

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

N-(1-Acetyl-r-7,c-9-diphenyl-4,8-dithia-1,2-diazaspiro[5.4]dec-2-en-3-yl)acetamide

D. Gayathri,^a D. Velmurugan,^{a*} S. Umamatheswari,^b S. Kabilan^b and K. Ravikumar^c

^aCentre of Advanced Study in Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai 600 025, India, ^bDepartment of Chemistry, Annamalai University, Annamalai Nagar 608 002, India, and ^cLaboratory of X-ray Crystallography, Indian Institute of Chemical Technology, Hyderabad 500 007, India
Correspondence e-mail: d_velu@yahoo.com

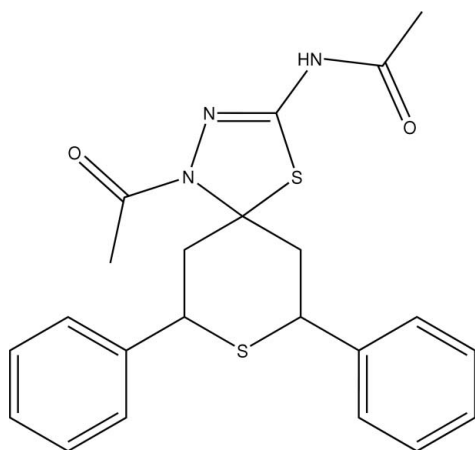
Received 16 December 2007; accepted 10 January 2008

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.039; wR factor = 0.116; data-to-parameter ratio = 19.5.

In the title compound, $\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_2\text{S}_2$, the five-membered ring is planar and the C_5S ring adopts a chair conformation. The crystal packing is stabilized by intermolecular $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ interactions, generating a chain and a centrosymmetric dimer, respectively.

Related literature

For related literature, see: Allen *et al.* (1987); Isaac *et al.* (2003); Pan *et al.* (2003); Jung *et al.* (2004); Foroumadi *et al.* (2002); Jalilian *et al.* (2002); Leung-Toung *et al.* (2003); Schmidt *et al.* (1970); Cremer & Pople (1975); Nardelli (1983); Singh *et al.* (2003).



Experimental

Crystal data

$\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_2\text{S}_2$
 $M_r = 425.55$
 Monoclinic, $P2_1/n$
 $a = 12.3310$ (7) Å
 $b = 16.0218$ (9) Å
 $c = 12.3852$ (7) Å
 $\beta = 116.714$ (1)°
 $V = 2185.7$ (2) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.27$ mm⁻¹
 $T = 293$ (2) K
 $0.25 \times 0.24 \times 0.22$ mm

Data collection

Bruker SMART APEX CCD
 area-detector diffractometer
 Absorption correction: none
 24434 measured reflections
 5139 independent reflections
 4587 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.116$
 $S = 0.97$
 5139 reflections
 264 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.31$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.17$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N3}-\text{H3}\cdots\text{O1}^{\text{i}}$	0.86	1.94	2.786 (2)	166
$\text{C5}-\text{H5}\cdots\text{O2}^{\text{ii}}$	0.98	2.49	3.446 (2)	163

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

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97 and PARST (Nardelli, 1995).

DG thanks CSIR, India, for the award of a Senior Research Fellowship. DV thanks DST, India, for a major research project, and acknowledges the Department of Science and Technology (DST-FIST) and the University Grants Commission (UGC), Government of India, for the provision of research facilities.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2527).

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
 Bruker (2001). SMART and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
 Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
 Foroumadi, A., Asadipour, A., Mirzaei, M., Karimi, J. & Emami, S. (2002). *II Farmaco*, **57**, 765–769.
 Isaac, M., Slassi, M., Xin, T., Arora, J., O'Brien, A., Edwards, L., MacLean, N., Wilson, J., Demshyshyn, L., Labrie, P., Naismith, A., Maddaford, S. P., Papac, D., Harrison, S., Wang, H., Draper, S. & Tehim, A. (2003). *Bioorg. Med. Chem. Lett.* **13**, 4409–4413.
 Jalilian, A. R., Sattari, S., Bineshmarvasti, M., Daneshlab, M. & Shafiee, A. (2002). *II Farmaco*, **58**, 63–68.
 Jung, K. Y., Kim, S. K., Gao, Z. G., Gross, A. S., Melman, N., Jacobson, K. A. & Kim, Y. C. (2004). *Bioorg. Med. Chem.* **12**, 613–623.

