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6,7-Diphenyl-5-thia-7-azaspiro[2.6]nonan-8-one 5,5-dioxide

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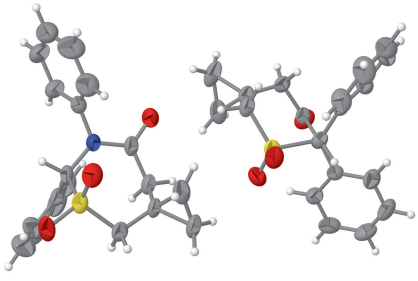
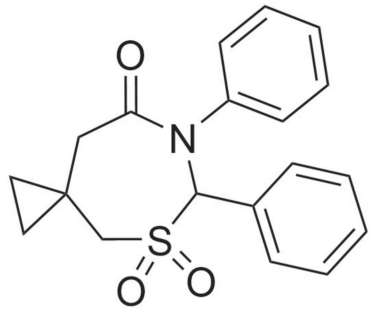
The racemic mixture of the title compound, $C_{19}H_{19}NO_3S$, crystallizes in space group $P\overline{1}$ with two homochiral molecules in each asymmetric unit. The seven-membered ring in both molecules is in a pucker-chair conformation. The extended structure exhibits C—H···O hydrogen bonds, of which two connect crystallographically independent molecules to generate a chain propagating along the *b*-axis direction. One C—H grouping of the cyclopropyl ring is in close contact with the phenyl ring of the neighboring independent molecule in C—H···π type interactions with carbon atom–ring-centroid distances of 3.544 (5) and 3.596 (4) Å. Other interactions are of the parallel–reciprocal type, with the chiral carbon atom of one molecule donating a proton to an oxygen atom of the sulfone group of a symmetry-related molecule and *vice-versa*. Symmetry-related molecular pairs also exhibit T-type interactions between aromatic rings with interplanar angles of 74.2 (2) and 69.2 (2)° and intercentroid distances of 4.965 (4) and 5.114 (4) Å.

3D view



Chemical scheme



Structure description

The seven-membered 1,3-thiazepan-4-one ring system, like the similar six-membered 1,3-thiazin-4-one and five-membered 1,3-thiazolidin-4-one systems, is biologically active and of potential medicinal use. For example, the Bristol-Myers Squibb ACE/NEP inhibitor omapatrilat ($C_{19}H_{24}N_2O_4S_2$) advanced to Phase II clinical trials (Graul *et al.*, 1999; Robl *et al.* 1997; Tabrizchi, 2001; Cozier *et al.*, 2018). Oxidation to the sulfone has been shown to change the biological activity of an isopenam 1,3-thiazepan-4-one (Hwu *et al.*, 1999). *S*-Oxides of 1,3-thiazin-4-ones have shown greater activity than the sulfides from which they were synthesized (Surrey *et al.*, 1958). Here we report the crystal structure of the sulfone derivative **1** (Silverberg, 2022) of 1,3-thiazepan-4-one **2** (Yennawar & Silverberg,

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···O2^{i}	0.98	2.29	3.242 (4)	165
C5—H5A···O6	0.97	2.53	3.460 (5)	161
C20—H20···O5^{ii}	0.98	2.35	3.310 (4)	166
C24—H24A···O3^{iii}	0.97	2.47	3.413 (5)	165

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

2013). Although we have isolated the corresponding sulfoxide **3** (Silverberg, 2022), we have not been able to form it selectively and have not yet obtained a crystal structure.

