

Synthesis and crystal structure of racemic (R^* , R^*)-2,2'-(1,4-phenylene)bis(3-phenyl-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one)

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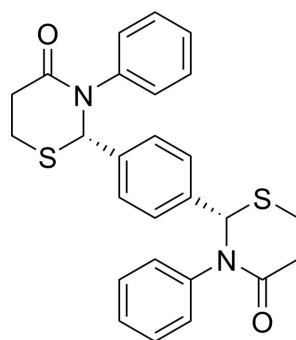
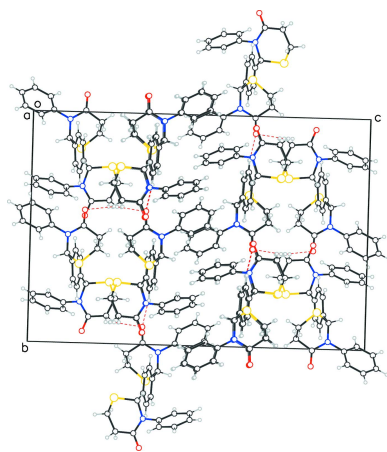
Supporting information: this article has supporting information at journals.iucr.org/e

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In the racemic title compound, $C_{26}H_{24}N_2O_2S_2$, one of the thiazine rings shows a twisted boat conformation ($Q = 0.743 \text{ \AA}$, $\theta = 92.1^\circ$) and the other a half-chair puckering ($Q = 0.669 \text{ \AA}$, $\theta = 54.3^\circ$). The terminal phenyl rings are almost parallel to each other [dihedral angle $21.71 (10)^\circ$]. Both of these rings are orthogonal to the central phenyl ring, subtending a dihedral angle of about 78° in each case. The extended structure is consolidated by C—H···O and C—H···S hydrogen bonds as well as aromatic ring interactions of parallel-displaced and T-type. The molecule has approximate C_2 local symmetry but this is not carried over to its three-dimensional structure or the intermolecular interactions.

1. Chemical context

Bis-heterocyclic compounds exhibit a variety of biological activities (Shaker, 2012). 2,2'-(1,4-Phenylene)-bis-(3-phenyl-1,3-thiazolidin-4-one), a phenylene-bridged bis-(1,3-thiazolidin-4-one) in which the bridging benzene ring is connected to C2 of each five-membered heterocycle, has been reported by three groups (Martani, 1956; Shaker, 1999; Mohammadi *et al.*, 2020). 2,2'-(1,4-Phenylene)-bis-(3-(4-fluorophenyl)-1,3-thiazolidin-4-one) has shown good antifungal activity (Abdel-Rahman & Ali, 2013). The only report of a phenylene-bridged bis-(1,3-thiazin-4-one) in which the bridging benzene ring is connected to C2 of each six-membered heterocycle is of two unsaturated derivatives of 2,2'-(1,4-phenylene)-bis-(3,4-dihydro-2*H*-1,3-thiazin-4-one) (Shaker *et al.*, 2010). We have previously reported the synthesis and crystal structure of saturated *meso*-3,3'-(1,4-phenylene)-bis-(2-phenyl-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one), in which the bridging benzene ring is connected to the nitrogen atom of each heterocycle (Yennawar, Moyer & Silverburg, 2018). Herein, we report the synthesis and crystal structure of the racemic title compound, $C_{26}H_{24}N_2O_2S_2$.



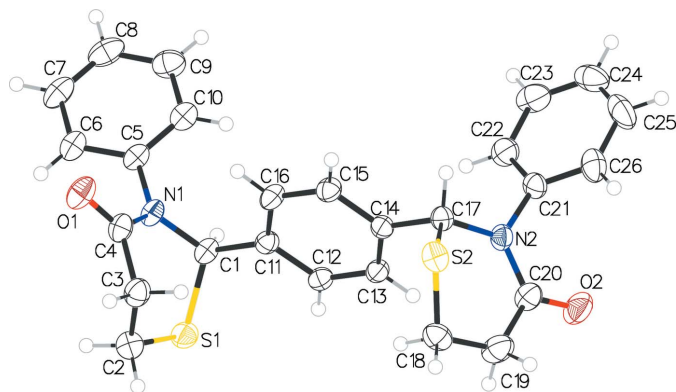


Figure 1
Displacement ellipsoid drawing at a 50% probability level of the title compound.

