



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

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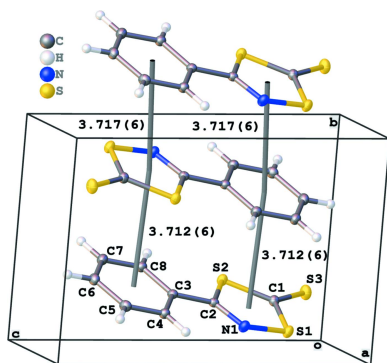
In the title compound, C₈H₅NS₃, the dihedral angle between the heterocyclic ring and the phenyl ring is 2.62 (5)°. In the extended structure, aromatic π - π stacking between the 1,4,2-dithiazole-5-thione moiety and the phenyl ring is observed [centroid-centroid distances = 3.717 (6) and 3.712 (6) Å]. 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

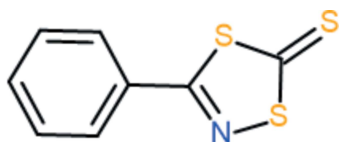
The preparation of derivatives of the 1,4,2-dithiazole-5-thione heterocycle was first described in 1967 in 9–14% yield (Behringer & Deichmann, 1967). Subsequent synthetic work (Greig *et al.*, 1985) allowed the synthesis of several derivatives in higher yields (21–29%). An investigation of the chemistry 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, $C_8H_5NS_3$.



2. Structural commentary

The structure of the title compound (Fig. 1) reveals that the heterocycle and the aromatic ring are essentially co-planar [$C8-C3-C2-S2 = -2.91(13)^\circ$]. The $C2-C3$ [1.4721(14) Å] bond is not significantly shorter than the accepted value for a Csp^2-Csp^2 single bond (1.48 Å) but it is longer than the average (1.45 ± 0.03 Å) of similar Csp^2-Csp^2 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).

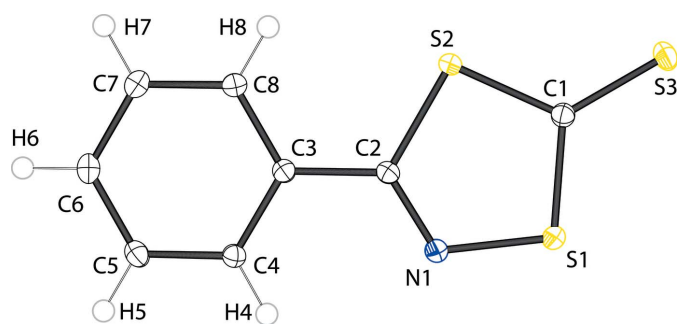


Figure 1

The molecular structure of the title compound, showing anisotropic displacement ellipsoids projected at 50% probability.

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 CS_2 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 ($C-S = 1.75 \pm 0.02$ Å and $C=S = 1.64 \pm 0.02$ Å) from the comparison heterocycle systems.

3. Supramolecular features

The extended structure of the title compound features $\pi-\pi$ centroid stacking (Fig. 2), six hydrogen-bonding interactions

