Synthesis and crystal structure of 3-phenyl-1,4,2-dithiazole-5-thione

Melbourne J. Schriver, a, * Tanner George b and Jason D. Masuda b

a Department of Chemistry, Crandall University, PO Box 6004, Moncton, New Brunswick, E1C 9L7, Canada, and
b Department of Chemistry, Saint Mary’s University, 923 Robie Street, Halifax, Nova Scotia, B3H 3C3, Canada.
* Correspondence e-mail: mel.schriver@crandallu.ca

In the title compound, C 8H 5NS 3, the dihedral angle between the heterocyclic ring and the phenyl ring is 2.62 (5)°. In the extended structure, aromatic π–π stacking between the 1,4,2-dithiazole-5-thione moiety and the phenyl ring is observed [centroid–centroid distances = 3.717 (6) and 3.712 (6) Å]. The almost planar molecules arrange themselves in parallel chains of head-to-tail molecules oriented by a network of weak C—H···S contacts close to the sum of their van der Waals radii within the chains. All the hydrogen atoms participate in hydrogen-bonding interactions with the sulfur and nitrogen atoms of adjacent molecules. C=S···S contacts between the chains that are significantly shorter than the sum of their van der Waals radii also impact the overall packing.

1. Chemical context

The preparation of derivatives of the 1,4,2-dithiazole-5-thione heterocycle was first described in 1967 in 9–14% yield (Behringer & Deichmann, 1967). Subsequent synthetic work (Greig et al., 1985) allowed the synthesis of several derivatives in higher yields (21–29%). An investigation of the chemistry of the ring system (Crosby et al., 2002) showed that the 1,4,2-dithiazole-5-thione ring is more thermally stable and less reactive than the electronically similar 1,3,4-oxathiazol-2-one ring but may be used as an alternate route to nitrile sulfides and the thermal cycloaddition with electron deficient alkynes and nitriles. The existing literature on the 1,4,2-dithiazole-5-thione heterocycle is limited to six accounts (Behringer & Deichmann, 1967; Noel & Vialle, 1967; Holm & Toubro, 1978; Greig et al., 1985; Wai & Sammes, 1990; Crosby et al., 2002), which do not include theoretical or crystal-structure determinations.

The 1,4,2-dithiazole-5-thione heterocycle is a member of a rich family of isomeric ring systems. Derivatives of 1,2,4-dithiazole-5-thione include xanthane hydride, which has been the subject of structural analysis (Stanford, 1963) and is used industrially as a sulfur-transfer agent in the vulcanization of rubber and the sulfuration of oligonucleotides. The crystal structure of the isomeric ring system 1,3,2-dithiazole-4-thione has also been reported (Oakley et al., 1987).

The incorporation of the preparation, isolation and structural characterization of heterocyclic compounds to demonstrate the chemistry of carboxylic acid derivatives in the undergraduate organic chemistry laboratory has been previously described (Nason et al., 2017). To date, our attention has been focused on the synthesis of derivatives of the 1,3,4-oxathiazol-2-one heterocycle because of the relative ease
of preparation and, until recently, the limited research studying the chemistry of the heterocycle family. In our search for a new focus heterocycle, the small library of existing publications on the 1,4,2-dithiazole-5-thione derivatives coupled to the relative ease of synthesis made this ring system a target for investigation and we now describe the synthesis and crystal structure of the title compound, C₈H₅NS₃.

2. Structural commentary

The structure of the title compound (Fig. 1) reveals that the heterocycle and the aromatic ring are essentially co-planar [C₈−C₃−C₂−S₂ = −2.91 (13)°]. The C₂−C₃ [1.4721 (14) Å] bond is not significantly shorter than the accepted value for a C-sp²–C-sp² single bond (1.48 Å) but it is longer than the average (1.45 ± 0.03 Å) of similar C-sp²–C-sp² inter-ring bonds found in the related oxathiazolone derivatives (Nason et al., 2017). The extension of π delocalization between the rings is sufficient to direct the observed co-planarity. The sum of the internal angles of the heterocyclic ring (539.9°) is almost ideal for five-membered rings (540°).