2. Structural commentary

The title compound has three phenyl rings (C5–C10, C11–C16 and C21–C26) alternating with two 1,3-thiazine rings, C1–C4/N1/S1 and C17–C20/N2/S2 (Fig. 1). In the arbitrarily chosen asymmetric molecule, atoms C1 and C17 both have an *R* configuration, but crystal symmetry generates a racemic *R,R* and *S,S* mixture. The terminal C5 and C21 phenyl rings are approximately parallel to each other with the interplanar

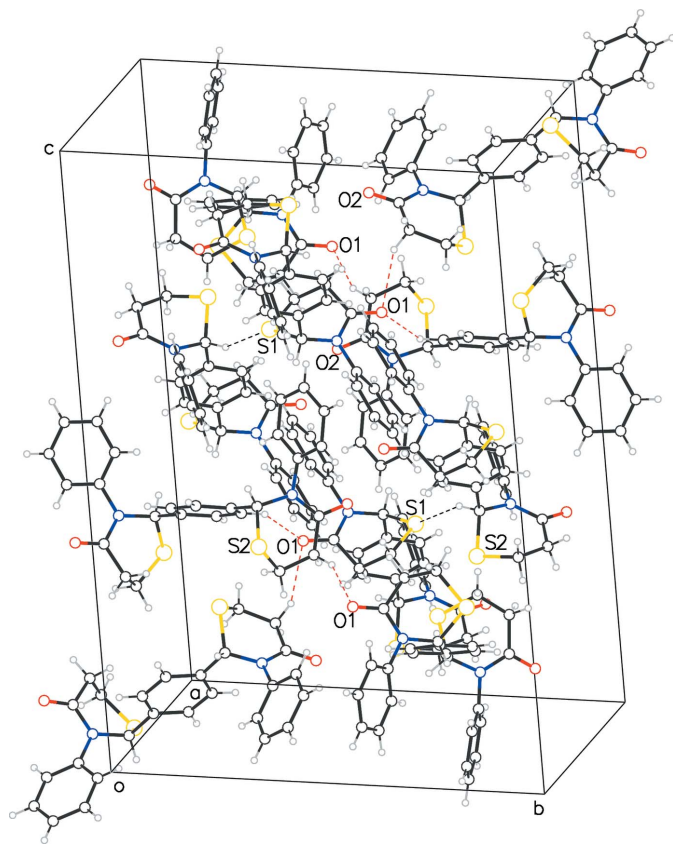


Figure 2
Crystal packing diagram showing C–H...O bonds as red dashed lines and C–H...S as black dashed lines.

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

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C19–H19A...O1 ⁱ	0.97	2.46	3.353 (3)	153
C17–H17...S1 ⁱⁱⁱ	0.98	2.62	3.5094 (19)	151
C13–H13...O1 ⁱⁱⁱ	0.93	2.52	3.280 (2)	139

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

angle being 21.71 (10)°. Each of these ‘bookend’ rings is orthogonal to the central phenyl ring subtending dihedral angles of 78.50 (9)° (C5/C11 rings) and 78.80 (9)° (C11/C21 rings). The thiazine ring containing atom S1 exhibits a twisted-boat pucker ($Q = 0.743$ Å, $\theta = 92.1^\circ$) while the ring containing S2 has a half-chair pucker ($Q = 0.669$ Å, $\theta = 54.3^\circ$) with atom S2 displaced from the plane defined by the remaining five atoms of the ring, by about 0.968 Å. Neither of these puckers are of the most favored type. Despite the different conformations of the heterocyclic rings, the molecule possesses approximate local *C*₂ symmetry with an r.m.s. deviation for the overlapping halves of the molecule of 0.261 Å but this local symmetry does not coincide with any crystallographic symmetry in the lattice. Consequently there is asymmetry in the intermolecular interactions (Fig. 2).

3. Supramolecular features

The surface of the molecule is dominated by hydrophobic regions with three phenyl rings alternating with two thiazine rings. The extended structure seems to be primarily a result of hydrophobic van der Waals interactions, further assisted by aromatic–aromatic interactions of parallel-displaced and T-type. Of the two sulfur and two oxygen atoms in each molecule, only one of each (O1 and S1) act as acceptors for C–H...O and C–H...S type intermolecular interactions (Table 1). The donor carbon atoms (C13, C17 and C19) are either members of the central phenyl ring or the other thiazine ring (containing O2 and S2). Thus although the molecule is chemically symmetric and the structure contains both enantiomers, the packing shows asymmetry in the interactions. A view down the *a*-axis direction (Fig. 3) shows layers of the aromatic rings and thiazine rings alternating with each other along the *c*-axis direction. It is worth noting the C–H...S interaction observed here is a hydrogen bond between non-traditional donor and acceptor atoms. Ghosh *et al.* (2020) have recently presented experimental and theoretical analyses of such interactions, and state that these type of interactions ‘exhibit all the characteristics of conventional hydrogen bonds’.

