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# 5,6-Di-2-thienyl-2,3-dihydropyrazine

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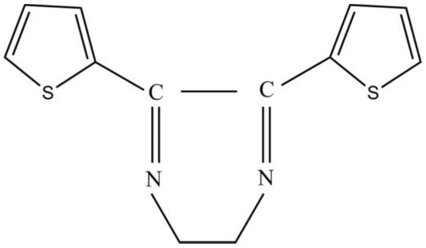
Key indicators: single-crystal X-ray study; $T$ = 100 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.032; $wR$ factor = 0.115; data-to-parameter ratio = 31.7.

In the title compound, $C_{12}H_{10}N_2S_2$, which was synthesized by the reaction of 2,2′-thenil and ethylenediamine, the dihedral angle between the two thiophene rings is 66.33 (9)°. In the crystal structure, intermolecular C—H⋯N hydrogen bonds link the molecules into infinite chains along the $b$ axis and weak C—H⋯$\pi$ interactions may further stabilize the structure.

## Related literature

For backgroud to thenils, see: Shimon *et al.* (1993). For related structures, see: Crundwell *et al.* (2002*a*,*b*, 2003); Linehan *et al.* (2003); Stacy *et al.* (2003). For bond-length data, see: Allen *et al.* (1987). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



## Experimental

### *Crystal data*

$C_{12}H_{10}N_2S_2$
$M_r$ = 246.34
Monoclinic, $P2_1$
$a$ = 5.5006 (9) Å
$b$ = 7.5246 (12) Å
$c$ = 14.116 (2) Å
$\beta$ = 97.902 (5)°
$V$ = 578.73 (16) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 0.43 mm$^{-1}$
$T$ = 100 K
0.32 × 0.26 × 0.08 mm

### *Data collection*

Bruker APEX DUO CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009) $T_{\min}$ = 0.875, $T_{\max}$ = 0.965
9583 measured reflections
4603 independent reflections
4295 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.022

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.115
$S$ = 1.20
4603 reflections
145 parameters
1 restraint
All H-atom parameters refined
$\Delta\rho_{\max}$ = 0.62 e Å$^{-3}$
$\Delta\rho_{\min}$ = −0.47 e Å$^{-3}$
Absolute structure: Flack (1983), with 1899 Friedel pairs
Flack parameter: 0.07 (6)

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

*Cg*2 is the centroid of the S2/C9–C12 ring.

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| C1—H1$A$⋯N1$^{\rm i}$ | 0.93 | 2.33 | 3.235 (3) | 163 |
| C2—H2$A$⋯$Cg2^{\rm ii}$ | 0.93 | 2.85 | 3.7737 (18) | 171 |

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5396).

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# supporting information

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## 5,6-Di-2-thienyl-2,3-dihydropyrazine

**Madhukar Hemamalini and Hoong-Kun Fun**

### S1. Comment

Thienyl-based guests have shown preferential inclusion into the host by keeping thienyl ring *S* atoms pointed away from the face of growing crystals, possibly to avoid unfavorable electrostatic interactions between sulfur lone pairs coplanar with the thiophene ring and molecules already incorporated into the growing crystal face (Shimon *et al.*, 1993). The structural studies on thenoins (Crundwell *et al.*, 2002*a*,*b*) and thenils (Crundwell *et al.*, 2003), and other thiophene-containing molecules such as 2,5-diphenyl-3,4-dithien-3-ylcyclopentadien-1-one (Linehan *et al.*, 2003) and 4-bromo-2-thiophenecarboxaldehyde (Stacy *et al.*, 2003) have been reported in the literature. In continuation of this area of study, the crystal structure of the title compound, (I), is reported here.

In the molecule of the title compound (Fig. 1), the bond lengths (Allen *et al.*, 1987) and angles are within normal ranges. The dihedral angle between the two thiophene rings S1/C1–C4 and S2/C9–C12 is 66.33 (9)°. In the crystal structure, intermolecular C—H···N hydrogen bonds (Table 1) link the molecules (Fig. 2) into infinite chains along the *b* axis, in which they may be effective in the stabilization of the structure. The crystal structure is further stabilized by C—H···$\pi$ interactions (Table 1), involving the S2/C9–C12 (centroid Cg2) ring.

### S2. Experimental

2,2′-thenil (55 mg) and ethylenediamine (15 mg) in ethanol/water (40 ml) were heated under reflux for 2 h with stirring. The resulting solution was then cooled to room temperature. After a few days of slow evaporation of the solvent, brown plates of (I) were obtained.