Within the heterocycle moiety, the molecule shows significant (p < 0.01) structural differences (Kooijman, 2005) to similar regions in the related oxathiazolone derivatives, and for reference, the comparison will be made to 5-phenyl-1,3,4-oxathiazol-2-one (Schriver et al., 1995). In the title compound, the C₂=N₁ double bond [1.2961 (13) Å] is significantly longer (and weaker) than in the oxathiazolone [1.268 (6) Å] while the C₁−S₁ bond [1.7248 (11) Å] is shorter [1.754 (5) Å]. These differences are consistent with a higher degree of π delocalization in the title heterocycle as compared to the oxathiazolone. The current π-island structural model for oxathiazolone heterocycles has been suggested to explain the decarboxylation to form the nitrile sulfides (Krayushkin et al., 2010) with longer, weaker endocyclic C−S bonds consistent with lower extrusion temperatures (Zhu et al., 2017).

Conversely, in the title molecule the C₁−S₁ bond is shorter and stronger, which is consistent with the observed resistance of 1,4,2-dithiazole-5-thiones to thermally extrude CS₂ to form nitrile sulfides (Greig et al., 1985). The endocyclic C−S bonds are significantly (p < 0.01) asymmetric with the C₁−S₁ bond the shortest of the three bonds, consistent with a higher bond order and π character while the C₁−S₂ bond [1.7363 (11) Å] is longer but not as long as the C₂−S₂ bond [1.7587 (10) Å]. This pattern of bond lengths is in agreement with a more extensive, and less localized, π delocalization in this heterocycle than in the comparable oxathiazolone derivatives.

Comparison of the structure of the title compound with the structures of the isomeric ring systems 1,2,4-dithiazole-5-thione (Stanford, 1963), 1,3,2-dithiazole-4-thione (Oakley et al., 1987), 1,2,3-dithiazole-5-thione (Constantinides et al., 2021) and the derivatives of 1,4,2-dithiazole (Oakley et al., 1993) reveal that the endocyclic C−S bonds in the heterocycle (average 1.74 ± 0.02 Å) and the exocyclic C₁−S₃ bond [1.6438 (11) Å] are all consistent with the distances expected based on the conventional Lewis structure and the statistical averages for comparable bond distances (C−S = 1.75 ±0.02 Å and C=\(\text{S} = 1.64 ± 0.02\) Å) from the comparison heterocycle systems.

3. Supramolecular features

The extended structure of the title compound features π–π centroid stacking (Fig. 2), six hydrogen-bonding interactions...
Table 1
Hydrogen-bond geometry (Å, °).

|       | D—H···A | D−H | H···A | D···A | D−H···A |
|-------|---------|------|-------|-------|---------|
| C4—H4···N1 | 0.95 | 2.89 | 3.6281 (14) | 136 |
| C5—H5···S1 | 0.95 | 3.04 | 3.8474 (11) | 144 |
| C5—H5···S2 | 0.95 | 2.96 | 3.6529 (11) | 131 |
| C6—H6···S3 | 0.95 | 3.11 | 3.7231 (12) | 124 |
| C7—H7···S3 | 0.95 | 3.06 | 3.9651 (12) | 159 |
| C8—H8···S2 | 0.95 | 3.10 | 3.9141 (11) | 145 |

Symmetry codes: (i) −x + 2, −y, −z + 1; (ii) x + 1, y, z + 1; (iii) −x, −y + 1, −z + 1.

(Table 1; Fig. 3) and one chain of sulfur-sulfur interactions (Fig. 4). The packing of two molecules across an inversion centre results in one of two centroid-stacking interactions. The molecules exist as co-planar and parallel chains of heterocycles, with supramolecular contacts confirmed by the statistically constant centroid-to-centroid distances between rings in different adjacent chains [3.717 (6) and 3.712 (6) Å] with the latter centroid-to-centroid distance across the inversion centre. The plane of the molecule is roughly perpendicular to the b axis and the molecular centroids form a chain-to-chain, stepwise angle [166.698 (17)°] on the a axis. Head-to-toe hydrogen-bonding interactions between C5 and C6 donors to the exocyclic thione S3 with H···S distances of 2.96 and 3.11 Å, respectively (Fig. 3) form the primary cohesion along the a- and c-axis directions. In addition, the rest of the phenyl ring hydrogen atoms are involved with side-on, out-of-plane step-wise hydrogen bonds between H4 and N1 (2.89 Å), H5···S1 (3.04 Å), H7···S3 (3.06 Å) and H8···S2 (3.10 Å). The sulfur-sulfur interactions occur as a chain out of plane between the thione S3 and S1 atoms within the ring (Fig. 4). While the observed H···S hydrogen bonding between the molecules is weak (Σ van der Waals radii S···H = 3.0 Å), they aid the orientation of the molecules within the out-of-plane chains. In contrast, the S···S contact distance [3.575 (11) Å] may appear to be close to the accepted sum of the van der Waals radii (3.6 Å) but when the known anisotropy of sulfur contacts [in plane S···S contact 3.20 Å and perpendicular S···S contact 4.06 Å (Constantinides et al., 2021)] are factored, it is revealed that the contact is a significant contributor to the supramolecular packing of the compound.