4. Database survey

A structure search was done in Scifinder, and a text search (‘1,3-thiazin-4-one’) was performed in the Cambridge Structural Database (Groom *et al.*, 2016; accessed October, 2021). Of the bis-heterocycles mentioned in the *Chemical context* section above, only our prior paper reports a crystal structure

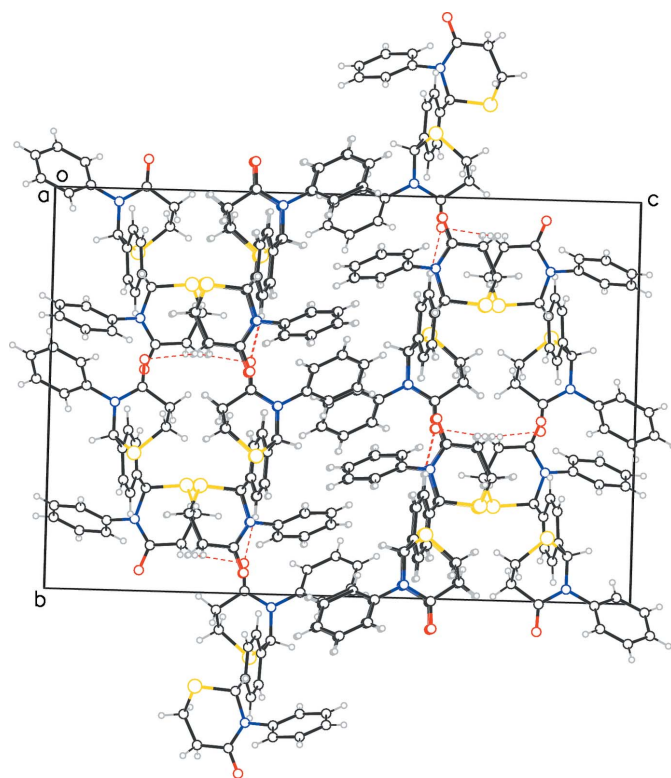


Figure 3
Crystal packing viewed down the *a*-axis direction showing alternate layering of aromatic rings and thiazine rings in the *c*-axis direction.

(Yennawar, Moyer & Silverburg, 2018). Crystal structures of monocyclic 2,3,5,6-tetrahydro-1,3-thiazin-4-ones have been reported for four 2,3-diaryl-1,3-thiazin-4-ones (Yennawar & Silverberg, 2014; Yennawar *et al.*, 2015; Yennawar, Bradley *et al.*, 2018), for a bicyclic azasugar 2,3-fused 1,3-thiazin-4-one (Li *et al.*, 2012) and a 2,2-dialkyl-1,3-thiazinone (Capps *et al.*, 1985). The thiazine rings in these structures exhibit varied puckering. There is a pucker 'between half-chair and envelope' in *meso*-3,3'-(1,4-phenylene)bis(2-phenyl-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one (Yennawar, Moyer & Silverberg 2018), an envelope in 2,3-diphenyl-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one (Yennawar & Silverberg, 2014), envelopes in (2*S*)-2-(3-nitrophenyl)-3-phenyl-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one and *rac*-2-(4-nitrophenyl)-3-phenyl-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one (Yennawar, Bradley *et al.*, 2018), a boat and a half-chair in *N*-[(2*S*,5*R*)-4-oxo-2,3-diphenyl-1,3-thiazinan-5-yl]acetamide (Yennawar *et al.*, 2015), a half-chair in (7*R*,8*R*,9*R*,9*aR*)-7,8,9-trihydroxyhexahydro-4*H*,6*H*-pyrido[2,1-*b*][1,3]thiazin-4-one (Li *et al.*, 2012), and a half-chair and a chair in methyl (2*R*,6*R*)-6-methoxy-4-oxo-2-(prop-1-en-2-yl)-1,3-thiazinane-2-carboxylate (Capps *et al.*, 1985).

5. Synthesis and crystallization

A two-necked 25 ml round-bottom flask was oven-dried, cooled under N₂, and charged with a stir bar. *N,N'*-(Benzene-

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₂₆ H ₂₄ N ₂ O ₂ S ₂
<i>M_r</i>	460.59
Crystal system, space group	Orthorhombic, <i>Pbca</i>
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.6963 (3), 17.6307 (4), 25.7044 (6)
<i>V</i> (Å ³)	4394.22 (19)
<i>Z</i>	8
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	2.41
Crystal size (mm)	0.34 × 0.30 × 0.16
Data collection	
Diffractometer	ROD, Synergy Custom system, HyPix-Arc 150
Absorption correction	Gaussian (<i>CrysAlis PRO</i> ; Rigaku OD, 2021)
<i>T_{min}</i> , <i>T_{max}</i>	0.59, 0.81
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	16911, 4317, 3910
<i>R_{int}</i>	0.035
(sin θ/λ) _{max} (Å ⁻¹)	0.627
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.040, 0.102, 1.05
No. of reflections	4317
No. of parameters	290
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.34, -0.30

Computer programs: *CrysAlis PRO* (Rigaku OD, 2021), *CrysAlis PRO* (Rigaku OD, 2021), *SHELXT2018* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), and *OLEX2* (Dolomanov *et al.*, 2009).

