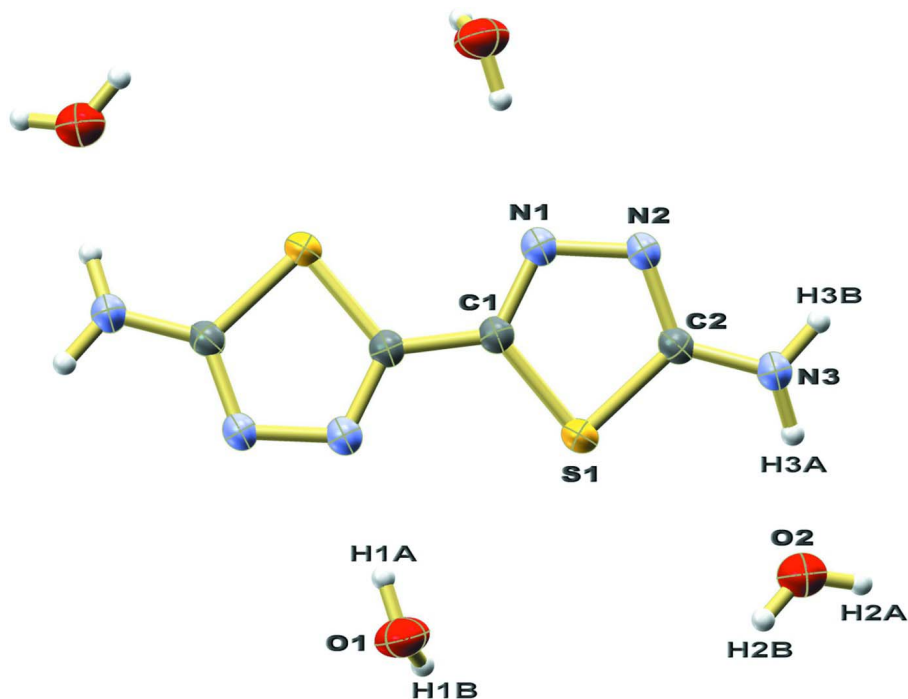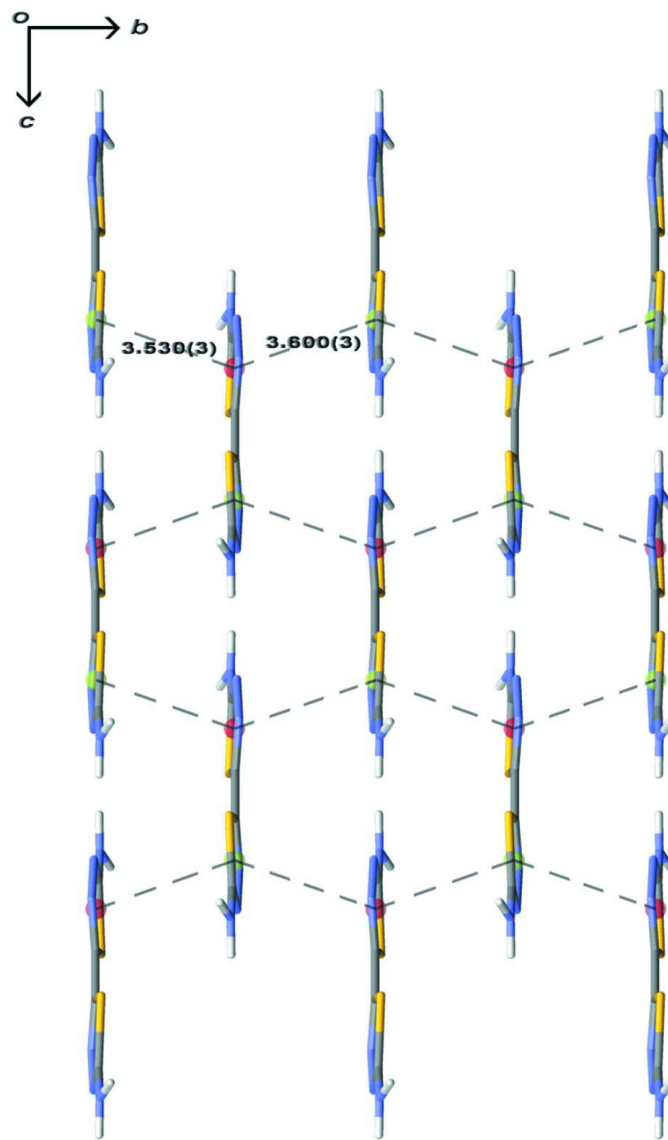


**Figure 1**

The molecular structure of (I) with displacement ellipsoids plotted at the 30% probability level. H atoms are omitted.