- Leung-Toung, R., Odzinska, J., Li, W., Lowrie, J., Kukreja, R., Desilets, D., Karimian, K. & Tam, T. F. (2003). *Bioorg. Med. Chem.* **11**, 5529–5537.
- Nardelli, M. (1983). *Acta Cryst.* **C39**, 1141–1142.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Pan, K., Scott, M. K., Lee, D. H. S., Fitzpatric, L. J., Crooke, J. J., Rivero, R. A., Rosenthal, D. I., Vaidya, A. H., Zhao, B. & Reiz, A. B. (2003). *Bioorg. Med. Chem.* **11**, 185–192.
- Schmidt, P., Eichenberger, K. & Schwiezer, E. (1970). *Chem. Abstr.* **72**, 318377u.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Singh, U., Raju, B., Lam, S., Zhou, J., Gadwood, R. C., Ford, C. W., Zurenko, G. E., Schaadt, R. D., Morin, S. E., Adams, W. J., Friis, J. M., Courtney, M., Palandra, J., Hackbarth, C. J., Lopez, S. *et al.* (2003). *Bioorg. Med. Chem. Lett.* **13**, 4209–4212.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supporting information

Acta Cryst. (2008). E64, o494–o495 [doi:10.1107/S1600536808001025]

***N*-(1-Acetyl-*r*-7,*c*-9-diphenyl-4,8-dithia-1,2-diazaspiro[5.4]dec-2-en-3-yl)acetamide**

D. Gayathri, D. Velmurugan, S. Umamatheswari, S. Kabilan and K. Ravikumar

S1. Comment

Tetrahydrothiopyrans play major roles in the field of medicinal chemistry (Isaac *et al.*, 2003). 1,3,4-Thiadiazoline nucleus, a biologically active heterocyclic ring, is also associated with a wide range of pharmacological activities (Pan *et al.*, 2003; Jung *et al.*, 2004; Foroumadi *et al.*, 2002; Jalilian *et al.*, 2002; Leung-Toung *et al.*, 2003). An essential component of the search for new leads in a drug-design programme is the synthesis of molecules, which is novel and resembles known biologically active molecules by virtue of the presence of certain pharmacophoric groups. Certain small heterocyclic molecules act as highly functionalized scaffolds and are pharmacophores of a number of biologically active and medicinally useful molecules. As the title compound (I) is of much biological importance, we have undertaken the crystal structure determination by X-ray diffraction.

The bond lengths and bond angles in (I) are comparable with those in the literature (Allen *et al.*, 1987). The sum of the bond angles around N1 atom [360.0 (3)°] indicates the sp^2 hybridization. The torsion angles C19—C18—N1—N2 [-0.1 (2)°] and C19—C18—N1—C3 [-179.3 (1)°] indicate that atoms C18 and C19 lie in the plane of the five membered ring (N1/N2/C20/S2/C3). Also the torsion angles C22—C21—N3—C20 [-177.3 (2)°], O2—C21—N3—C20 [2.4 (3)°], C21—N3—C20—S2 [2.3 (2)°] and C21—N3—C20—N2 [-178.1 (2)°] indicate that the substituted moiety at C20 lie in the plane of the ring to which it is attached. The dihedral angle between the two phenyl rings in the structure is about 77.6 (1)° which clearly indicates that the two phenyl rings are nearly perpendicular to each other.

The six membered ring C1—C5/S1 adopts chair conformation with the puckering parameters (Cremer & Pople, 1975) and the smallest displacement asymmetry parameters (Nardelli, 1983) being $q_2 = 0.117$ (1) Å, $q_3 = 0.651$ (1) Å; $Q_T = 0.661$ (1) Å and $\theta = 10.2$ (1)°.

The crystal packing is stabilized N—H...O and C—H...O intermolecular interaction generating a chain of C(7) and a centrosymmetric dimer of $R_2^2(18)$ ring, respectively.

S2. Experimental

2,6-Diphenyltetrahydrothiopyran-4-one thiosemicarbazone (0.025 mol) was treated with freshly distilled acetic anhydride and the mixture was refluxed for 8 h on a water bath (363–373 K). The removal of solvent from the cooled reaction mixture in vacuo afforded 4-acetyl-2-acetylamino-5-spiro-((*r*)-2,(*c*)-6-diphenyltetrahydrothiopyran-4-yl)-4,5-dihydro-[1,3,4]thiadiazole which was purified in neutral alumina column using n-hexane-ethyl acetate (4:1) as eluent. The pure compound was recrystallized from ethanol [m.p.: 399 K].