1,4-diylidimethylidene)dianiline (0.572 g, 3.00 mmol) and 3-mercaptopropionic acid (0.7432 g, 7.50 mmol) were added. 2-Methyltetrahydrofuran (2.3 ml) was added and the solution was stirred. Pyridine (2.4 ml, 30 mmol) was added. Finally, 2,4,6-tripropyl-1,3,5,2,4,6-trioxatriphosphorinane-2,4,6-trioxide (T3P) in 2-methyltetrahydrofuran (50 weight percent; 9.2 ml, 15 mmol) was added. The reaction was stirred at room temperature and followed by TLC, then poured into a separatory funnel with dichloromethane (20 ml). The mixture was washed with water (10 ml). The aqueous fraction was then extracted twice with dichloromethane (10 ml each). The organics were combined and washed with saturated sodium bicarbonate (10 ml) and then saturated sodium chloride (10 ml). The organic fraction was dried over sodium sulfate and concentrated under vacuum to give a pale yellow crude solid. Recrystallization from ethanol solution gave two crops of off-white solid (0.4715 g and 0.1087 g, total 0.5802 g, 42%). m.p. 476.3–483.7 K (decomp.). Crystals suitable for X-ray analysis were grown by slow evaporation from ethanol solution.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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References

- Abdel-Rahman, R. M. & Ali, T. E. (2013). *Monatsh. Chem.* **144**, 1243–1252.
- Capps, N. K., Davies, G. M., Hitchcock, P. B. & Young, D. W. (1985). *J. Chem. Soc. Chem. Commun.* pp. 843–845.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Ghosh, S., Chopra, P. & Wategaonkar, S. (2020). *Phys. Chem. Chem. Phys.* **22**, 17482–17493.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Li, X., Qin, Z., Yang, T., Zhang, H., Wei, S., Li, C., Chen, H. & Meng, M. (2012). *Bioorg. Med. Chem. Lett.* **22**, 2712–2716.
- Martani, A. (1956). *Ann. Chim.* **46**, 256–262.
- Mohammadi, R., Alamgholiloo, H., Gholipour, B., Rostamnia, S., Khaksar, S., Farajzadeh, M. & Shokouhimehr, M. (2020). *J. Photochem. Photobiol. Chem.* **402**, 112786.
- Rigaku OD (2021). *CrysAlis PRO*. Rigaku Oxford Diffraction Ltd, Yarnton, England.
- Shaker, R. M. (1999). *Phosphorus Sulfur Silicon*, **149**, 7–14.
- Shaker, R. M. (2012). *Arkivoc*, **i**, 1–44.
- Shaker, R. M., Ibrahim, Y. R., Abdel-Latif, F. F. & Hamoda, A. (2010). *Z. Naturforsch. Teil B*, **65**, 1148–1154.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Yennawar, H. P., Bradley, H. G., Perhonitch, K. C., Reppert, H. E. & Silverberg, L. J. (2018). *Acta Cryst.* **E74**, 454–457.
- Yennawar, H. P., Moyer, Q. J. & Silverberg, L. J. (2018). *Acta Cryst.* **E74**, 1497–1499.
- Yennawar, H. P. & Silverberg, L. J. (2014). *Acta Cryst.* **E70**, o133.
- Yennawar, H. P., Singh, H. & Silverberg, L. J. (2015). *Acta Cryst.* **E71**, 62–64.

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Synthesis and crystal structure of racemic (*R*^{*},*R*^{*})-2,2'-(1,4-phenylene)bis(3-phenyl-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one)

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2021); cell refinement: *CrysAlis PRO* (Rigaku OD, 2021); data reduction: *CrysAlis PRO* (Rigaku OD, 2021); program(s) used to solve structure: *SHELXT2018* (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).

(*R,R*)/(*S,S*)-2,2'-(1,4-Phenylene)bis(3-phenyl-3,4,5,6-tetrahydro-2*H*-1,3-thiazin-4-one)

Crystal data

C₂₆H₂₄N₂O₂S₂

M_r = 460.59

Orthorhombic, *Pbca*

a = 9.6963 (3) Å

b = 17.6307 (4) Å

c = 25.7044 (6) Å

V = 4394.22 (19) Å³

Z = 8

F(000) = 1936

D_x = 1.392 Mg m⁻³

Cu *Kα* radiation, λ = 1.54184 Å

Cell parameters from 13210 reflections

θ = 3.0–74.7°

μ = 2.41 mm⁻¹

T = 173 K

Block, colorless

0.34 × 0.30 × 0.16 mm

Data collection

ROD, Synergy Custom system, HyPix-Arc 150 diffractometer

Radiation source: Rotating-anode X-ray tube

Detector resolution: 10.0000 pixels mm⁻¹

ω scans

Absorption correction: gaussian

(CrysAlisPro; Rigaku OD, 2021)

T_{min} = 0.59, *T_{max}* = 0.81

16911 measured reflections

4317 independent reflections

3910 reflections with *I* > 2σ(*I*)