**Figure 2**

Centriod-centriod interaction distances between thiadiazoline rings in packing plot down *a* axis. Water layers are omitted.

**Figure 3**

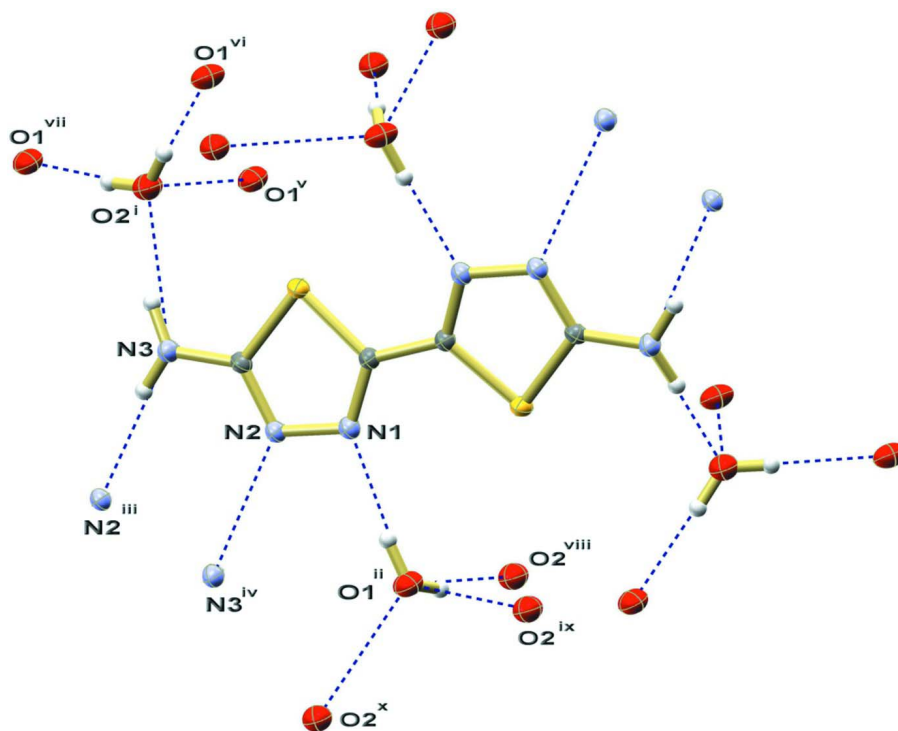The interactions of the [5,5′-amine-(2,2′-1,3,4-thiadiazole)] tetrahydrate compound. Symmetry code: i= $x$, $y$ - 1,$z$; ii = 1 - $x$,$y$,1.5 - $z$; iii = 1 - $x$, $y$ 2.5 - $z$; iv = 1 - $x$, $y$, 2.5 - $z$; v = $x$, -$y$, 1/2 + $z$; vi = 1/2 - $x$, 1/2 - $y$, 1 - $z$; vii = 1/2 - $x$, $y$ - 1/2, 1 - $z$; viii = 1 - $x$, 1 - $y$, 2 - $z$; ix = 1/2 + $x$, $y$ - 1/2, $z$; x = 1/2 + $x$, 1.5 - $y$, 1/2 - $z$.
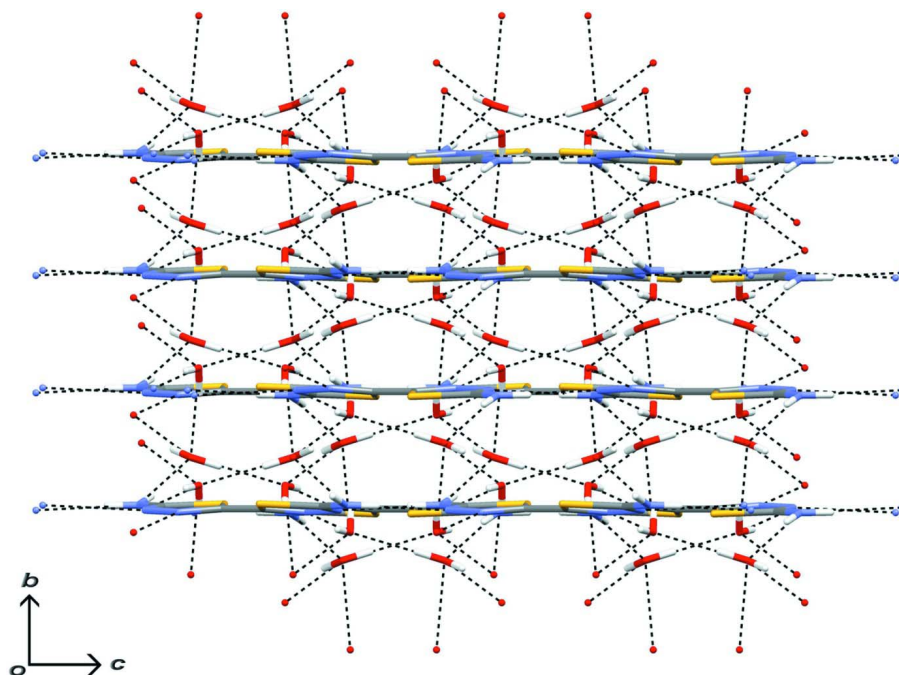
**Figure 4**

