Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Synthesis and structure of 5,5′-(trisulfane-1,3-diyl)-bis(1,3,4-thiadiazol-2-amine)

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Received 16 April 2026
Accepted 25 May 2026

Edited by W. T. A. Harrison, University of Aberdeen, United Kingdom

Keywords: 1,3,4-thiadiazole; crystal structure; noncovalent interactions.

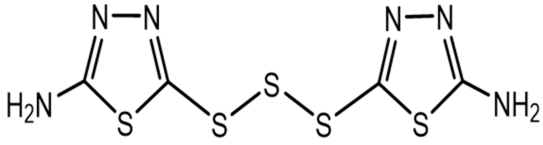
CCDC reference: 2556705

Supporting information: this article has supporting information at journals.iucr.org/e

The title compound, $C_4H_4N_6S_5$, consists of two 1,3,4-thiadiazol-2-amine moieties bridged by a trisulfanediyl group [S—S—S = 107.98 (6)°]. The conformation is supported by an intramolecular π–π stacking interaction. In the crystal, N—H···N hydrogen bonds link the molecules, enclosing $R_2^2(8)$ and $R_5^5(31)$ ring motifs, into infinite channels/tubes propagating along the *b*-axis direction. Hirshfeld surface analysis revealed that the most important contributions for the crystal packing are from S···S (33.6%) and H···N/N···H (32.8%) interactions.

1. Chemical context

1,3,4-Thiadiazole ($C_2H_2N_2S$) is a five-membered heterocyclic aromatic compound containing two nitrogen atoms and one sulfur atom. In order to improve the functional properties of 1,3,4- thiadiazoles, substituents can be attached at the 2- and 5-positions, enabling the creation of diverse bioactive compounds (*e.g.*, antibacterial, anticancer) from a stable, electron-deficient, five-membered heterocyclic ring (Hu *et al.*, 2014). Common synthesis methods include the cyclization of thiosemicarbazides or diacylhydrazines, as well as nucleophilic substitution and C—H activation to introduce various substituents (Hu *et al.*, 2014; Kumar *et al.*, 2024). In this work, we describe the synthesis and structure of the title compound, $C_4H_4N_6S_5$ (**I**), prepared by the oxidation of 5-amino-1,3,4-thiadiazole-2-thiol with 30% H_2O_2.



2. Structural commentary

Compound (**I**) consists of two 1,3,4-thiadiazol-2-amine moieties bridged by the trisulfanediyl group (Fig. 1) with the S2—S3—S4 bridging angle of 107.98 (6)°. The S2—S3 [2.0478 (16) Å] and S3—S4 [2.0705 (16) Å] and S2—C2 [1.766 (5) Å] and S4—C3 [1.755 (16) Å] bond lengths are slightly different, while the C2—S2—S3 [101.91 (15)°] and C3—S4—S3 [100.29 (15)°] bond angles are significantly different. The *A* (N1/N2/S1/C1/C2) and *B* (N4/N5/S5/C3/C4) rings are oriented at a dihedral angle of 5.15 (13)°, with a

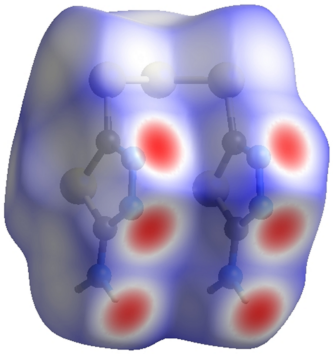


Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···N4^{i}	0.86	2.12	2.969 (6)	171
N3—H3B···N2^{ii}	0.86	2.25	3.099 (6)	170
N6—H6A···N5^{ii}	0.86	2.16	3.021 (5)	174
N6—H6B···N1^{i}	0.86	2.16	3.015 (6)	171

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

centroid–centroid separation of 3.621 (2) Å (slippage 1.336 Å), indicative of an intramolecular π–π stacking interaction. The key torsion angles associated with the trisulfide bridge are C2—S2—S3—S4 = 81.8 (3) and S2—S3—S4—C3 = −79.3 (3)°.