4. Database survey
A search of the Cambridge Structural Database (Version 5.41, September 2021; Groom et al., 2016) revealed that there are six crystal structures reported for molecules containing the neutral 1,4,2-dithiazole heterocyclic ring (Chu et al., 1993; Oakley et al., 1993, 1994; Feng et al., 2016). The thione moiety in the structure of 3-phenyl-1,4,2-dithiazole-5-thione, however, makes this the first crystal structure reported for this heterocyclic system with a thione substituent at the C1 position.

5. Synthesis and crystallization
A solution of trichloromethanesulfenyl chloride (10.17 g, 22.81 mmol) in chloroform (10.17 g) was added dropwise to a warmed solution of thiobenzamide (6.161 g, 44.91 mmol) in chloroform (240 ml) according to a literature procedure (Greig et al., 1985). The reaction mixture was refluxed for 4 h followed by evaporation in a crystallizing dish to a yellow–orange residue (7.002 g). The crude product was recrystallized twice in 95% ethanol to give the product as bright-yellow crystalline needles (Fig. 5) (1.235 g, 5.84 mmol, 13.0%)
Table 2
Experimental details.

| Crystal data | Chemical formula | C₈H₅NS₃ |
|--------------|------------------|---------|
| Mₐ | 211.31 |
| Crystal system, space group | Triclinic, PTT |
| Temperature (K) | 100 |
| a, b, c (Å) | 5.7955 (4), 7.3789 (5), 10.0344 (7) |
| α, β, γ (°) | 89.459 (3), 89.719 (2), 78.956 (2) |
| V (Å³) | 421.15 (5) |
| Z | 2 |
| Radiation type | Mo Kα |
| μ (mm⁻¹) | 0.81 |
| Crystal size (mm) | 0.2 × 0.12 × 0.05 |

| Data collection | Diffractometer | Bruker APEXI CCD |
|-----------------|-----------------|------------------|
| T_{min} T_{max} | 0.654, 0.748 |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 49509, 4085, 3322 |
| R_{int} | 0.064 |
| (sinθ/λ)_{max} (Å⁻¹) | 0.833 |

| Refinement | R(F² > 2σ(F²)), wR(F²), S | 0.031, 0.074, 1.03 |
| No. of reflections | 4085 |
| No. of parameters | 109 |
| H-atom treatment | H-atom parameters constrained |
| Δρ_{max}, Δρ_{min} (e Å⁻³) | 0.63, −0.39 |

Computer programs: APEX4 and SAINT (Bruker, 2019), SHELXT2014/5 (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b) and OLEX2 (Dolomanov et al., 2009).

suitable for crystallographic analysis. R₁ (CH₂Cl₂) = 0.671; UV–visible (CH₂Cl₂) λ_{max} nm (log ε): 256 (4.29), 361 (4.20), ¹H NMR 60 MHz, CDCl₃ δ = 7.53 ppm (multiplet).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were geometrically placed (C−H = 0.95 Å) and refined as riding atoms with U_{iso}(H) = 1.2U_{eq}(C).

Acknowledgements

We thank Katherine N. Robertson for helpful discussions.

Funding information

MJS would like to acknowledge the support of Crandall University and the Stephen and Ella Steeves Research Fund for operating funds. JDM would like to acknowledge the Natural Science and Engineering Council of Canada (NSERC) for operating funds and Saint Mary’s University for supporting the purchase of the SCXRD instrument.