S3. Refinement

All H-atoms were refined using a riding model with $d(C-H) = 0.93$ Å, $U_{iso} = 1.2U_{eq}$ (C) for aromatic, 0.98 Å, $U_{iso} = 1.2U_{eq}$ (C) for CH, 0.97 Å, $U_{iso} = 1.2U_{eq}$ (C) for CH₂, 0.96 Å, $U_{iso} = 1.5U_{eq}$ (C) for CH₃ atoms and 0.86 Å, $U_{iso} = 1.2U_{eq}$ (N) for

the NH group.

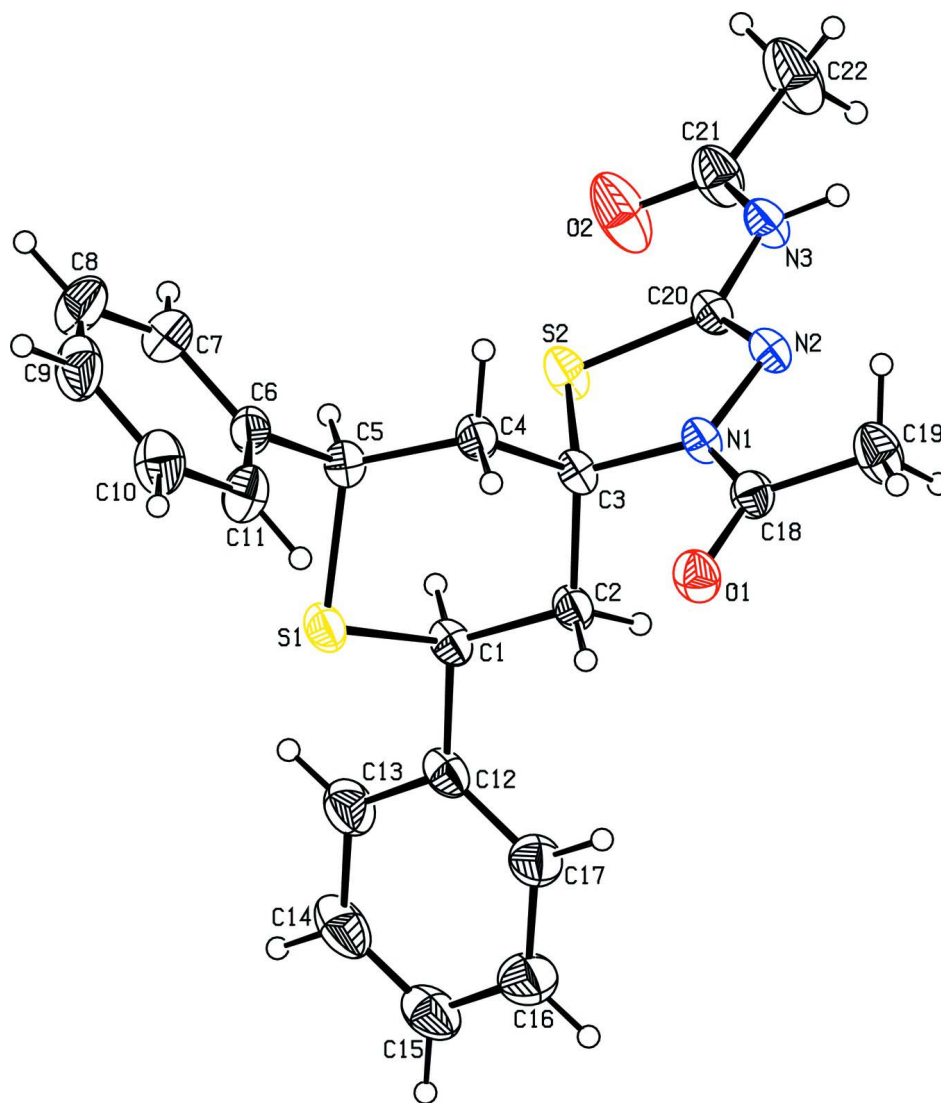


Figure 1

The molecular structure of (I), with atom labels and 30% probability displacement ellipsoids.