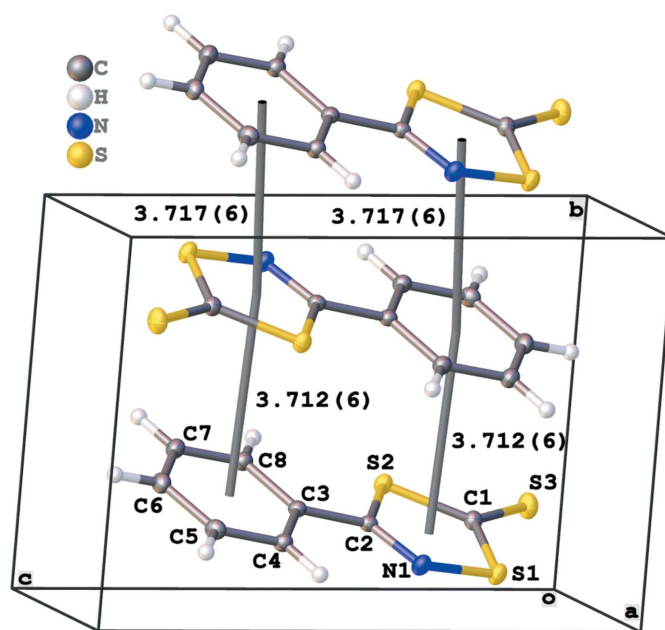


Figure 2

Packing diagram illustrating centroid-stacking interactions down the b -axis direction (a) between parallel-aligned ring systems with co-planar molecules flipped across an inversion centre [centroid-to-centroid distance = $3.712(6)$ Å] and packed back to back [centroid-to-centroid distance = $3.717(6)$ Å]. The three molecules are staggered with an angle of $166.698(17)^\circ$ and two molecules fit within the the $P1$ unit cell.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C4-H4\cdots N1^i$	0.95	2.89	3.6281 (14)	136
$C5-H5\cdots S1^i$	0.95	3.04	3.8474 (11)	144
$C5-H5\cdots S3^{ii}$	0.95	2.96	3.6529 (11)	131
$C6-H6\cdots S3^{ii}$	0.95	3.11	3.7231 (12)	124
$C7-H7\cdots S3^{iii}$	0.95	3.06	3.9651 (12)	159
$C8-H8\cdots S2^{iii}$	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-tail hydrogen-bonding interactions between C5 and C6 donors to the exocyclic thione S3 with $H\cdots S$ 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 \cdots S1 (3.04 Å), H7 \cdots S3 (3.06 Å) and H8 \cdots 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 $H\cdots S$ hydrogen bonding between the molecules is weak (Σ van der Waals radii $S\cdots H = 3.0$ Å), they aid the orientation of the molecules within the out-of-plane chains. In contrast, the $S\cdots S$ 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 $S\cdots S$ contact 3.20 Å and perpendicular $S\cdots S$ 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.

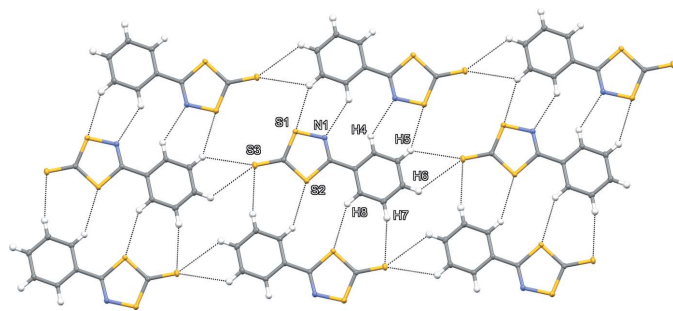


Figure 3
 A packing diagram of the title compound showing hydrogen bonding in head-to-tail chains with flanking interactions where all possible hydrogen-bond donors and acceptors are participating in hydrogen bonds.

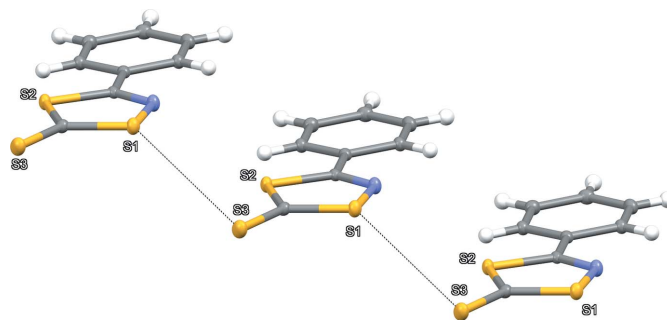


Figure 4
 A packing diagram of the title compound showing interchain $S\cdots S$ contacts of 3.575 (11) Å and the stepwise progression of the chains going down the b -axis, stepping towards the a -axis.

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 trichloromethanesulfonyl 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%)

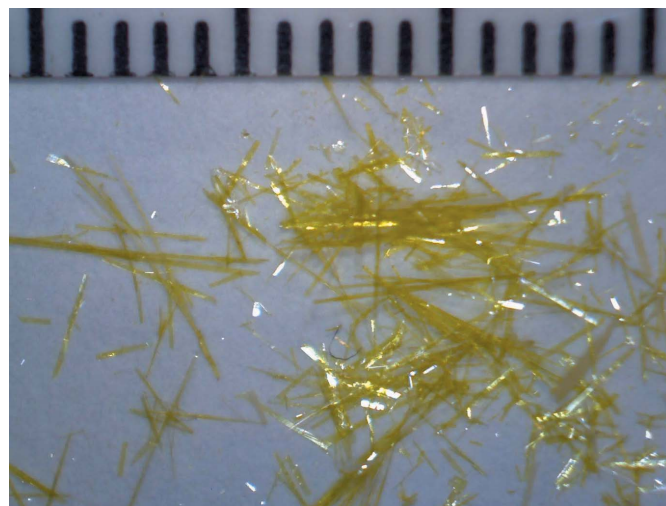


Figure 5
 A photograph of crystals of the title compound (1 mm reference scale).