References

Behringer, H. & Deichmann, D. (1967). Tetrahedron Lett. 8, 1013–1017.
Bruker (2019). APEX4 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
Cha, S.-L., Wai, K.-F., Lai, T.-F. & Sammes, M. P. (1993). Tetrahedron Lett. 34, 847–850.
Constantinides, C. P., Koyioni, M., Bazzi, F., Manoli, M., Lawson, D. B. & Koutentis, P. A. (2021). Molecules, 26, 5875.
Crosby, J., Grant, K. J., Greig, D. J., Paton, R. M., Rankin, J. G. & Ross, J. F. (2002). Arkivoc, pp. 121–129.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). J. Appl. Cryst. 42, 339–341.
Feng, Y., Zou, M., Song, R., Shao, X., Li, Z. & Qian, X. (2016). J. Org. Chem. 81, 10321–10327.
Greig, D. J., McPherson, M., Paton, R. M. & Crosby, J. (1985). J. Chem. Soc. Perkin Trans. 1, pp. 1205–1208.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). Acta Cryst. B72, 171–179.
Holm, A. & Toubro, N. H. (1978). J. Chem. Soc. Perkin Trans. 1, pp. 1445–1449.
Kooijman, H. (2005). Interpretation of Crystal Structure Determinations. Utrecht University.
Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). J. Appl. Cryst. 48, 3–10.
Krayushkin, M. M., Kalik, M. A. & Vorontsova, L. G. (2010). Chem. Heterocycl. Compd. 46, 484–489.
Nason, T. R., Schriver, M. J., Hendsbee, A. D. & Masuda, J. D. (2017). Acta Cryst. E73, 1298–1301.
Noel, D. & Vialle, J. (1967). Bull. Soc. Chim. Fr. p. 2239.
Oakley, R. T., Koenig, H. & Cordes, A. W. (1987). Acta Cryst. C43, 2468–2469.
Oakley, R. T., Richardson, J. F. & Spence, R. E. (1993). J. Chem. Soc. Chem. Commun. pp. 1226–1227.
Oakley, R. T., Richardson, J. F., Spence, R. E. v. H. (1994). J. Org. Chem. 59, 2997–3002.
Schriver, M. J. & Zaworotko, M. J. (1995). J. Chem. Crystallogr. 25, 25–28.
Sheldrick, G. M. (2015a). Acta Cryst. A71, 3–8.
Sheldrick, G. M. (2015b). Acta Cryst. C71, 3–8.
Stanford, R. H. (1963). Acta Cryst. 16, 1157–1162.
Wai, K. F. & Sammes, M. P. (1990). J. Chem. Soc. Perkin Trans. 1, pp. 808–809.
Zhu, S., Schriver, M. J., Hendsbee, A. D. & Masuda, J. D. (2017). Acta Cryst. E73, 1726–1731.
Synthesis and crystal structure of 3-phenyl-1,4,2-dithiazole-5-thione

Melbourne J. Schriver, Tanner George and Jason D. Masuda

Computing details

Data collection: APEX4 (Bruker, 2019); cell refinement: SAINT (Bruker, 2019); data reduction: SAINT (Bruker, 2019); program(s) used to solve structure: SHELXT2014/5 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

3-Phenyl-5H-1,4,2-dithiazole-5-thione

Crystal data

C8H5NS3  
Mr = 211.31  
Triclinic, P1  
a = 5.7955 (4) Å  
b = 7.3789 (5) Å  
c = 10.0344 (7) Å  
α = 89.459 (3)°  
β = 89.719 (2)°  
γ = 78.956 (2)°  
V = 421.15 (5) Å³  
Z = 2  
F(000) = 216  
Dx = 1.666 Mg m⁻³  
Mo Kα radiation, λ = 0.71073 Å  
Cell parameters from 9861 reflections  
θ = 2.8–39.7°  
µ = 0.81 mm⁻¹  
T = 100 K  
Needle, yellow  
θmax = 36.3°, θmin = 2.0°  
0.2 × 0.12 × 0.05 mm

Data collection

Bruker APEXII CCD  
diffractometer  
φ and ω scans  
Absorption correction: multi-scan  
(SADABS; Krause et al., 2015)  
Tmin = 0.654, Tmax = 0.748  
49509 measured reflections  
4085 independent reflections  
3322 reflections with I > 2σ(I)  
Rint = 0.064  
θmax = 36.3°, θmin = 2.0°  
h = −9→9  
k = −12→12  
l = −16→16