The asymmetric unit of **1** is comprised of two independent molecules (*A* containing C1 and *B* containing C20, Fig. 1), each consisting of a cyclopropane ring, a pair of phenyl rings and a seven-membered heterocycle displaying a chair-pucker conformation in both molecules. For the C1 molecule, $q(2)$ = 0.463 (4) Å, $q(3)$ = 0.728 (3) Å, $\varphi(2)$ = 92.7 (4)°, $\varphi(3)$ = 336.2 (3)° and the total puckering amplitude Q = 0.863 (3) Å, with equivalent data of 0.444 (4) Å, 0.729 (3) Å, 90.2 (4)°, 335.4 (3)° and 0.853 (3) Å, respectively for the C20 molecule. We reported similar puckering of the 1,3-thiazepan-4-one ring previously (Yennawar *et al.*, 2019). The stereogenic centers (C1 and C20) in the arbitrarily chosen asymmetric unit both have *R* configurations but crystal symmetry generates a racemic mixture.

The packing of **1** is consolidated by a number of C—H···O and C—H···π type interactions (Fig. 2 and Table 1). One pair of C—H···O bonds, C5—H5A···O6 [C···O = 3.460 (5) Å, C—H···O = 161°] and C24—H24A···O3 [3.413 (5) Å and 165°], wherein the carbonyl oxygen atom of one molecule accepts a C—H grouping of the heterocycle of another, form a chain of alternating crystallographically independent molecules along the *b* axis direction. Independent neighbors along the [10$\bar{1}$] direction participate in C—H···π type interactions (Tsuzuki, 2000) wherein a C—H moiety (C18/C38) of the cyclopropyl ring makes a close contact [C···π = 3.596 (5) and 3.544 (4) Å] with the centroid of an adjacent phenyl ring (C25–C30 and C6–C11, respectively]. Additionally, parallel *give-and-take* C—H···O interactions are seen between the symmetry-related pairs of molecules wherein the chiral carbon atom (C1 and C20) of one donates a proton to one of the sulfone oxygen atoms (O2 and O5, respectively) on the heterocyclic ring of its neighbor in a reciprocal fashion.

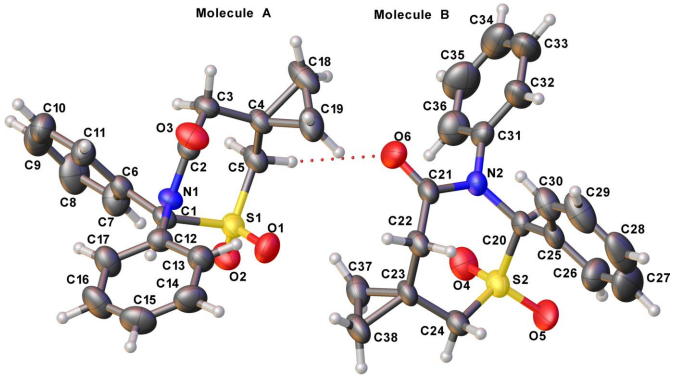


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. C—H···O interactions are shown as dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{19}H_{19}NO_3S$
M_r	341.41
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	298
a, b, c (Å)	10.125 (5), 11.222 (5), 15.995 (7)
α, β, γ (°)	79.117 (8), 83.484 (9), 72.829 (8)
V (Å^3)	1701.8 (13)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.21
Crystal size (mm)	0.14 × 0.10 × 0.05
Data collection	
Diffractometer	Bruker *SMART* CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.698, 0.9
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15037, 7728, 3674
R_{int}	0.060
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.669
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.079, 0.207, 0.91
No. of reflections	7728
No. of parameters	433
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.74, −0.45

Computer programs: *SMART* and *SAINT* (Bruker, 2001), *SHELXS* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015), and *OLEX2* (Dolomanov *et al.*, 2009).