### S3. Refinement

All H atoms were positioned geometrically (C—H = 0.93 or 0.97 Å) and were refined using a riding model, with $U_{\rm iso}$(H) = 1.2 or 1.5$U_{\rm eq}$(C). In the absence of significant anomalous scattering effects, 1899 Friedel pairs were merged.

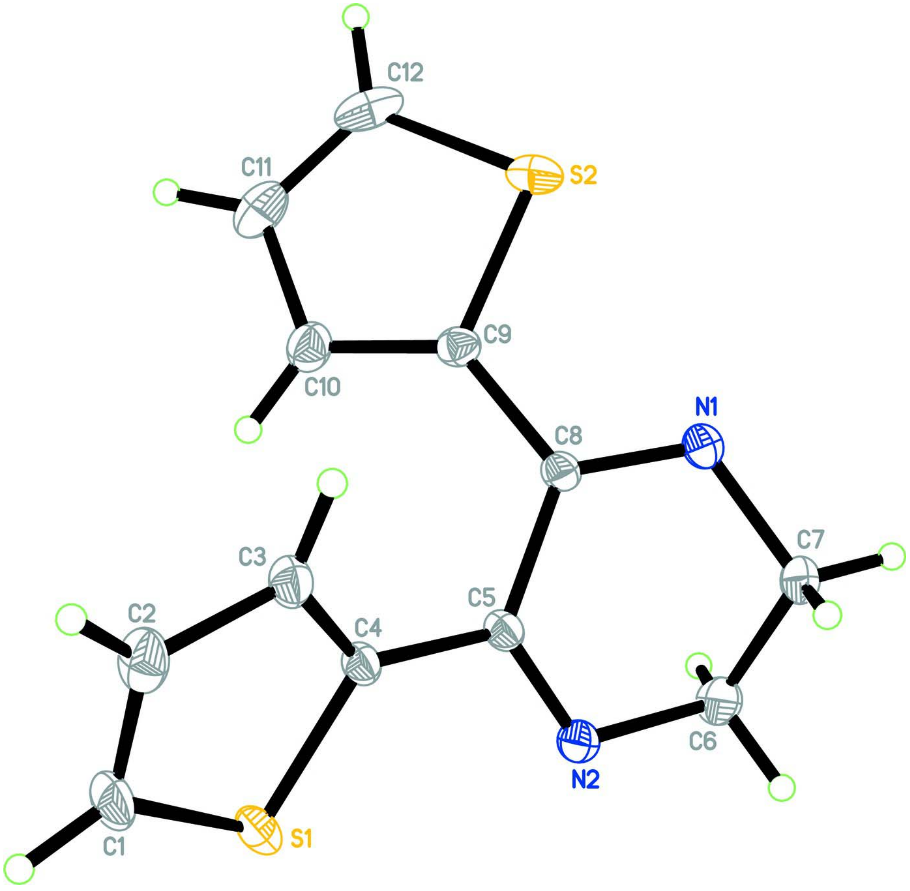

**Figure 1**

The asymmetric unit of (I) with displacement ellipsoids drawn at the 50% probability level.