The interactions packing plot down *a* axis.
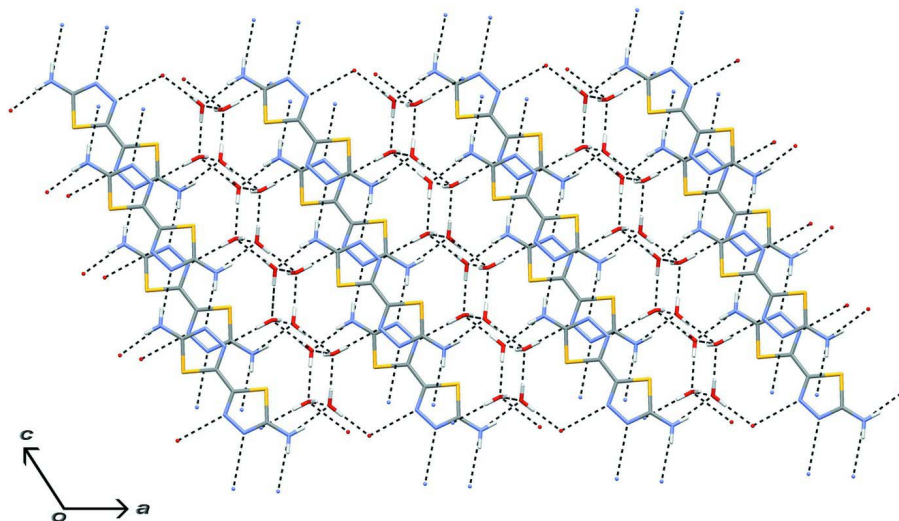


**Figure 5**

The interactions packing plot down *b* axis.
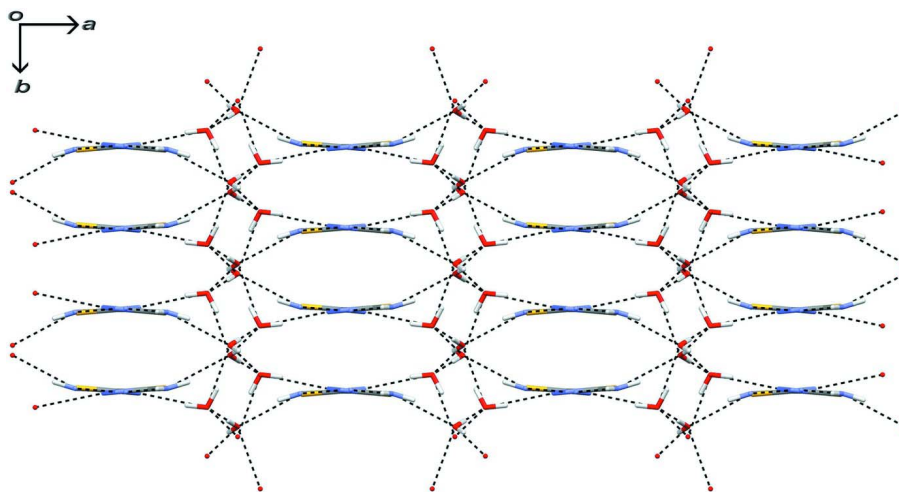


**Figure 6**

The interactions packing plot down *c* axis.