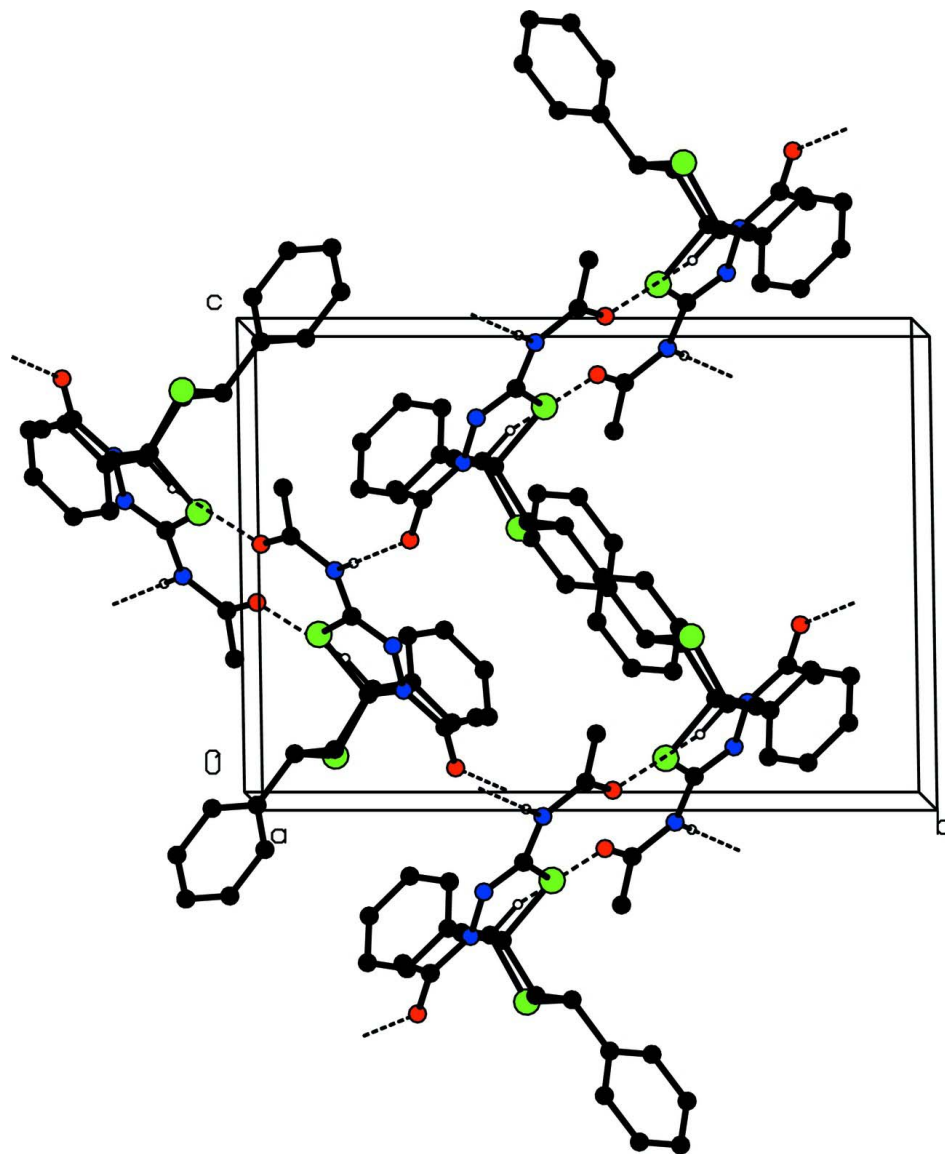


Figure 2

The packing of (I), viewed down the *a* axis, showing N—H \cdots O and C—H \cdots O intermolecular interactions. H atoms not involved in hydrogen bonding have been omitted.

***N*-(1-Acetyl-*r*-7,*c*-9-diphenyl-4,8-dithia-1,2-diazaspiro[5.4]dec-2-en-3-yl)acetamide**

Crystal data

$C_{22}H_{23}N_3O_2S_2$

$M_r = 425.55$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 12.3310$ (7) Å

$b = 16.0218$ (9) Å

$c = 12.3852$ (7) Å

$\beta = 116.714$ (1)°

$V = 2185.7$ (2) Å³

$Z = 4$

$F(000) = 896$

$D_x = 1.293$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2504 reflections