Synthesis and crystallization

6,7-Diphenyl-5-thia-7-azaspiro[2.6]nonan-8-one **2** (Yennawar & Silverberg, 2013) (0.0831 g, 0.267 mmol) was dissolved in

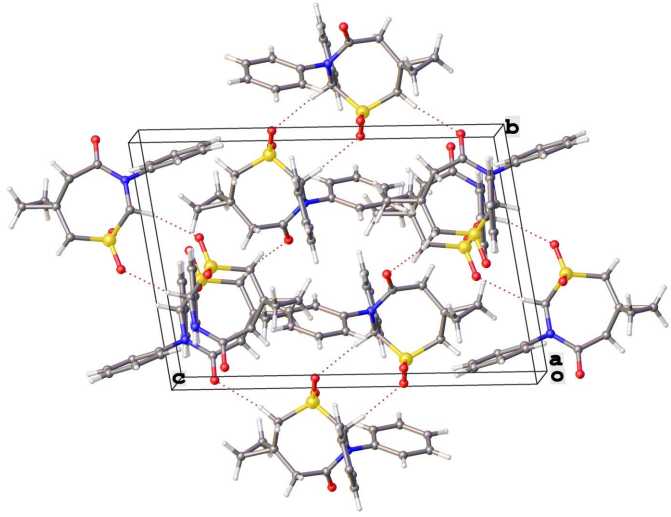


Figure 2
Packing diagram viewing down *a* axis, showing C—H···O hydrogen bonds between molecules.

glacial acetic acid (1.2 ml). An aqueous solution of $KMnO_4$ (0.0853 g, 0.535 mmol in 1.45 ml water) was added dropwise at room temperature with vigorous stirring. The reaction was followed by TLC. Solid sodium bisulfite ($NaHSO_3/Na_2S_20_5$) was added until the solution remained colorless. 1.45 ml of water were added and stirred for 10 min. The mixture was extracted with CH_2Cl_2 (3 × 5 ml). The organics were combined and washed once with sat. NaCl. The solution was dried over Na_2SO_4 and filtered. The product **1** was purified by chromatography in a silica gel microcolumn [0.0638 g, 70% yield. m.p. 186.6–187.7°C (decomposition)]. Crystals were grown by slow evaporation of an ethanol solution.

Refinement

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

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full crystallographic data

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Crystal data

$C_{19}H_{19}NO_3S$
M_r = 341.41
Triclinic, $P\overline{1}$
a = 10.125 (5) Å
b = 11.222 (5) Å
c = 15.995 (7) Å
α = 79.117 (8)°
β = 83.484 (9)°
γ = 72.829 (8)°
V = 1701.8 (13) Å^3
Z = 4
$F(000)$ = 720
D_x = 1.332 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1788 reflections
θ = 2.4–25.1°
μ = 0.21 mm^{-1}
T = 298 K
Block, colorless
0.14 × 0.10 × 0.05 mm

Data collection

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.34 pixels mm^{-1}
phi and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.698, T_{max} = 0.9
15037 measured reflections
7728 independent reflections
3674 reflections with $I > 2\sigma(I)$
R_{int} = 0.060
θ_{max} = 28.4°, θ_{min} = 1.3°
h = −11→13
k = −14→15
l = −21→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.079
$wR(F^2)$ = 0.207
S = 0.91
7728 reflections
433 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.74 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

Special details

Experimental. The data collection nominally covered a full sphere of reciprocal space by a combination of 5 sets of ω scans each set at different φ and/or 2θ angles and each scan (30 s exposure) covering -0.300° degrees in ω. The crystal to detector distance was 5.82 cm.

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.

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 $F^2 > 2\text{sigma}(F^2)$ 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.