Refinement

Refinement on F²  
Least-squares matrix: full  
R[F² > 2σ(F²)] = 0.031  
wR(F²) = 0.074  
S = 1.03  
4085 reflections  
109 parameters  
0 restraints  
Hydrogen site location: inferred from neighbour sites  
H-atom parameters constrained  
w = 1/[σ²(Fo²) + (0.0293P)² + 0.2221P]  
where P = (Fo² + 2Fe²)/3  
(Δ/σ)max = 0.001  
Δρmax = 0.63 e Å⁻³  
Δρmin = −0.39 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      | Uiso* / Ueq |
|----|--------|--------|--------|-------------|
| S1 | 0.59859 (5) | 0.10273 (4) | 0.20602 (3) | 0.01367 (6) |
| S2 | 0.23050 (4) | 0.29112 (4) | 0.36958 (3) | 0.01254 (6) |
| S3 | 0.12785 (5) | 0.22623 (4) | 0.08266 (3) | 0.01711 (6) |
| N1 | 0.67826 (16) | 0.13417 (13) | 0.36131 (9) | 0.01333 (16) |
| C1 | 0.30604 (19) | 0.20788 (15) | 0.21084 (10) | 0.01200 (17) |
| C2 | 0.2316 (18) | 0.22144 (14) | 0.43743 (10) | 0.01050 (16) |
| C3 | 0.55288 (18) | 0.26295 (14) | 0.57773 (10) | 0.01094 (16) |
| C4 | 0.77430 (18) | 0.20050 (14) | 0.63514 (10) | 0.01211 (17) |
| H4 | 0.898918 | 0.133069 | 0.583378 | 0.015* |
| C5 | 0.81060 (19) | 0.23770 (15) | 0.76809 (11) | 0.01428 (18) |
| H5 | 0.960741 | 0.195896 | 0.806938 | 0.017* |
| C6 | 0.6283 (2) | 0.33594 (15) | 0.84490 (11) | 0.01488 (18) |
| H6 | 0.653943 | 0.359485 | 0.936024 | 0.018* |
| C7 | 0.4088 (2) | 0.39949 (15) | 0.78795 (11) | 0.01443 (18) |
| H7 | 0.284614 | 0.467081 | 0.839959 | 0.017* |
| C8 | 0.37177 (19) | 0.36371 (14) | 0.65470 (10) | 0.01259 (17) |
| H8 | 0.222345 | 0.408062 | 0.615693 | 0.015* |

**Atomic displacement parameters (Å²)**

|    | U¹¹ | U¹² | U¹³ | U¹² | U¹³ | U¹³ |
|----|-----|-----|-----|-----|-----|-----|
| S1 | 0.01186 (11) | 0.01664 (12) | 0.01185 (11) | −0.00088 (9) | 0.00020 (8) | −0.00335 (8) |
| S2 | 0.00949 (10) | 0.01580 (12) | 0.01156 (10) | −0.00040 (8) | −0.00086 (8) | −0.00118 (8) |
| S3 | 0.01444 (12) | 0.02474 (14) | 0.01221 (11) | −0.00380 (10) | −0.00353 (9) | 0.00023 (9) |
| N1 | 0.0115 (4) | 0.0153 (4) | 0.0124 (4) | −0.0004 (3) | −0.0012 (3) | −0.0028 (3) |
| C1 | 0.0116 (4) | 0.0132 (4) | 0.0115 (4) | −0.0033 (3) | 0.0001 (3) | −0.0004 (3) |
| C2 | 0.0103 (4) | 0.0095 (4) | 0.0118 (4) | −0.0020 (3) | −0.0009 (3) | 0.0005 (3) |
| C3 | 0.0116 (4) | 0.0096 (4) | 0.0116 (4) | −0.0020 (3) | −0.0006 (3) | −0.0001 (3) |
| C4 | 0.0116 (4) | 0.0119 (4) | 0.0124 (4) | −0.0013 (3) | −0.0008 (3) | −0.0007 (3) |
| C5 | 0.0143 (4) | 0.0142 (4) | 0.0142 (4) | −0.0025 (4) | −0.0036 (3) | 0.0005 (3) |
| C6 | 0.0188 (5) | 0.0147 (4) | 0.0118 (4) | −0.0047 (4) | −0.0013 (4) | −0.0011 (3) |
| C7 | 0.0164 (5) | 0.0137 (4) | 0.0132 (4) | −0.0026 (4) | 0.0016 (3) | −0.0017 (3) |
| C8 | 0.0119 (4) | 0.0124 (4) | 0.0130 (4) | −0.0014 (3) | 0.0001 (3) | −0.0005 (3) |