R_{int} = 0.035

θ_{max} = 75.2°, θ_{min} = 3.4°

h = -11→10

k = -21→21

l = -31→22

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.040

wR(*F*²) = 0.102

S = 1.05

4317 reflections

290 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.043*P*)² + 2.8735*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.34 e Å⁻³

Δρ_{min} = -0.30 e Å⁻³

Extinction correction: SHELXL2018/3

(Sheldrick 2015b),

F_c^{*} = *kF_c*[1 + 0.001*xF_c*²λ³/sin(2θ)]^{-1/4}

Extinction coefficient: 0.00067 (6)

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.03452 (5)	0.15757 (3)	0.35406 (2)	0.03576 (14)
S2	0.74104 (5)	0.23378 (3)	0.26135 (2)	0.03303 (14)
O1	0.17980 (17)	-0.07596 (8)	0.34004 (5)	0.0405 (4)
O2	0.73414 (19)	0.44837 (8)	0.33902 (6)	0.0498 (4)
N1	0.17158 (16)	0.03164 (8)	0.38871 (6)	0.0285 (3)
N2	0.74004 (16)	0.32127 (9)	0.34850 (6)	0.0282 (3)
C1	0.17917 (19)	0.11440 (10)	0.38934 (7)	0.0283 (4)
H1	0.166679	0.129095	0.425801	0.034*
C2	0.0161 (2)	0.09064 (12)	0.30065 (8)	0.0396 (5)
H2A	-0.063280	0.058472	0.306954	0.048*
H2B	0.000097	0.118287	0.268585	0.048*
C3	0.1439 (2)	0.04154 (11)	0.29466 (7)	0.0351 (4)
H3A	0.133360	0.009144	0.264420	0.042*
H3B	0.223572	0.073762	0.289008	0.042*
C4	0.1679 (2)	-0.00726 (11)	0.34247 (7)	0.0315 (4)
C5	0.1762 (2)	-0.00729 (10)	0.43785 (7)	0.0289 (4)
C6	0.0811 (2)	-0.06443 (10)	0.44850 (8)	0.0330 (4)
H6	0.015814	-0.078494	0.423799	0.040*
C7	0.0854 (2)	-0.09993 (11)	0.49658 (8)	0.0401 (5)
H7	0.023888	-0.139005	0.503783	0.048*
C8	0.1797 (3)	-0.07817 (12)	0.53393 (8)	0.0441 (5)
H8	0.181054	-0.102412	0.566059	0.053*
C9	0.2717 (2)	-0.02062 (12)	0.52368 (8)	0.0417 (5)
H9	0.334019	-0.005143	0.549063	0.050*
C10	0.2710 (2)	0.01427 (11)	0.47510 (8)	0.0351 (4)
H10	0.334578	0.052247	0.467703	0.042*
C11	0.31846 (18)	0.14655 (10)	0.37342 (6)	0.0257 (4)
C12	0.33492 (19)	0.22501 (10)	0.37044 (7)	0.0262 (4)
H12	0.259894	0.256443	0.377028	0.031*
C13	0.46121 (18)	0.25695 (10)	0.35783 (6)	0.0262 (4)
H13	0.470079	0.309434	0.356459	0.031*
C14	0.57488 (19)	0.21130 (10)	0.34719 (6)	0.0251 (4)
C15	0.5598 (2)	0.13267 (10)	0.35063 (7)	0.0289 (4)
H15	0.634864	0.101322	0.343891	0.035*
C16	0.4333 (2)	0.10086 (10)	0.36410 (7)	0.0302 (4)
H16	0.425202	0.048454	0.366908	0.036*
C17	0.71351 (19)	0.24304 (10)	0.33082 (7)	0.0267 (4)
H17	0.783403	0.211186	0.347587	0.032*
C18	0.6139 (2)	0.30351 (11)	0.24347 (7)	0.0362 (4)