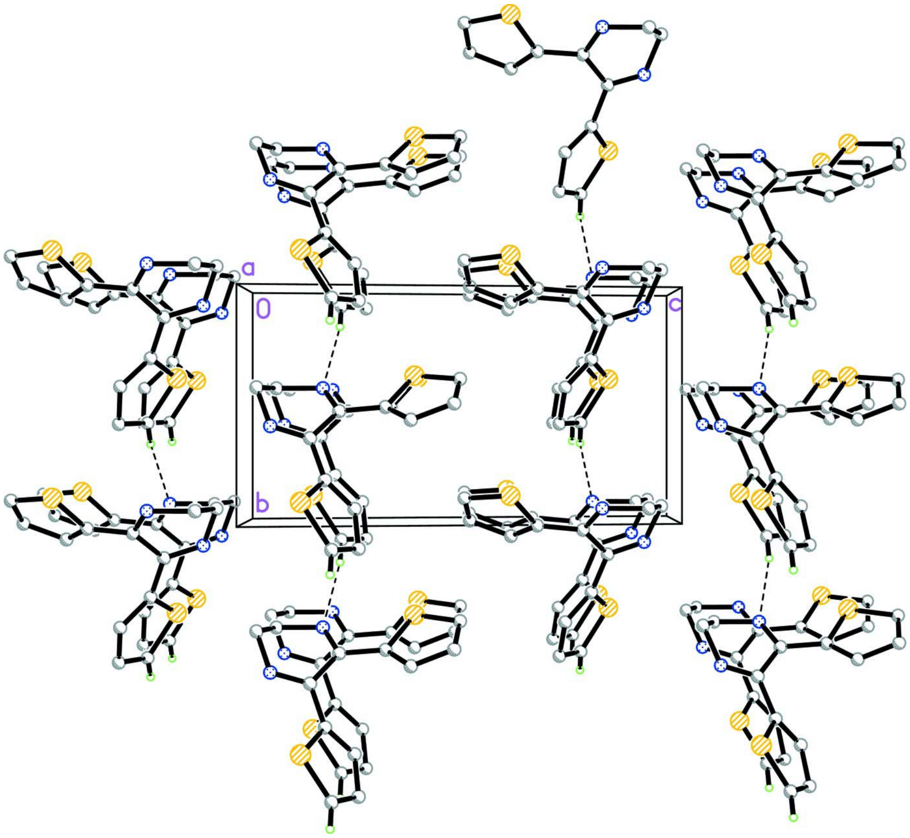

**Figure 2**

The crystal packing of (I), showing hydrogen-bonded (dashed lines) networks. H atoms are not involving the hydrogen bond interactions are omitted for clarity.

## 5,6-Di-2-thienyl-2,3-dihydropyrazine

### *Crystal data*

$C_{12}H_{10}N_2S_2$
$M_r = 246.34$
Monoclinic, $P2_1$
Hall symbol: P 2yb
$a = 5.5006$ (9) Å
$b = 7.5246$ (12) Å
$c = 14.116$ (2) Å
$\beta = 97.902$ (5)°
$V = 578.73$ (16) Å$^3$
$Z = 2$

$F(000) = 256$
$D_x = 1.414$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5014 reflections
$\theta = 2.9$–34.8°
$\mu = 0.43$ mm$^{-1}$
$T = 100$ K
Plate, brown
0.32 × 0.26 × 0.08 mm

### *Data collection*

Bruker APEX DUO CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{\min} = 0.875$, $T_{\max} = 0.965$

9583 measured reflections
4603 independent reflections
4295 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.022$
$\theta_{\max} = 35.1°$, $\theta_{\min} = 1.5°$
$h = -8\rightarrow8$
$k = -12\rightarrow12$
$l = -22\rightarrow22$

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | All H-atom parameters refined |
| $R[F^2 > 2\sigma(F^2)] = 0.032$ | $w = 1/[\sigma^2(F_o^2) + (0.0632P)^2 + 0.0559P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.115$ | $(\Delta/\sigma)_{max} < 0.001$ |
| $S = 1.20$ | $\Delta\rho_{max} = 0.62$ e Å$^{-3}$ |
| 4603 reflections | $\Delta\rho_{min} = -0.47$ e Å$^{-3}$ |
| 145 parameters | Absolute structure: Flack (1983), with 1899 Friedel pairs |
| 1 restraint | Absolute structure parameter: 0.07 (6) |
| Primary atom site location: structure-invariant direct methods | |
| Secondary atom site location: difference Fourier map | |

*Special details*

**Experimental**. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

**Geometry**. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 | 0.53730 (6) | 0.88379 (6) | 0.15567 (3) | 0.02249 (9) |
| S2 | −0.08370 (7) | 0.37500 (7) | 0.39261 (3) | 0.02435 (10) |
| N1 | −0.1511 (2) | 0.42753 (19) | 0.18646 (9) | 0.0176 (2) |
| N2 | 0.2016 (2) | 0.58341 (19) | 0.08083 (8) | 0.0167 (2) |
| C1 | 0.5372 (3) | 1.0745 (3) | 0.22117 (12) | 0.0256 (3) |
| H1A | 0.6518 | 1.1651 | 0.2206 | 0.031* |
| C2 | 0.3468 (3) | 1.0777 (2) | 0.27490 (12) | 0.0225 (3) |
| H2A | 0.3166 | 1.1719 | 0.3143 | 0.027* |
| C3 | 0.2025 (3) | 0.9222 (2) | 0.26367 (10) | 0.0176 (2) |
| H3A | 0.0665 | 0.9026 | 0.2948 | 0.021* |
| C4 | 0.2854 (2) | 0.8021 (2) | 0.20133 (9) | 0.0141 (2) |
| C5 | 0.1765 (2) | 0.6334 (2) | 0.16622 (10) | 0.0141 (2) |
| C6 | 0.0602 (3) | 0.4259 (2) | 0.04601 (10) | 0.0199 (3) |
| H6A | 0.1494 | 0.3194 | 0.0686 | 0.024* |
| H6B | 0.0373 | 0.4245 | −0.0234 | 0.024* |
| C7 | −0.1875 (3) | 0.4280 (2) | 0.08163 (10) | 0.0192 (3) |
| H7A | −0.2783 | 0.5333 | 0.0582 | 0.023* |
| H7B | −0.2817 | 0.3244 | 0.0579 | 0.023* |
| C8 | 0.0286 (2) | 0.5231 (2) | 0.22635 (9) | 0.0136 (2) |
| C9 | 0.0980 (3) | 0.5061 (2) | 0.32993 (9) | 0.0148 (2) |
| C10 | 0.3080 (3) | 0.5582 (2) | 0.38767 (10) | 0.0199 (3) |