**2,2′-Bi-1,3,4-thiadiazole-5,5′-diamine tetrahydrate**

*Crystal data*

| | |
|---|---|
| $C_4H_4N_6S_2$·$4H_2O$ | $V = 1149.7$ (6) Å$^3$ |
| $M_r = 272.32$ | $Z = 4$ |
| Monoclinic, $C2/c$ | $F(000) = 568$ |
| Hall symbol: -C 2yc | $D_x = 1.573$ Mg m$^{-3}$ |
| $a = 19.977$ (6) Å | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $b = 6.678$ (2) Å | Cell parameters from 1375 reflections |
| $c = 9.328$ (3) Å | $\theta = 2.2$–27.5° |
| $\beta = 112.514$ (6)° | $\mu = 0.48$ mm$^{-1}$ |

$T$ = 293 K

Rod, colourless

$0.29 \times 0.06 \times 0.03$ mm

*Data collection*

| | |
|---|---|
| Bruker APEX CCD diffractometer | 5047 measured reflections |
| Radiation source: fine-focus sealed tube | 1015 independent reflections |
| Graphite monochromator | 902 reflections with $I > 2\sigma(I)$ |
| Frames, each covering 0.3 ° in $\omega$ scans | $R_{int}$ = 0.040 |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2003) | $\theta_{max}$ = 25.0°, $\theta_{min}$ = 2.2° |
| | $h = -23 \rightarrow 23$ |
| | $k = -7 \rightarrow 7$ |
| $T_{min}$ = 0.659, $T_{max}$ = 1.000 | $l = -11 \rightarrow 11$ |

*Refinement*

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.034

$wR(F^2)$ = 0.091

$S$ = 1.12

1015 reflections

91 parameters

6 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

$w = 1/[\sigma^2(F_o^2) + (0.046P)^2 + 0.8924P]$ where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max}$ = 0.36 e Å$^{-3}$

$\Delta\rho_{min}$ = −0.29 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 $F^2 > 2\sigma(F^2)$ 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$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| S1 | 0.40277 (3) | 0.22880 (9) | 0.80732 (6) | 0.0302 (2) |
| C1 | 0.49090 (11) | 0.2498 (3) | 0.8184 (2) | 0.0254 (5) |
| C2 | 0.43905 (11) | 0.2386 (3) | 1.0092 (2) | 0.0250 (5) |
| N1 | 0.53913 (9) | 0.2631 (2) | 0.9582 (2) | 0.0275 (4) |
| N2 | 0.51008 (10) | 0.2557 (3) | 1.0700 (2) | 0.0278 (4) |
| N3 | 0.39755 (11) | 0.2341 (3) | 1.0925 (2) | 0.0346 (5) |
| H3A | 0.3518 (10) | 0.196 (4) | 1.049 (3) | 0.042* |
| H3B | 0.4198 (14) | 0.236 (4) | 1.194 (2) | 0.042* |
| O1 | 0.30903 (9) | 0.3504 (3) | 0.3923 (2) | 0.0468 (5) |
| H1A | 0.3539 (10) | 0.338 (5) | 0.434 (3) | 0.056* |
| H1B | 0.2881 (16) | 0.242 (3) | 0.391 (4) | 0.056* |
| O2 | 0.25880 (9) | 1.0305 (3) | 0.9186 (2) | 0.0451 (5) |
| H2A | 0.2393 (14) | 0.997 (5) | 0.977 (3) | 0.054* |