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₈ H ₅ NS ₃
<i>M_r</i>	211.31
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.7955 (4), 7.3789 (5), 10.0344 (7)
α , β , γ (°)	89.459 (3), 89.719 (2), 78.956 (2)
<i>V</i> (Å ³)	421.15 (5)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.81
Crystal size (mm)	0.2 × 0.12 × 0.05
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.654, 0.748
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	49509, 4085, 3322
<i>R_{int}</i>	0.064
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.833
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.031, 0.074, 1.03
No. of reflections	4085
No. of parameters	109
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (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. *R_f* (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) = 1.2*U*_{eq}(C).

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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

$C_8H_5NS_3$	$Z = 2$
$M_r = 211.31$	$F(000) = 216$
Triclinic, $P\bar{1}$	$D_x = 1.666 \text{ Mg m}^{-3}$
$a = 5.7955 (4) \text{ \AA}$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$b = 7.3789 (5) \text{ \AA}$	Cell parameters from 9861 reflections
$c = 10.0344 (7) \text{ \AA}$	$\theta = 2.8\text{--}39.7^\circ$
$\alpha = 89.459 (3)^\circ$	$\mu = 0.81 \text{ mm}^{-1}$
$\beta = 89.719 (2)^\circ$	$T = 100 \text{ K}$
$\gamma = 78.956 (2)^\circ$	Needle, yellow
$V = 421.15 (5) \text{ \AA}^3$	$0.2 \times 0.12 \times 0.05 \text{ mm}$

Data collection

Bruker APEXII CCD diffractometer	4085 independent reflections
φ and ω scans	3322 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Krause <i>et al.</i> , 2015)	$R_{\text{int}} = 0.064$
$T_{\text{min}} = 0.654$, $T_{\text{max}} = 0.748$	$\theta_{\text{max}} = 36.3^\circ$, $\theta_{\text{min}} = 2.0^\circ$
49509 measured reflections	$h = -9 \rightarrow 9$
	$k = -12 \rightarrow 12$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.031$	$w = 1/[\sigma^2(F_o^2) + (0.0293P)^2 + 0.2221P]$
$wR(F^2) = 0.074$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{\text{max}} = 0.001$
4085 reflections	$\Delta\rho_{\text{max}} = 0.63 \text{ e \AA}^{-3}$
109 parameters	$\Delta\rho_{\text{min}} = -0.39 \text{ e \AA}^{-3}$
0 restraints	
Primary atom site location: dual	

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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	0.51316 (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 (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
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 (\AA , $^\circ$)

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

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
N1—S1—C1	100.79 (5)	C5—C4—H4	120.1
C1—S2—C2	95.54 (5)	C4—C5—H5	119.7
C2—N1—S1	115.28 (8)	C4—C5—C6	120.51 (10)
S1—C1—S2	110.12 (6)	C6—C5—H5	119.7
S3—C1—S1	124.34 (6)	C5—C6—H6	120.0
S3—C1—S2	125.54 (7)	C7—C6—C5	119.96 (10)
N1—C2—S2	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)	C8—C7—C6	119.80 (10)
C4—C3—C2	119.78 (9)	C8—C7—H7	120.1
C8—C3—C2	120.68 (9)	C3—C8—H8	119.8
C8—C3—C4	119.54 (9)	C7—C8—C3	120.48 (10)
C3—C4—H4	120.1	C7—C8—H8	119.8
C5—C4—C3	119.70 (10)		
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—S3	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—N1	-1.49 (9)	C8—C3—C4—C5	0.67 (15)
C1—S2—C2—C3	178.91 (8)		

Hydrogen-bond geometry (\AA , $^\circ$)

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

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