Atoms N3, N6, S2 and S4 are displaced by 0.076 (4), −0.062 (4), 0.0182 (11) and −0.1483 (12) Å, respectively, from their corresponding ring planes. The C1—N3 [1.338 (6) Å] and C4—N6 [1.320 (6) Å] bond lengths are a little longer than a typical C=N double bond (*e.g.* 1.27–1.30 Å) in imines and oximes with more orbital overlap indicating partial double bond (*e.g.*, 1.35–1.38 Å for pyridine and amides) character due to resonance delocalization. On the other hand, the S1—C1—N3 [120.6 (3)°] and S5—C4—N6 [123.5 (3)°], N1—C1—N3 [125.2 (4)°] and N4—C4—N6 [123.7 (4)°], S1—C1—N1 [114.2 (4)°] and S5—C4—N4 [112.8 (3)°], C1—N1—N2 [111.4 (4)°] and C4—N4—N5 [112.6 (3)°] bond angles are significantly different.

3. Supramolecular features

In the crystal, N—H···N hydrogen bonds (Table 1) link the molecules, enclosing $R_2^2(8)$ and $R_5^5(31)$ ring motifs (Fig. 2*a*), into infinite channels/tubes propagating along the *b*-axis direction (Fig. 2*b*). No intermolecular π–π stacking or C—H···π interactions are observed.

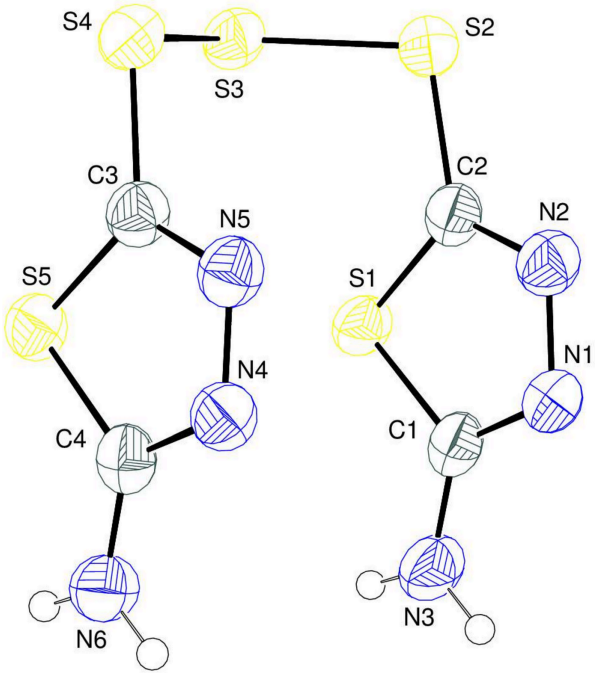


Figure 1
The molecular structure of (**I**) showing 50% probability ellipsoids.