**Geometric parameters (Å, °)**

|    |    |    |    |    |    |
|----|----|----|----|----|----|
| S1—N1 | 1.6583 (9) | C4—H4 | 0.9500 |
| S1—C1 | 1.7248 (11) | C4—C5 | 1.3896 (14) |
| S2—C1 | 1.7363 (11) | C5—H5 | 0.9500 |
| Bond                  | Length (Å) | Bond                  | Length (Å) |
|----------------------|------------|----------------------|------------|
| S2—C2                | 1.7587 (10)   | C5—C6                | 1.3945 (16) |
| S3—C1                | 1.6418 (11)   | C6—H6                | 0.9500     |
| N1—C2                | 1.2961 (13)   | C6—C7                | 1.3926 (16) |
| C2—C3                | 1.4721 (14)   | C7—H7                | 0.9500     |
| C3—C4                | 1.4024 (14)   | C7—C8                | 1.3910 (15) |
| C3—C8                | 1.3981 (14)   | C8—H8                | 0.9500     |

| C2—N1—C1            | 100.79 (5)    | C5—C4—H4            | 120.1      |
| C1—S2—C2            | 95.54 (5)     | C4—C5—H5            | 119.7      |
| N1—C2—S1            | 115.28 (8)    | C4—C5—C6            | 120.51 (10) |
| S3—C1—C2            | 124.34 (6)    | C6—C5—H5            | 119.7      |
| S3—C1—S2            | 125.54 (7)    | C5—C6—H6            | 120.0      |
| S2—C2—S1            | 118.25 (8)    | C7—C6—H6            | 120.0      |
| N1—C2—C3            | 122.66 (9)    | C6—C7—H7            | 120.1      |
| C3—C2—S2            | 119.09 (8)    | C6—C7—C6            | 119.80 (10) |
| C4—C3—C2            | 119.78 (9)    | C8—C7—H7            | 120.1      |
| C8—C3—C2            | 120.68 (9)    | C8—C7—C3            | 120.48 (10) |
| C3—C4—H4            | 120.1         | C7—C8—H8            | 119.8      |
| C5—C4—C3            | 119.70 (10)   |                      |            |

| Bond                  | Angle (°)     | Bond                  | Angle (°)  |
|----------------------|--------------|----------------------|------------|
| S1—N1—C2—S2         | 0.97 (12)    | C2—S2—C1—S1         | 1.38 (6)   |
| S1—N1—C2—C3         | −179.44 (8)  | C2—S2—C1—S3         | −178.33 (8) |
| S2—C2—C3—C4         | 176.91 (8)   | C2—C3—C4—C5         | −179.15 (9) |
| S2—C2—C3—C8         | −2.91 (13)   | C2—C3—C8—C7         | 178.73 (10) |
| N1—S1—C1—S2         | −1.05 (7)    | C3—C4—C5—C6         | 0.27 (16)  |
| N1—S1—C1—C3         | 178.66 (7)   | C4—C3—C8—C7         | −1.09 (15) |
| N1—C2—C3—C4         | −2.67 (15)   | C4—C5—C6—C7         | −0.80 (16) |
| N1—C2—C3—C8         | 177.51 (10)  | C5—C6—C7—C8         | 0.38 (16)  |
| C1—S1—N1—C2         | 0.08 (9)     | C6—C7—C8—C3         | 0.57 (16)  |
| C1—S2—C2—C1         | −1.49 (9)    | C8—C3—C4—C5         | 0.67 (15)  |
| C1—S2—C2—C3         | 178.91 (8)   |                      |            |

### Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|-------|-------|---------|
| C4—H4···N1i | 0.95 | 2.89  | 3.6281 (14) | 136 |
| C5—H5···S1i | 0.95 | 3.04  | 3.8474 (11) | 144 |
| C5—H5···S3ii | 0.95 | 2.96  | 3.6529 (11) | 131 |
| C6—H6···S3ii | 0.95 | 3.11  | 3.7231 (12) | 124 |
| C7—H7···S3iii | 0.95 | 3.06  | 3.9651 (12) | 159 |
| C8—H8···S2iii | 0.95 | 3.10  | 3.9141 (11) | 145 |

Symmetry codes: (i) x+2, y, z+1; (ii) x+1, y, z+1; (iii) −x, −y+1, −z+1.