H18A	0.612491	0.308869	0.205912	0.043*
H18B	0.523504	0.286260	0.254475	0.043*
C19	0.6438 (3)	0.37990 (12)	0.26799 (8)	0.0437 (5)
H19A	0.703209	0.407306	0.244148	0.052*
H19B	0.557206	0.407369	0.269383	0.052*
C20	0.7086 (2)	0.38557 (11)	0.32129 (7)	0.0344 (4)
C21	0.81722 (19)	0.32632 (10)	0.39613 (7)	0.0292 (4)
C22	0.7625 (2)	0.29558 (11)	0.44129 (7)	0.0370 (5)
H22	0.672942	0.276680	0.441353	0.044*
C23	0.8408 (3)	0.29297 (12)	0.48625 (8)	0.0495 (6)
H23	0.804317	0.271700	0.516364	0.059*
C24	0.9725 (3)	0.32179 (13)	0.48645 (10)	0.0544 (7)
H24	1.024965	0.320241	0.516726	0.065*
C25	1.0268 (3)	0.35300 (14)	0.44176 (11)	0.0533 (6)
H25	1.115824	0.372603	0.442092	0.064*
C26	0.9499 (2)	0.35544 (12)	0.39634 (9)	0.0408 (5)
H26	0.987103	0.376435	0.366260	0.049*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0283 (2)	0.0316 (2)	0.0474 (3)	0.00307 (19)	0.0025 (2)	0.0052 (2)
S2	0.0318 (3)	0.0391 (3)	0.0282 (2)	-0.0025 (2)	0.00399 (18)	-0.00733 (18)
O1	0.0579 (10)	0.0262 (7)	0.0374 (7)	-0.0022 (7)	0.0097 (7)	-0.0020 (6)
O2	0.0725 (11)	0.0269 (7)	0.0501 (9)	-0.0046 (7)	-0.0080 (8)	-0.0010 (6)
N1	0.0342 (8)	0.0225 (7)	0.0286 (7)	-0.0038 (6)	0.0052 (6)	0.0026 (6)
N2	0.0314 (8)	0.0254 (8)	0.0277 (7)	-0.0048 (6)	-0.0017 (6)	-0.0021 (6)
C1	0.0321 (10)	0.0225 (8)	0.0304 (9)	-0.0007 (7)	0.0045 (8)	0.0019 (7)
C2	0.0385 (11)	0.0382 (11)	0.0421 (11)	-0.0035 (9)	-0.0049 (9)	0.0039 (9)
C3	0.0407 (11)	0.0331 (10)	0.0313 (10)	-0.0044 (8)	0.0014 (8)	0.0012 (8)
C4	0.0329 (10)	0.0285 (9)	0.0330 (9)	-0.0039 (8)	0.0064 (8)	0.0002 (8)
C5	0.0346 (10)	0.0229 (8)	0.0290 (9)	0.0015 (7)	0.0058 (8)	0.0015 (7)
C6	0.0379 (10)	0.0261 (9)	0.0351 (10)	-0.0013 (8)	0.0095 (8)	-0.0002 (8)
C7	0.0504 (13)	0.0279 (9)	0.0420 (11)	0.0014 (9)	0.0165 (10)	0.0067 (8)
C8	0.0612 (15)	0.0378 (11)	0.0332 (10)	0.0099 (10)	0.0122 (10)	0.0095 (9)
C9	0.0518 (13)	0.0408 (11)	0.0326 (10)	0.0060 (10)	-0.0011 (9)	-0.0002 (9)
C10	0.0400 (11)	0.0298 (9)	0.0356 (10)	-0.0005 (8)	0.0029 (8)	0.0022 (8)
C11	0.0288 (9)	0.0252 (8)	0.0231 (8)	-0.0007 (7)	0.0004 (7)	0.0017 (7)
C12	0.0288 (9)	0.0234 (8)	0.0265 (8)	0.0026 (7)	0.0007 (7)	0.0001 (7)
C13	0.0305 (9)	0.0220 (8)	0.0262 (8)	-0.0010 (7)	-0.0015 (7)	0.0009 (7)
C14	0.0280 (9)	0.0256 (9)	0.0219 (8)	-0.0018 (7)	-0.0023 (7)	-0.0003 (6)
C15	0.0294 (9)	0.0241 (9)	0.0332 (9)	0.0030 (7)	0.0014 (7)	-0.0005 (7)
C16	0.0341 (10)	0.0208 (8)	0.0356 (9)	0.0009 (7)	0.0033 (8)	0.0023 (7)
C17	0.0281 (9)	0.0252 (8)	0.0267 (8)	-0.0015 (7)	-0.0022 (7)	-0.0027 (7)
C18	0.0369 (11)	0.0454 (11)	0.0264 (9)	-0.0007 (9)	-0.0027 (8)	0.0000 (8)
C19	0.0611 (15)	0.0363 (11)	0.0338 (10)	0.0019 (10)	-0.0029 (10)	0.0048 (8)
C20	0.0409 (11)	0.0306 (10)	0.0319 (9)	-0.0011 (8)	0.0023 (8)	0.0012 (8)
C21	0.0311 (9)	0.0266 (8)	0.0301 (9)	0.0000 (7)	-0.0038 (8)	-0.0064 (7)

C22	0.0467 (12)	0.0331 (10)	0.0312 (10)	-0.0020 (9)	-0.0043 (9)	-0.0030 (8)
C23	0.0799 (18)	0.0361 (11)	0.0324 (11)	0.0070 (11)	-0.0132 (11)	-0.0047 (9)
C24	0.0692 (17)	0.0415 (12)	0.0526 (14)	0.0158 (12)	-0.0321 (13)	-0.0159 (11)
C25	0.0395 (12)	0.0482 (13)	0.0723 (16)	0.0015 (10)	-0.0205 (12)	-0.0260 (12)
C26	0.0372 (11)	0.0368 (10)	0.0485 (12)	-0.0057 (9)	0.0006 (9)	-0.0121 (9)

Geometric parameters (Å, °)