$\theta = 1.9$ – 28.0 °

$\mu = 0.27$ mm⁻¹

$T = 293$ K

Block, colourless

$0.25 \times 0.24 \times 0.22$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	4587 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.020$
Radiation source: fine-focus sealed tube	$\theta_{\text{max}} = 28.0^\circ$, $\theta_{\text{min}} = 1.9^\circ$
Graphite monochromator	$h = -15 \rightarrow 15$
ω scans	$k = -21 \rightarrow 21$
24434 measured reflections	$l = -16 \rightarrow 16$
5139 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.038$	H-atom parameters constrained
$wR(F^2) = 0.116$	$w = 1/[\sigma^2(F_o^2) + (0.0759P)^2 + 0.4937P]$
$S = 0.97$	where $P = (F_o^2 + 2F_c^2)/3$
5139 reflections	$(\Delta/\sigma)_{\text{max}} = 0.031$
264 parameters	$\Delta\rho_{\text{max}} = 0.31 \text{ e } \text{\AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.17 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.81098 (11)	0.05407 (8)	0.11215 (12)	0.0408 (3)
H1	0.8386	0.0188	0.1844	0.049*
C2	0.91557 (11)	0.11046 (8)	0.12512 (12)	0.0409 (3)
H2A	0.8872	0.1490	0.0575	0.049*
H2B	0.9794	0.0766	0.1221	0.049*
C3	0.96801 (10)	0.16028 (8)	0.24349 (11)	0.0377 (3)
C4	0.87477 (11)	0.21761 (8)	0.25620 (12)	0.0405 (3)
H4A	0.9135	0.2456	0.3338	0.049*
H4B	0.8499	0.2601	0.1938	0.049*
C5	0.76159 (11)	0.17236 (8)	0.24675 (12)	0.0403 (3)
H5	0.7863	0.1315	0.3124	0.048*
C6	0.67241 (12)	0.23270 (8)	0.25743 (12)	0.0418 (3)
C7	0.64638 (16)	0.22878 (12)	0.35475 (15)	0.0586 (4)
H7	0.6834	0.1886	0.4143	0.070*
C8	0.5648 (2)	0.28496 (14)	0.36371 (19)	0.0752 (5)
H8	0.5471	0.2818	0.4291	0.090*
C9	0.51035 (17)	0.34484 (12)	0.2773 (2)	0.0690 (5)

H9	0.4571	0.3827	0.2850	0.083*
C10	0.53404 (16)	0.34912 (11)	0.17975 (19)	0.0632 (4)
H10	0.4963	0.3893	0.1203	0.076*
C11	0.61498 (15)	0.29289 (10)	0.17013 (16)	0.0538 (4)
H11	0.6309	0.2958	0.1036	0.065*
C12	0.76348 (11)	-0.00201 (8)	0.00198 (13)	0.0448 (3)
C13	0.68438 (16)	-0.06649 (11)	-0.00790 (18)	0.0625 (4)
H13	0.6616	-0.0749	0.0534	0.075*
C14	0.63888 (17)	-0.11863 (11)	-0.1084 (2)	0.0719 (5)
H14	0.5863	-0.1617	-0.1135	0.086*
C15	0.67076 (16)	-0.10715 (11)	-0.19984 (19)	0.0681 (5)
H15	0.6392	-0.1416	-0.2675	0.082*
C16	0.74988 (18)	-0.04419 (12)	-0.19032 (18)	0.0693 (5)
H16	0.7728	-0.0364	-0.2516	0.083*
C17	0.79604 (16)	0.00785 (10)	-0.09063 (15)	0.0578 (4)
H17	0.8498	0.0501	-0.0857	0.069*
C18	1.07172 (12)	0.27042 (8)	0.17789 (12)	0.0411 (3)
C19	1.18800 (14)	0.31368 (11)	0.20301 (17)	0.0606 (4)
H19A	1.2396	0.2764	0.1865	0.091*
H19B	1.2279	0.3303	0.2863	0.091*
H19C	1.1711	0.3621	0.1524	0.091*
C20	1.17574 (11)	0.13205 (8)	0.41606 (11)	0.0382 (3)
C21	1.28104 (14)	0.04085 (11)	0.58940 (16)	0.0602 (4)
C22	1.40213 (17)	0.02732 (16)	0.6959 (2)	0.0910 (8)
H22A	1.3910	0.0001	0.7593	0.137*
H22B	1.4412	0.0802	0.7244	0.137*
H22C	1.4517	-0.0070	0.6723	0.137*
N1	1.07548 (9)	0.21007 (7)	0.25605 (9)	0.0385 (2)
N2	1.18656 (9)	0.19210 (7)	0.35415 (10)	0.0391 (2)
N3	1.27755 (10)	0.10526 (8)	0.51668 (10)	0.0459 (3)
H3	1.3443	0.1316	0.5348	0.055*
S1	0.68373 (3)	0.11763 (2)	0.10259 (3)	0.04552 (11)
S2	1.03376 (3)	0.08660 (2)	0.37248 (3)	0.04760 (12)
O1	0.97614 (9)	0.28782 (7)	0.08854 (9)	0.0496 (2)
O2	1.19260 (12)	-0.00139 (10)	0.56887 (15)	0.0911 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0315 (6)	0.0393 (6)	0.0463 (6)	-0.0006 (5)	0.0128 (5)	-0.0023 (5)
C2	0.0295 (6)	0.0440 (7)	0.0462 (7)	-0.0014 (5)	0.0144 (5)	-0.0066 (5)
C3	0.0275 (5)	0.0391 (6)	0.0415 (6)	-0.0027 (4)	0.0111 (5)	-0.0001 (5)
C4	0.0334 (6)	0.0417 (6)	0.0454 (6)	-0.0017 (5)	0.0169 (5)	-0.0033 (5)
C5	0.0356 (6)	0.0420 (6)	0.0441 (6)	-0.0007 (5)	0.0187 (5)	0.0010 (5)
C6	0.0362 (6)	0.0436 (6)	0.0495 (7)	-0.0049 (5)	0.0228 (5)	-0.0037 (5)
C7	0.0614 (9)	0.0688 (10)	0.0551 (8)	-0.0016 (8)	0.0347 (8)	-0.0018 (7)
C8	0.0779 (12)	0.0931 (14)	0.0782 (12)	-0.0035 (11)	0.0560 (11)	-0.0175 (11)
C9	0.0560 (9)	0.0644 (10)	0.1010 (14)	-0.0014 (8)	0.0481 (10)	-0.0211 (10)