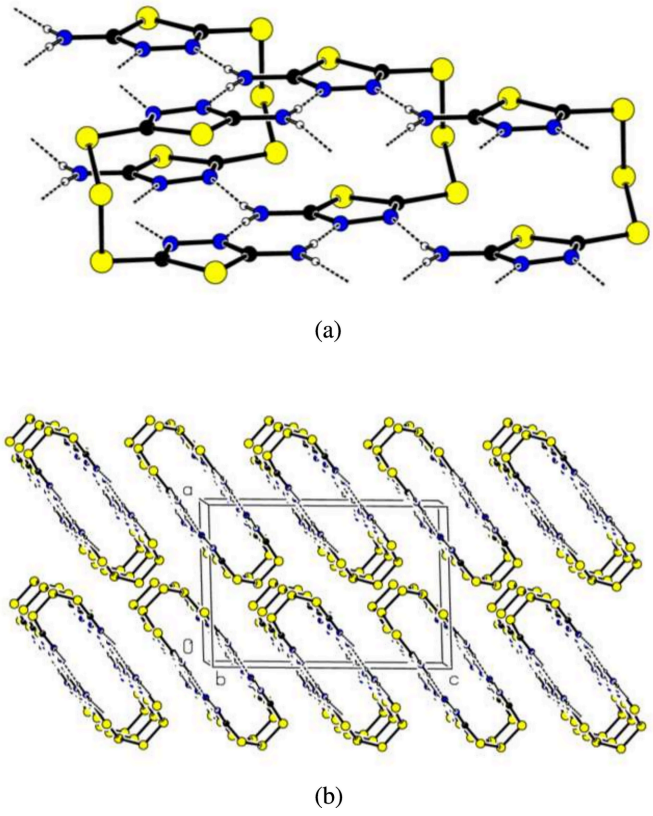


Figure 2
Partial packing diagrams for (**I**) showing N—H···N hydrogen bonds as dashed lines with (*a*) the $R_2^2(8)$ and $R_5^5(31)$ ring motifs and (*b*) the infinite channels/tubes viewed along the *b*-axis direction.

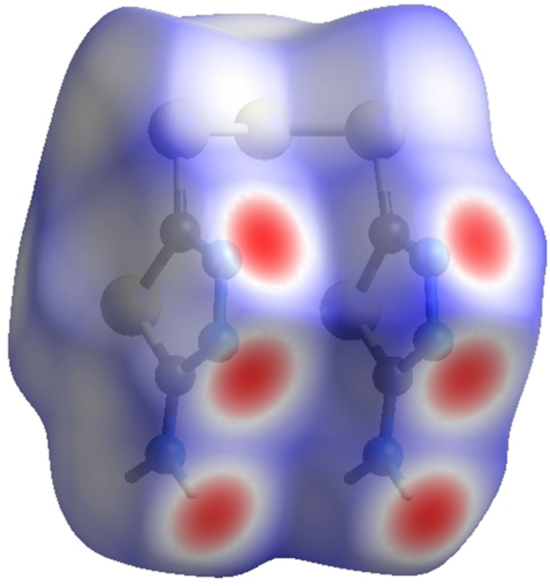


Figure 3
View of the three-dimensional Hirshfeld surface for (**I**) plotted over d_{norm} in the range −0.51 to 1.25 a.u.

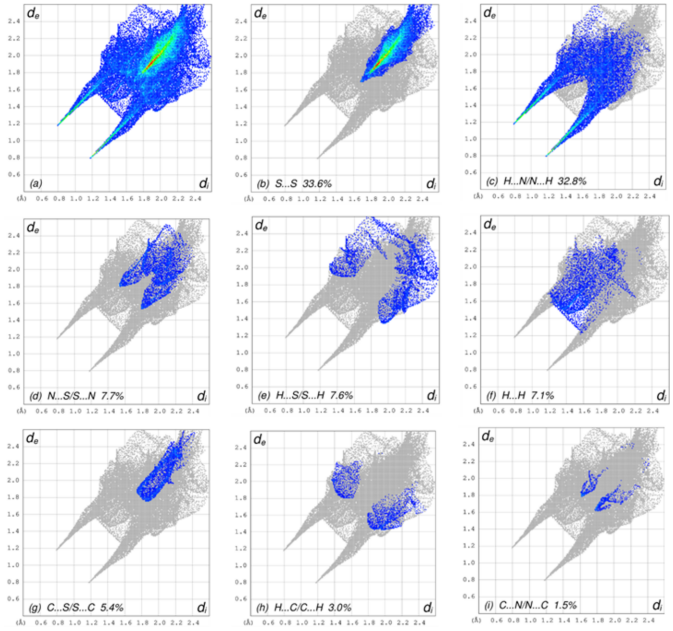


Figure 4
The two-dimensional fingerprint plots for (**I**), showing (*a*) all interactions, and delineated into different contact types (*b*)–(*i*). The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