| | | | | |
|---|---|---|---|---|
| H10A | 0.4286 | 0.6292 | 0.3670 | 0.024* |
| C11 | 0.3203 (4) | 0.4914 (3) | 0.48252 (11) | 0.0272 (3) |
| H11A | 0.4496 | 0.5144 | 0.5307 | 0.033* |
| C12 | 0.1220 (4) | 0.3904 (3) | 0.49497 (11) | 0.0296 (4) |
| H12A | 0.1007 | 0.3360 | 0.5524 | 0.036* |

*Atomic displacement parameters ($Å^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.02124 (15) | 0.02353 (19) | 0.02375 (16) | −0.01080 (15) | 0.00690 (12) | −0.00227 (15) |
| S2 | 0.02570 (17) | 0.0293 (2) | 0.01976 (15) | −0.00416 (17) | 0.00917 (12) | 0.00490 (16) |
| N1 | 0.0195 (5) | 0.0164 (5) | 0.0168 (4) | −0.0061 (4) | 0.0022 (4) | −0.0014 (4) |
| N2 | 0.0188 (5) | 0.0166 (5) | 0.0151 (5) | −0.0038 (4) | 0.0037 (4) | −0.0023 (4) |
| C1 | 0.0311 (8) | 0.0176 (7) | 0.0264 (7) | −0.0130 (6) | −0.0022 (6) | 0.0022 (6) |
| C2 | 0.0283 (7) | 0.0127 (6) | 0.0246 (6) | −0.0012 (6) | −0.0030 (5) | −0.0006 (5) |
| C3 | 0.0178 (5) | 0.0161 (6) | 0.0186 (5) | −0.0030 (5) | 0.0010 (4) | −0.0018 (5) |
| C4 | 0.0142 (5) | 0.0126 (6) | 0.0151 (5) | −0.0027 (4) | 0.0007 (4) | 0.0008 (4) |
| C5 | 0.0138 (5) | 0.0131 (6) | 0.0154 (5) | −0.0023 (4) | 0.0019 (4) | 0.0006 (4) |
| C6 | 0.0256 (6) | 0.0162 (6) | 0.0181 (5) | −0.0039 (5) | 0.0042 (5) | −0.0054 (5) |
| C7 | 0.0203 (6) | 0.0200 (7) | 0.0164 (5) | −0.0066 (5) | 0.0001 (4) | −0.0024 (5) |
| C8 | 0.0154 (5) | 0.0113 (5) | 0.0141 (5) | −0.0022 (4) | 0.0027 (4) | 0.0000 (4) |
| C9 | 0.0180 (5) | 0.0129 (6) | 0.0140 (5) | −0.0001 (5) | 0.0036 (4) | 0.0004 (4) |
| C10 | 0.0205 (6) | 0.0206 (7) | 0.0173 (5) | −0.0006 (5) | −0.0017 (5) | 0.0012 (5) |
| C11 | 0.0331 (8) | 0.0304 (9) | 0.0163 (6) | 0.0034 (7) | −0.0030 (5) | 0.0006 (6) |
| C12 | 0.0399 (8) | 0.0353 (10) | 0.0151 (5) | 0.0070 (9) | 0.0087 (5) | 0.0054 (7) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| S1—C1 | 1.707 (2) | C4—C5 | 1.461 (2) |
| S1—C4 | 1.7201 (14) | C5—C8 | 1.5040 (19) |
| S2—C12 | 1.7124 (19) | C6—C7 | 1.516 (2) |
| S2—C9 | 1.7317 (14) | C6—H6A | 0.9700 |
| N1—C8 | 1.2874 (18) | C6—H6B | 0.9700 |
| N1—C7 | 1.4658 (19) | C7—H7A | 0.9700 |
| N2—C5 | 1.2880 (18) | C7—H7B | 0.9700 |
| N2—C6 | 1.465 (2) | C8—C9 | 1.4652 (19) |
| C1—C2 | 1.375 (3) | C9—C10 | 1.376 (2) |
| C1—H1A | 0.9300 | C10—C11 | 1.423 (2) |
| C2—C3 | 1.411 (2) | C10—H10A | 0.9300 |
| C2—H2A | 0.9300 | C11—C12 | 1.361 (3) |
| C3—C4 | 1.382 (2) | C11—H11A | 0.9300 |
| C3—H3A | 0.9300 | C12—H12A | 0.9300 |
| | | | |
| C1—S1—C4 | 92.13 (8) | C7—C6—H6B | 109.7 |
| C12—S2—C9 | 91.82 (8) | H6A—C6—H6B | 108.2 |
| C8—N1—C7 | 115.50 (12) | N1—C7—C6 | 109.29 (12) |
| C5—N2—C6 | 115.48 (12) | N1—C7—H7A | 109.8 |
| C2—C1—S1 | 111.76 (12) | C6—C7—H7A | 109.8 |