C10	0.0539 (9)	0.0514 (9)	0.0889 (12)	0.0088 (7)	0.0362 (9)	0.0020 (8)
C11	0.0528 (8)	0.0531 (8)	0.0657 (9)	0.0082 (6)	0.0358 (7)	0.0066 (7)
C12	0.0320 (6)	0.0397 (6)	0.0537 (7)	0.0014 (5)	0.0113 (5)	-0.0061 (5)
C13	0.0533 (9)	0.0579 (9)	0.0740 (10)	-0.0153 (7)	0.0267 (8)	-0.0141 (8)
C14	0.0498 (9)	0.0556 (10)	0.0958 (14)	-0.0159 (7)	0.0200 (9)	-0.0223 (9)
C15	0.0498 (9)	0.0622 (10)	0.0776 (11)	0.0029 (7)	0.0156 (8)	-0.0305 (9)
C16	0.0708 (11)	0.0702 (11)	0.0666 (10)	-0.0030 (9)	0.0305 (9)	-0.0223 (9)
C17	0.0576 (9)	0.0522 (8)	0.0635 (9)	-0.0072 (7)	0.0272 (8)	-0.0143 (7)
C18	0.0370 (6)	0.0392 (6)	0.0463 (6)	0.0018 (5)	0.0180 (5)	0.0003 (5)
C19	0.0461 (8)	0.0560 (9)	0.0721 (10)	-0.0088 (7)	0.0198 (7)	0.0140 (7)
C20	0.0289 (5)	0.0389 (6)	0.0415 (6)	-0.0018 (4)	0.0111 (5)	-0.0034 (5)
C21	0.0413 (7)	0.0576 (9)	0.0678 (10)	0.0010 (6)	0.0121 (7)	0.0199 (7)
C22	0.0484 (9)	0.1010 (16)	0.0918 (14)	-0.0008 (10)	0.0032 (9)	0.0505 (13)
N1	0.0269 (5)	0.0415 (5)	0.0417 (5)	-0.0022 (4)	0.0107 (4)	0.0011 (4)
N2	0.0278 (5)	0.0422 (5)	0.0402 (5)	-0.0023 (4)	0.0089 (4)	-0.0015 (4)
N3	0.0308 (5)	0.0494 (6)	0.0463 (6)	-0.0035 (4)	0.0073 (4)	0.0060 (5)
S1	0.02991 (17)	0.0501 (2)	0.0527 (2)	-0.00154 (12)	0.01512 (14)	-0.00724 (14)
S2	0.03201 (17)	0.0476 (2)	0.0523 (2)	-0.00652 (12)	0.00926 (14)	0.00873 (14)
O1	0.0386 (5)	0.0543 (6)	0.0509 (5)	0.0070 (4)	0.0156 (4)	0.0104 (4)
O2	0.0511 (7)	0.0829 (9)	0.1081 (11)	-0.0123 (6)	0.0081 (7)	0.0488 (8)