4. Hirshfeld surface analysis

The intermolecular interactions in the crystal were further visualized by carrying out a Hirshfeld surface (HS) analysis using *CrystalExplorer* 17.5 (Spackman *et al.*, 2021). Fig. 3 shows the Hirshfeld surface with several neighboring molecules in the crystal. The white surface indicates contacts with distances equal to the sum of van der Waals radii, and the red and blue colours indicate distances shorter (in close contact) or longer (distinct contacts) than the van der Waals radii, respectively. The red spots indicate their roles as the respective donors and/or acceptor atoms in hydrogen bonding, as discussed above; they also appear as the blue and red regions corresponding to positive and negative potentials on the HS mapped over electrostatic potential as shown in Fig. S1. The blue and red regions indicate positive (hydrogen-bond donors) and negative (hydrogen-bond acceptors) electrostatic potentials. The overall two-dimensional fingerprint plots are shown in Fig. 4*a* and those delineated into different contact types are illustrated in Fig. 4*b*–*i*. According to the two-dimensional fingerprint plots, S···S and H···N/N···H contacts make the most significant contributions to the HS, at 33.6% and 32.8%, respectively.

5. Synthesis and crystallization

Hydrogen peroxide (30%, 10.4 ml) was added dropwise to a solution of 2-amino-5-mercapto-1,3,4-thiadiazole (0.20 mol) in the mixed solvents of ethanol (40 ml) and water (20 ml) at room temperature (Fig. 5). The mixture was stirred for 3 h, giving a precipitate. The precipitate was filtered off, dried and recrystallized from a *N*,*N*-dimethylformamide (DMF) solution to yield the title compound as a yellow solid. Yellow block-like single crystals of (**I**) suitable for single-crystal X-ray diffraction were grown by slow evaporation from DMF at room temperature. Yield: 58% (based on 2-amino-5-mercapto-1,3,4-thiadiazole). Analysis (%) calculated for $C_4H_4N_6S_5$, calculated (observed): C 16.21 (16.18), H 1.36 (1.34), N 28.35 (28.33). IR (ATR, 298 K, cm^{-1}): 3123, 3260 and 3402 ν(N—H), 1595 and 1614 ν(C=N). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 7.66 and 7.83 (4H, 2 NH_2). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, ppm): δ 157.2 and 148.6.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_4H_4N_6S_5$
M_r	296.43
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	11.0300 (4), 5.9139 (2), 16.2881 (7)
β (°)	92.406 (4)
V (Å^3)	1061.54 (7)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	9.89
Crystal size (mm)	0.16 × 0.12 × 0.08
Data collection	
Diffractometer	XtaLAB Synergy, Single source at home/near, HyPix3000
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2020)
T_{min}, T_{max}	0.380, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8905, 2054, 1675
R_{int}	0.078
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.615
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.069, 0.202, 1.00
No. of reflections	2054
No. of parameters	136
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.77, −0.66

Computer programs: *CrysAlis PRO* (Rigaku OD, 2020), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2016/6* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydrogen-atom positions were calculated geometrically at distances of N—H = 0.86 Å and refined using a riding model. The constraint U_{iso}(H) = 1.2U_{eq}(N) was applied in all cases.

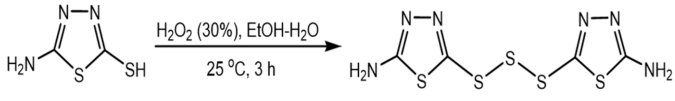


Figure 5
Synthesis scheme for (**I**).

Acknowledgements

The author's contributions are as follows. Conceptualization, ANB and TH; synthesis, AA and BT; X-ray analysis, BT, JA and TH; Hirshfeld surface analysis, TH; writing (review and editing of the manuscript) ANA, ANB and TH; supervision, TH and ANB.

Funding information

This work has been supported by the Azerbaijan Medical University and Baku Engineering University. TH is also grateful to Hacettepe University Scientific Research Project Unit (grant No. 013 D04 602 004).