| | | | |
|---|---|---|---|
| C2—C1—H1A | 124.1 | N1—C7—H7B | 109.8 |
| S1—C1—H1A | 124.1 | C6—C7—H7B | 109.8 |
| C1—C2—C3 | 112.51 (15) | H7A—C7—H7B | 108.3 |
| C1—C2—H2A | 123.7 | N1—C8—C9 | 117.84 (12) |
| C3—C2—H2A | 123.7 | N1—C8—C5 | 120.25 (12) |
| C4—C3—C2 | 112.59 (13) | C9—C8—C5 | 121.61 (12) |
| C4—C3—H3A | 123.7 | C10—C9—C8 | 130.47 (13) |
| C2—C3—H3A | 123.7 | C10—C9—S2 | 110.85 (10) |
| C3—C4—C5 | 128.94 (12) | C8—C9—S2 | 118.02 (10) |
| C3—C4—S1 | 110.99 (11) | C9—C10—C11 | 112.61 (15) |
| C5—C4—S1 | 119.83 (10) | C9—C10—H10A | 123.7 |
| N2—C5—C4 | 118.67 (13) | C11—C10—H10A | 123.7 |
| N2—C5—C8 | 120.18 (13) | C12—C11—C10 | 112.55 (15) |
| C4—C5—C8 | 121.10 (11) | C12—C11—H11A | 123.7 |
| N2—C6—C7 | 109.89 (12) | C10—C11—H11A | 123.7 |
| N2—C6—H6A | 109.7 | C11—C12—S2 | 112.16 (12) |
| C7—C6—H6A | 109.7 | C11—C12—H12A | 123.9 |
| N2—C6—H6B | 109.7 | S2—C12—H12A | 123.9 |

| | | | |
|---|---|---|---|
| C4—S1—C1—C2 | −1.31 (14) | C7—N1—C8—C5 | 3.3 (2) |
| S1—C1—C2—C3 | 0.95 (19) | N2—C5—C8—N1 | −29.3 (2) |
| C1—C2—C3—C4 | 0.1 (2) | C4—C5—C8—N1 | 148.07 (15) |
| C2—C3—C4—C5 | −175.19 (14) | N2—C5—C8—C9 | 144.36 (15) |
| C2—C3—C4—S1 | −1.03 (16) | C4—C5—C8—C9 | −38.3 (2) |
| C1—S1—C4—C3 | 1.33 (12) | N1—C8—C9—C10 | 163.90 (16) |
| C1—S1—C4—C5 | 176.10 (12) | C5—C8—C9—C10 | −9.9 (2) |
| C6—N2—C5—C4 | −172.06 (13) | N1—C8—C9—S2 | −5.87 (19) |
| C6—N2—C5—C8 | 5.4 (2) | C5—C8—C9—S2 | −179.66 (11) |
| C3—C4—C5—N2 | 147.03 (16) | C12—S2—C9—C10 | −0.12 (14) |
| S1—C4—C5—N2 | −26.69 (19) | C12—S2—C9—C8 | 171.56 (13) |
| C3—C4—C5—C8 | −30.4 (2) | C8—C9—C10—C11 | −170.37 (16) |
| S1—C4—C5—C8 | 155.92 (11) | S2—C9—C10—C11 | −0.03 (18) |
| C5—N2—C6—C7 | 37.17 (19) | C9—C10—C11—C12 | 0.2 (2) |
| C8—N1—C7—C6 | 38.97 (19) | C10—C11—C12—S2 | −0.3 (2) |
| N2—C6—C7—N1 | −60.13 (17) | C9—S2—C12—C11 | 0.26 (17) |
| C7—N1—C8—C9 | −170.61 (13) | | |

### *Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C1—H1*A*···N1$^{i}$ | 0.93 | 2.33 | 3.235 (3) | 163 |
| C2—H2*A*···*Cg*2$^{ii}$ | 0.93 | 2.85 | 3.7737 (18) | 171 |

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