Geometric parameters (Å, °)

C1—C12	1.5145 (18)	C12—C13	1.388 (2)
C1—C2	1.5228 (17)	C13—C14	1.391 (3)
C1—S1	1.8292 (13)	C13—H13	0.9300
C1—H1	0.9800	C14—C15	1.368 (3)
C2—C3	1.5337 (17)	C14—H14	0.9300
C2—H2A	0.9700	C15—C16	1.371 (3)
C2—H2B	0.9700	C15—H15	0.9300
C3—N1	1.4937 (15)	C16—C17	1.383 (2)
C3—C4	1.5341 (17)	C16—H16	0.9300
C3—S2	1.8543 (13)	C17—H17	0.9300
C4—C5	1.5297 (17)	C18—O1	1.2324 (16)
C4—H4A	0.9700	C18—N1	1.3541 (17)
C4—H4B	0.9700	C18—C19	1.4941 (19)
C5—C6	1.5140 (18)	C19—H19A	0.9600
C5—S1	1.8268 (13)	C19—H19B	0.9600
C5—H5	0.9800	C19—H19C	0.9600
C6—C11	1.383 (2)	C20—N2	1.2742 (17)
C6—C7	1.3811 (19)	C20—N3	1.3808 (16)
C7—C8	1.391 (3)	C20—S2	1.7427 (12)
C7—H7	0.9300	C21—O2	1.209 (2)
C8—C9	1.368 (3)	C21—N3	1.3577 (19)
C8—H8	0.9300	C21—C22	1.499 (2)
C9—C10	1.366 (3)	C22—H22A	0.9600
C9—H9	0.9300	C22—H22B	0.9600
C10—C11	1.389 (2)	C22—H22C	0.9600

C10—H10	0.9300	N1—N2	1.3924 (14)
C11—H11	0.9300	N3—H3	0.8600
C12—C17	1.384 (2)		
C12—C1—C2	114.40 (11)	C17—C12—C13	117.78 (14)
C12—C1—S1	107.39 (8)	C17—C12—C1	122.70 (12)
C2—C1—S1	109.74 (9)	C13—C12—C1	119.52 (14)
C12—C1—H1	108.4	C12—C13—C14	120.71 (17)
C2—C1—H1	108.4	C12—C13—H13	119.6
S1—C1—H1	108.4	C14—C13—H13	119.6
C1—C2—C3	112.51 (11)	C15—C14—C13	120.66 (16)
C1—C2—H2A	109.1	C15—C14—H14	119.7
C3—C2—H2A	109.1	C13—C14—H14	119.7
C1—C2—H2B	109.1	C14—C15—C16	119.07 (16)
C3—C2—H2B	109.1	C14—C15—H15	120.5
H2A—C2—H2B	107.8	C16—C15—H15	120.5
N1—C3—C4	109.89 (10)	C15—C16—C17	120.78 (18)
N1—C3—C2	110.53 (10)	C15—C16—H16	119.6
C4—C3—C2	113.35 (10)	C17—C16—H16	119.6
N1—C3—S2	103.09 (8)	C16—C17—C12	120.99 (16)
C4—C3—S2	110.51 (9)	C16—C17—H17	119.5
C2—C3—S2	108.99 (9)	C12—C17—H17	119.5
C5—C4—C3	114.11 (10)	O1—C18—N1	121.01 (12)
C5—C4—H4A	108.7	O1—C18—C19	121.52 (13)
C3—C4—H4A	108.7	N1—C18—C19	117.46 (12)
C5—C4—H4B	108.7	C18—C19—H19A	109.5
C3—C4—H4B	108.7	C18—C19—H19B	109.5
H4A—C4—H4B	107.6	H19A—C19—H19B	109.5
C6—C5—C4	111.36 (11)	C18—C19—H19C	109.5
C6—C5—S1	107.98 (9)	H19A—C19—H19C	109.5
C4—C5—S1	111.28 (9)	H19B—C19—H19C	109.5
C6—C5—H5	108.7	N2—C20—N3	118.63 (11)
C4—C5—H5	108.7	N2—C20—S2	119.44 (9)
S1—C5—H5	108.7	N3—C20—S2	121.93 (10)
C11—C6—C7	118.41 (14)	O2—C21—N3	121.95 (14)
C11—C6—C5	120.91 (12)	O2—C21—C22	123.48 (16)
C7—C6—C5	120.67 (13)	N3—C21—C22	114.57 (14)
C6—C7—C8	120.03 (17)	C21—C22—H22A	109.5
C6—C7—H7	120.0	C21—C22—H22B	109.5
C8—C7—H7	120.0	H22A—C22—H22B	109.5
C9—C8—C7	120.65 (16)	C21—C22—H22C	109.5
C9—C8—H8	119.7	H22A—C22—H22C	109.5
C7—C8—H8	119.7	H22B—C22—H22C	109.5
C8—C9—C10	120.14 (16)	C18—N1—N2	118.39 (10)
C8—C9—H9	119.9	C18—N1—C3	124.27 (10)
C10—C9—H9	119.9	N2—N1—C3	117.33 (10)
C9—C10—C11	119.39 (17)	C20—N2—N1	110.68 (10)
C9—C10—H10	120.3	C21—N3—C20	125.43 (12)