S1—C2	1.819 (2)	C10—H10	0.9300
S1—C1	1.8355 (19)	C11—C12	1.395 (2)
S2—C18	1.801 (2)	C11—C16	1.395 (2)
S2—C17	1.8130 (18)	C12—C13	1.386 (2)
O1—C4	1.218 (2)	C12—H12	0.9300
O2—C20	1.223 (2)	C13—C14	1.392 (3)
N1—C4	1.373 (2)	C13—H13	0.9300
N1—C5	1.438 (2)	C14—C15	1.397 (2)
N1—C1	1.461 (2)	C14—C17	1.516 (2)
N2—C20	1.367 (2)	C15—C16	1.393 (3)
N2—C21	1.438 (2)	C15—H15	0.9300
N2—C17	1.475 (2)	C16—H16	0.9300
C1—C11	1.521 (2)	C17—H17	0.9800
C1—H1	0.9800	C18—C19	1.515 (3)
C2—C3	1.519 (3)	C18—H18A	0.9700
C2—H2A	0.9700	C18—H18B	0.9700
C2—H2B	0.9700	C19—C20	1.510 (3)
C3—C4	1.518 (3)	C19—H19A	0.9700
C3—H3A	0.9700	C19—H19B	0.9700
C3—H3B	0.9700	C21—C26	1.385 (3)
C5—C10	1.380 (3)	C21—C22	1.387 (3)
C5—C6	1.393 (3)	C22—C23	1.384 (3)
C6—C7	1.386 (3)	C22—H22	0.9300
C6—H6	0.9300	C23—C24	1.374 (4)
C7—C8	1.380 (3)	C23—H23	0.9300
C7—H7	0.9300	C24—C25	1.378 (4)
C8—C9	1.377 (3)	C24—H24	0.9300
C8—H8	0.9300	C25—C26	1.386 (3)
C9—C10	1.392 (3)	C25—H25	0.9300
C9—H9	0.9300	C26—H26	0.9300
C2—S1—C1	100.30 (9)	C11—C12—H12	119.4
C18—S2—C17	95.12 (9)	C12—C13—C14	120.70 (16)
C4—N1—C5	121.52 (15)	C12—C13—H13	119.6
C4—N1—C1	120.65 (15)	C14—C13—H13	119.6
C5—N1—C1	117.73 (14)	C13—C14—C15	118.60 (17)
C20—N2—C21	120.05 (15)	C13—C14—C17	122.92 (16)
C20—N2—C17	125.39 (15)	C15—C14—C17	118.47 (16)
C21—N2—C17	114.27 (14)	C16—C15—C14	120.49 (17)
N1—C1—C11	114.46 (15)	C16—C15—H15	119.8

N1—C1—S1	111.73 (13)	C14—C15—H15	119.8
C11—C1—S1	113.03 (12)	C15—C16—C11	120.88 (16)
N1—C1—H1	105.6	C15—C16—H16	119.6
C11—C1—H1	105.6	C11—C16—H16	119.6
S1—C1—H1	105.6	N2—C17—C14	114.48 (15)
C3—C2—S1	111.48 (14)	N2—C17—S2	111.22 (12)
C3—C2—H2A	109.3	C14—C17—S2	111.76 (12)
S1—C2—H2A	109.3	N2—C17—H17	106.2
C3—C2—H2B	109.3	C14—C17—H17	106.2
S1—C2—H2B	109.3	S2—C17—H17	106.2
H2A—C2—H2B	108.0	C19—C18—S2	111.69 (15)
C4—C3—C2	111.48 (16)	C19—C18—H18A	109.3
C4—C3—H3A	109.3	S2—C18—H18A	109.3
C2—C3—H3A	109.3	C19—C18—H18B	109.3
C4—C3—H3B	109.3	S2—C18—H18B	109.3
C2—C3—H3B	109.3	H18A—C18—H18B	107.9
H3A—C3—H3B	108.0	C20—C19—C18	121.05 (17)
O1—C4—N1	122.58 (17)	C20—C19—H19A	107.1
O1—C4—C3	122.46 (17)	C18—C19—H19A	107.1
N1—C4—C3	114.94 (16)	C20—C19—H19B	107.1
C10—C5—C6	120.24 (18)	C18—C19—H19B	107.1
C10—C5—N1	119.90 (16)	H19A—C19—H19B	106.8
C6—C5—N1	119.81 (17)	O2—C20—N2	121.00 (18)
C7—C6—C5	118.79 (19)	O2—C20—C19	118.84 (18)
C7—C6—H6	120.6	N2—C20—C19	120.15 (17)
C5—C6—H6	120.6	C26—C21—C22	119.81 (19)
C8—C7—C6	121.00 (19)	C26—C21—N2	120.64 (18)
C8—C7—H7	119.5	C22—C21—N2	119.31 (17)
C6—C7—H7	119.5	C23—C22—C21	120.1 (2)
C9—C8—C7	120.08 (19)	C23—C22—H22	119.9
C9—C8—H8	120.0	C21—C22—H22	119.9
C7—C8—H8	120.0	C24—C23—C22	120.1 (2)
C8—C9—C10	119.6 (2)	C24—C23—H23	120.0
C8—C9—H9	120.2	C22—C23—H23	120.0
C10—C9—H9	120.2	C23—C24—C25	120.0 (2)
C5—C10—C9	120.27 (19)	C23—C24—H24	120.0
C5—C10—H10	119.9	C25—C24—H24	120.0
C9—C10—H10	119.9	C24—C25—C26	120.6 (2)
C12—C11—C16	118.17 (16)	C24—C25—H25	119.7
C12—C11—C1	119.09 (16)	C26—C25—H25	119.7
C16—C11—C1	122.66 (15)	C21—C26—C25	119.4 (2)
C13—C12—C11	121.12 (17)	C21—C26—H26	120.3
C13—C12—H12	119.4	C25—C26—H26	120.3
C4—N1—C1—C11	-72.6 (2)	C13—C14—C15—C16	0.4 (3)
C5—N1—C1—C11	103.92 (18)	C17—C14—C15—C16	-178.19 (16)
C4—N1—C1—S1	57.5 (2)	C14—C15—C16—C11	1.2 (3)
C5—N1—C1—S1	-126.00 (15)	C12—C11—C16—C15	-1.9 (3)