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supporting information

Acta Cryst. (2026). E**82** [https://doi.org/10.1107/S2056989026005517]

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Computing details

5,5′-(Trisulfane-1,3-diyl)bis(1,3,4-thiadiazol-2-amine)

Crystal data

$C_4H_4N_6S_5$
M_r = 296.43
Monoclinic, $P2_1/c$
a = 11.0300 (4) Å
b = 5.9139 (2) Å
c = 16.2881 (7) Å
β = 92.406 (4)°
V = 1061.54 (7) Å^3
Z = 4
$F(000)$ = 600
D_x = 1.855 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 3057 reflections
θ = 4.0–71.0°
μ = 9.89 mm^{-1}
T = 293 K
Block, colourless
0.16 × 0.12 × 0.08 mm

Data collection

XtaLAB Synergy, Single source at home/near, HyPix3000 diffractometer
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2020)
T_{min} = 0.380, T_{max} = 1.000
8905 measured reflections
2054 independent reflections
1675 reflections with $I > 2\sigma(I)$
R_{int} = 0.078
θ_{max} = 71.5°, θ_{min} = 4.0°
h = −13→13
k = −7→7
l = −19→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.069
$wR(F^2)$ = 0.202
S = 1.00
2054 reflections
136 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1567P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.77 e Å^{-3}
$\Delta\rho_{min}$ = −0.66 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S3	0.47315 (9)	0.7178 (2)	0.31102 (7)	0.0452 (4)
S5	0.21531 (10)	0.30438 (19)	0.26530 (7)	0.0457 (4)
S1	0.33652 (10)	0.49558 (19)	0.47085 (7)	0.0451 (4)
S4	0.33425 (11)	0.75476 (18)	0.22253 (7)	0.0464 (4)
S2	0.44180 (10)	0.93820 (19)	0.40475 (7)	0.0488 (4)
N2	0.2520 (3)	0.8882 (7)	0.5007 (2)	0.0466 (9)
N4	0.0612 (3)	0.5350 (6)	0.3441 (2)	0.0438 (8)
N5	0.1361 (3)	0.6891 (6)	0.3097 (2)	0.0444 (8)
N1	0.1785 (4)	0.7401 (7)	0.5423 (3)	0.0473 (9)
N6	0.0369 (4)	0.1443 (6)	0.3578 (3)	0.0489 (9)
H6B	−0.023827	0.161979	0.388611	0.059*
H6A	0.061155	0.010410	0.345985	0.059*
N3	0.1525 (4)	0.3479 (7)	0.5594 (3)	0.0549 (11)
H3A	0.090114	0.365799	0.588721	0.066*
H3B	0.178061	0.214081	0.548935	0.066*
C4	0.0930 (4)	0.3226 (7)	0.3287 (3)	0.0409 (9)
C1	0.2097 (4)	0.5284 (8)	0.5301 (3)	0.0431 (10)
C2	0.3355 (4)	0.7875 (8)	0.4616 (3)	0.0417 (9)
C3	0.2197 (4)	0.5970 (8)	0.2674 (3)	0.0417 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S3	0.0374 (6)	0.0526 (7)	0.0465 (7)	0.0010 (4)	0.0108 (5)	−0.0029 (5)
S5	0.0428 (6)	0.0443 (6)	0.0507 (7)	0.0035 (4)	0.0097 (5)	−0.0090 (5)
S1	0.0425 (6)	0.0455 (6)	0.0481 (7)	0.0052 (4)	0.0121 (5)	−0.0021 (4)
S4	0.0486 (7)	0.0500 (7)	0.0408 (7)	−0.0005 (4)	0.0061 (5)	0.0013 (5)
S2	0.0502 (7)	0.0490 (7)	0.0479 (7)	−0.0088 (5)	0.0100 (5)	−0.0070 (5)
N2	0.0414 (19)	0.051 (2)	0.048 (2)	0.0010 (16)	0.0068 (16)	−0.0047 (18)
N4	0.0376 (17)	0.0445 (19)	0.050 (2)	0.0026 (15)	0.0063 (15)	−0.0057 (16)
N5	0.0423 (18)	0.049 (2)	0.042 (2)	0.0024 (16)	0.0005 (15)	−0.0024 (16)
N1	0.047 (2)	0.049 (2)	0.047 (2)	−0.0013 (16)	0.0141 (17)	−0.0069 (16)
N6	0.0481 (19)	0.042 (2)	0.057 (2)	0.0034 (16)	0.0115 (17)	−0.0026 (17)
N3	0.062 (2)	0.047 (2)	0.058 (3)	0.0075 (19)	0.023 (2)	−0.0003 (18)
C4	0.0351 (19)	0.047 (2)	0.041 (2)	0.0045 (16)	−0.0028 (17)	−0.0067 (18)
C1	0.043 (2)	0.050 (2)	0.037 (2)	0.0039 (18)	0.0058 (17)	−0.0066 (18)
C2	0.040 (2)	0.046 (2)	0.039 (2)	0.0009 (17)	0.0032 (17)	−0.0053 (18)
C3	0.039 (2)	0.044 (2)	0.043 (2)	0.0025 (17)	0.0041 (17)	−0.0028 (18)