| | | | |
|---|---|---|---|
| H2B | 0.2376 (14) | 1.067 (4) | 0.827 (2) | 0.054* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0234 (3) | 0.0449 (4) | 0.0199 (3) | 0.0004 (2) | 0.0057 (2) | −0.0007 (2) |
| C1 | 0.0253 (11) | 0.0284 (11) | 0.0227 (11) | 0.0003 (8) | 0.0096 (9) | 0.0001 (8) |
| C2 | 0.0270 (11) | 0.0256 (11) | 0.0206 (11) | 0.0016 (8) | 0.0071 (9) | −0.0001 (8) |
| N1 | 0.0273 (10) | 0.0324 (10) | 0.0230 (10) | 0.0002 (7) | 0.0100 (8) | 0.0004 (7) |
| N2 | 0.0269 (9) | 0.0364 (11) | 0.0203 (9) | 0.0005 (7) | 0.0093 (8) | 0.0002 (7) |
| N3 | 0.0275 (10) | 0.0542 (13) | 0.0232 (10) | −0.0021 (8) | 0.0109 (9) | −0.0003 (9) |
| O1 | 0.0292 (9) | 0.0543 (12) | 0.0501 (11) | −0.0052 (8) | 0.0076 (8) | 0.0054 (9) |
| O2 | 0.0356 (10) | 0.0546 (11) | 0.0420 (11) | −0.0013 (8) | 0.0113 (8) | 0.0006 (9) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| S1—C1 | 1.729 (2) | N3—H3A | 0.882 (17) |
| S1—C2 | 1.741 (2) | N3—H3B | 0.875 (17) |
| C1—N1 | 1.294 (3) | O1—H1A | 0.834 (18) |
| C1—C1$^i$ | 1.455 (4) | O1—H1B | 0.833 (17) |
| C2—N2 | 1.316 (3) | O2—H2A | 0.815 (17) |
| C2—N3 | 1.337 (3) | O2—H2B | 0.834 (17) |
| N1—N2 | 1.375 (3) | | |
| | | | |
| C1—S1—C2 | 86.53 (10) | C2—N2—N1 | 111.99 (17) |
| C1—S1—C2 | 86.53 (10) | C2—N2—N1 | 111.99 (17) |
| N1—C1—C1$^i$ | 122.9 (2) | C2—N3—H3A | 120.2 (17) |
| N1—C1—S1 | 114.49 (16) | C2—N3—H3A | 120.2 (17) |
| C1$^i$—C1—S1 | 122.6 (2) | C2—N3—H3B | 117.0 (19) |
| N2—C2—N3 | 123.9 (2) | C2—N3—H3B | 117.0 (19) |
| N2—C2—S1 | 113.78 (16) | H3A—N3—H3B | 121 (3) |
| N3—C2—S1 | 122.30 (17) | H1A—O1—H1B | 111 (3) |
| C1—N1—N2 | 113.20 (17) | H2A—O2—H2B | 126 (3) |
| | | | |
| C2—S1—C1—N1 | −0.35 (15) | C1$^i$—C1—N1—N2 | −178.63 (10) |
| C2—S1—C1—N1 | −0.35 (15) | S1—C1—N1—N2 | 0.6 (2) |
| C2—S1—C1—C1$^i$ | 178.91 (8) | N3—C2—N2—N1 | −178.00 (19) |
| C2—S1—C1—C1$^i$ | 178.91 (8) | S1—C2—N2—N1 | 0.4 (2) |
| C1—S1—C2—N2 | −0.02 (16) | C1—N1—N2—C2 | −0.6 (2) |
| C1—S1—C2—N3 | 178.36 (19) | C1—N1—N2—C2 | −0.6 (2) |

Symmetry code: (i) −x+1, y, −z+3/2.

*Hydrogen-bond geometry (Å, º)*

| D—H⋯A | D—H | H⋯A | D⋯A | D—H⋯A |
|---|---|---|---|---|
| N3—H3A⋯O2$^{ii}$ | 0.88 (2) | 2.11 (2) | 2.953 (3) | 161 (2) |
| N3—H3B⋯N2$^{iii}$ | 0.88 (2) | 2.12 (2) | 2.981 (3) | 170 (3) |
| O1—H1A⋯N1$^i$ | 0.83 (2) | 2.05 (2) | 2.872 (3) | 171 (3) |

| | | | | |
|---|---|---|---|---|
| O1—H1$B$···O2$^{iv}$ | 0.83 (2) | 1.96 (2) | 2.780 (3) | 168 (3) |
| O2—H2$A$···O1$^{v}$ | 0.82 (2) | 2.07 (2) | 2.867 (3) | 167 (3) |
| O2—H2$B$···O1$^{vi}$ | 0.83 (2) | 1.97 (2) | 2.806 (3) | 178 (3) |

Symmetry codes: (i) $-x+1$, $y$, $-z+3/2$; (ii) $x$, $y-1$, $z$; (iii) $-x+1$, $y$, $-z+5/2$; (iv) $x$, $-y+1$, $z-1/2$; (v) $-x+1/2$, $y+1/2$, $-z+3/2$; (vi) $-x+1/2$, $-y+3/2$, $-z+1$.