C2—S1—C1—N1	-37.28 (14)	C1—C11—C16—C15	-178.66 (16)
C2—S1—C1—C11	93.55 (14)	C20—N2—C17—C14	-90.8 (2)
C1—S1—C2—C3	-17.14 (16)	C21—N2—C17—C14	95.38 (18)
S1—C2—C3—C4	63.06 (19)	C20—N2—C17—S2	37.1 (2)
C5—N1—C4—O1	-6.2 (3)	C21—N2—C17—S2	-136.75 (13)
C1—N1—C4—O1	170.11 (18)	C13—C14—C17—N2	25.7 (2)
C5—N1—C4—C3	172.13 (17)	C15—C14—C17—N2	-155.73 (16)
C1—N1—C4—C3	-11.5 (3)	C13—C14—C17—S2	-101.90 (17)
C2—C3—C4—O1	125.2 (2)	C15—C14—C17—S2	76.68 (18)
C2—C3—C4—N1	-53.2 (2)	C18—S2—C17—N2	-59.40 (14)
C4—N1—C5—C10	132.03 (19)	C18—S2—C17—C14	69.93 (14)
C1—N1—C5—C10	-44.4 (2)	C17—S2—C18—C19	57.69 (16)
C4—N1—C5—C6	-50.7 (3)	S2—C18—C19—C20	-33.8 (3)
C1—N1—C5—C6	132.83 (18)	C21—N2—C20—O2	-6.6 (3)
C10—C5—C6—C7	-1.3 (3)	C17—N2—C20—O2	179.90 (19)
N1—C5—C6—C7	-178.50 (17)	C21—N2—C20—C19	172.13 (18)
C5—C6—C7—C8	1.6 (3)	C17—N2—C20—C19	-1.4 (3)
C6—C7—C8—C9	-0.3 (3)	C18—C19—C20—O2	178.1 (2)
C7—C8—C9—C10	-1.4 (3)	C18—C19—C20—N2	-0.6 (3)
C6—C5—C10—C9	-0.4 (3)	C20—N2—C21—C26	-61.7 (2)
N1—C5—C10—C9	176.87 (18)	C17—N2—C21—C26	112.5 (2)
C8—C9—C10—C5	1.7 (3)	C20—N2—C21—C22	124.0 (2)
N1—C1—C11—C12	177.14 (15)	C17—N2—C21—C22	-61.8 (2)
S1—C1—C11—C12	47.7 (2)	C26—C21—C22—C23	-0.9 (3)
N1—C1—C11—C16	-6.1 (2)	N2—C21—C22—C23	173.43 (18)
S1—C1—C11—C16	-135.58 (15)	C21—C22—C23—C24	0.9 (3)
C16—C11—C12—C13	0.9 (3)	C22—C23—C24—C25	-0.3 (3)
C1—C11—C12—C13	177.79 (16)	C23—C24—C25—C26	-0.2 (3)
C11—C12—C13—C14	0.7 (3)	C22—C21—C26—C25	0.4 (3)
C12—C13—C14—C15	-1.4 (3)	N2—C21—C26—C25	-173.87 (19)
C12—C13—C14—C17	177.14 (15)	C24—C25—C26—C21	0.2 (3)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C19—H19A...O1 ⁱ	0.97	2.46	3.353 (3)	153
C17—H17...S1 ⁱⁱ	0.98	2.62	3.5094 (19)	151
C13—H13...O1 ⁱⁱⁱ	0.93	2.52	3.280 (2)	139

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