Geometric parameters (Å, º)

S3—S4	2.0705 (16)	N4—N5	1.366 (5)
S3—S2	2.0478 (16)	N4—C4	1.331 (5)
S5—C4	1.737 (4)	N5—C3	1.294 (6)
S5—C3	1.732 (5)	N1—C1	1.315 (6)
S1—C1	1.744 (4)	N6—H6B	0.8600
S1—C2	1.733 (5)	N6—H6A	0.8600
S4—C3	1.755 (4)	N6—C4	1.320 (6)
S2—C2	1.766 (5)	N3—H3A	0.8600
N2—N1	1.389 (5)	N3—H3B	0.8600
N2—C2	1.287 (6)	N3—C1	1.338 (6)
S2—S3—S4	107.98 (6)	C1—N3—H3B	120.0
C3—S5—C4	87.0 (2)	N4—C4—S5	112.8 (3)
C2—S1—C1	86.2 (2)	N6—C4—S5	123.5 (3)
C3—S4—S3	100.29 (15)	N6—C4—N4	123.7 (4)
C2—S2—S3	101.91 (15)	N1—C1—S1	114.2 (4)
C2—N2—N1	113.2 (4)	N1—C1—N3	125.2 (4)
C4—N4—N5	112.6 (3)	N3—C1—S1	120.6 (3)
C3—N5—N4	113.2 (4)	S1—C2—S2	123.1 (3)
C1—N1—N2	111.4 (4)	N2—C2—S1	114.8 (4)
H6B—N6—H6A	120.0	N2—C2—S2	122.0 (4)
C4—N6—H6B	120.0	S5—C3—S4	122.9 (2)
C4—N6—H6A	120.0	N5—C3—S5	114.3 (3)
H3A—N3—H3B	120.0	N5—C3—S4	122.7 (4)
C1—N3—H3A	120.0		
S3—S4—C3—S5	−78.2 (3)	N1—N2—C2—S2	−179.3 (3)
S3—S4—C3—N5	97.0 (4)	C4—S5—C3—S4	174.1 (3)
S3—S2—C2—S1	33.6 (3)	C4—S5—C3—N5	−1.4 (3)
S3—S2—C2—N2	−147.6 (4)	C4—N4—N5—C3	1.9 (6)
N2—N1—C1—S1	3.1 (5)	C1—S1—C2—S2	−179.4 (3)
N2—N1—C1—N3	−177.1 (4)	C1—S1—C2—N2	1.8 (4)
N4—N5—C3—S5	0.0 (5)	C2—S1—C1—N1	−2.7 (4)
N4—N5—C3—S4	−175.5 (3)	C2—S1—C1—N3	177.4 (4)
N5—N4—C4—S5	−3.0 (5)	C2—N2—N1—C1	−1.7 (6)
N5—N4—C4—N6	177.6 (4)	C3—S5—C4—N4	2.5 (3)
N1—N2—C2—S1	−0.4 (5)	C3—S5—C4—N6	−178.1 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···N4^{i}	0.86	2.12	2.969 (6)	171
N3—H3*B*···N2^{ii}	0.86	2.25	3.099 (6)	170

N6—H6*A*···N5^{ii}	0.86	2.16	3.021 (5)	174
N6—H6*B*···N1^{i}	0.86	2.16	3.015 (6)	171

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