C11—C10—H10	120.3	C21—N3—H3	117.3
C6—C11—C10	121.36 (15)	C20—N3—H3	117.3
C6—C11—H11	119.3	C5—S1—C1	98.36 (6)
C10—C11—H11	119.3	C20—S2—C3	89.43 (6)
C12—C1—C2—C3	-174.88 (10)	C15—C16—C17—C12	-0.2 (3)
S1—C1—C2—C3	64.36 (12)	C13—C12—C17—C16	0.9 (2)
C1—C2—C3—N1	176.11 (10)	C1—C12—C17—C16	-179.42 (15)
C1—C2—C3—C4	-60.01 (14)	O1—C18—N1—N2	178.81 (12)
C1—C2—C3—S2	63.50 (12)	C19—C18—N1—N2	-0.07 (18)
N1—C3—C4—C5	-179.06 (10)	O1—C18—N1—C3	-0.5 (2)
C2—C3—C4—C5	56.72 (14)	C19—C18—N1—C3	-179.34 (13)
S2—C3—C4—C5	-65.95 (12)	C4—C3—N1—C18	-64.69 (15)
C3—C4—C5—C6	-178.82 (11)	C2—C3—N1—C18	61.15 (15)
C3—C4—C5—S1	-58.29 (13)	S2—C3—N1—C18	177.50 (10)
C4—C5—C6—C11	65.69 (17)	C4—C3—N1—N2	116.04 (12)
S1—C5—C6—C11	-56.76 (15)	C2—C3—N1—N2	-118.12 (11)
C4—C5—C6—C7	-114.40 (15)	S2—C3—N1—N2	-1.78 (12)
S1—C5—C6—C7	123.16 (13)	N3—C20—N2—N1	179.47 (11)
C11—C6—C7—C8	-0.5 (2)	S2—C20—N2—N1	-0.92 (15)
C5—C6—C7—C8	179.61 (16)	C18—N1—N2—C20	-177.50 (11)
C6—C7—C8—C9	-0.5 (3)	C3—N1—N2—C20	1.82 (15)
C7—C8—C9—C10	1.2 (3)	O2—C21—N3—C20	2.4 (3)
C8—C9—C10—C11	-0.8 (3)	C22—C21—N3—C20	-177.33 (18)
C7—C6—C11—C10	0.8 (2)	N2—C20—N3—C21	-178.11 (15)
C5—C6—C11—C10	-179.28 (14)	S2—C20—N3—C21	2.3 (2)
C9—C10—C11—C6	-0.2 (3)	C6—C5—S1—C1	178.14 (9)
C2—C1—C12—C17	-11.55 (19)	C4—C5—S1—C1	55.64 (10)
S1—C1—C12—C17	110.50 (14)	C12—C1—S1—C5	176.47 (9)
C2—C1—C12—C13	168.17 (13)	C2—C1—S1—C5	-58.62 (10)
S1—C1—C12—C13	-69.78 (15)	N2—C20—S2—C3	-0.11 (11)
C17—C12—C13—C14	-0.6 (2)	N3—C20—S2—C3	179.49 (11)
C1—C12—C13—C14	179.65 (15)	N1—C3—S2—C20	0.98 (8)
C12—C13—C14—C15	-0.3 (3)	C4—C3—S2—C20	-116.40 (9)
C13—C14—C15—C16	1.0 (3)	C2—C3—S2—C20	118.42 (9)
C14—C15—C16—C17	-0.8 (3)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3 \cdots O1 ⁱ	0.86	1.94	2.786 (2)	166
C5—H5 \cdots O2 ⁱⁱ	0.98	2.49	3.446 (2)	163

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