The hydrogen atoms were placed geometrically (C—H = 0.93–0.98 Å) and refined as riding on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.90079 (10)	0.56246 (8)	0.12862 (6)	0.0407 (3)
S2	0.60160 (10)	0.07781 (8)	0.36592 (6)	0.0434 (3)
O1	0.7581 (3)	0.5998 (2)	0.11179 (17)	0.0541 (7)
O2	0.9835 (3)	0.4395 (2)	0.11397 (17)	0.0523 (7)
O3	0.7584 (3)	0.9752 (2)	0.11388 (16)	0.0535 (7)
O4	0.7454 (3)	0.0349 (2)	0.38132 (17)	0.0552 (8)
O5	0.5248 (3)	−0.0146 (2)	0.38104 (18)	0.0598 (8)
O6	0.7253 (3)	0.4160 (3)	0.38174 (17)	0.0608 (8)
N1	0.8788 (3)	0.8038 (2)	0.05663 (18)	0.0350 (7)
N2	0.6102 (3)	0.2742 (3)	0.43865 (18)	0.0376 (7)
C1	0.9765 (3)	0.6790 (3)	0.0601 (2)	0.0359 (8)
H1	0.9802	0.6593	0.0026	0.043*
C2	0.8408 (4)	0.8715 (3)	0.1232 (2)	0.0376 (8)
C3	0.8994 (4)	0.8121 (3)	0.2094 (2)	0.0410 (9)
H3A	0.8795	0.8772	0.2449	0.049*
H3B	0.9993	0.7805	0.2013	0.049*
C4	0.8430 (4)	0.7046 (3)	0.2561 (2)	0.0404 (9)
C5	0.9171 (4)	0.5762 (3)	0.2345 (2)	0.0460 (10)
H5A	0.8808	0.5137	0.2728	0.055*
H5B	1.0146	0.5575	0.2440	0.055*
C6	1.1264 (3)	0.6682 (3)	0.0744 (2)	0.0385 (9)
C7	1.2248 (4)	0.5528 (4)	0.0859 (3)	0.0578 (12)
H7	1.1992	0.4790	0.0887	0.069*
C8	1.3633 (4)	0.5460 (5)	0.0933 (3)	0.0738 (15)
H8	1.4290	0.4676	0.1019	0.089*
C9	1.4028 (5)	0.6529 (5)	0.0882 (3)	0.0714 (14)
H9	1.4948	0.6479	0.0938	0.086*
C10	1.3073 (4)	0.7666 (4)	0.0749 (3)	0.0608 (12)
H10	1.3346	0.8398	0.0711	0.073*
C11	1.1706 (4)	0.7764 (4)	0.0669 (2)	0.0474 (10)
H11	1.1071	0.8558	0.0565	0.057*
C12	0.8103 (4)	0.8537 (3)	−0.0220 (2)	0.0375 (9)
C13	0.6711 (4)	0.8734 (4)	−0.0242 (3)	0.0497 (10)
H13	0.6188	0.8561	0.0258	0.060*

C14	0.6076 (4)	0.9188 (4)	−0.1002 (3)	0.0612 (12)
H14	0.5128	0.9318	−0.1015	0.073*
C15	0.6851 (5)	0.9450 (4)	−0.1743 (3)	0.0640 (13)
H15	0.6424	0.9773	−0.2256	0.077*
C16	0.8237 (5)	0.9233 (4)	−0.1722 (3)	0.0629 (12)
H16	0.8766	0.9376	−0.2226	0.076*
C17	0.8872 (4)	0.8802 (4)	−0.0959 (3)	0.0527 (11)
H17	0.9817	0.8691	−0.0946	0.063*
C18	0.7895 (5)	0.7086 (4)	0.3475 (3)	0.0662 (13)
H18A	0.8042	0.6290	0.3865	0.079*
H18B	0.7934	0.7796	0.3726	0.079*
C19	0.6911 (4)	0.7337 (4)	0.2799 (3)	0.0598 (12)
H19A	0.6348	0.8200	0.2640	0.072*
H19B	0.6457	0.6694	0.2779	0.072*
C20	0.5201 (3)	0.1954 (3)	0.4352 (2)	0.0378 (9)
H20	0.5210	0.1453	0.4925	0.045*
C21	0.6467 (4)	0.3572 (3)	0.3713 (2)	0.0422 (9)
C22	0.5898 (4)	0.3741 (3)	0.2860 (2)	0.0427 (9)
H22A	0.6076	0.4488	0.2507	0.051*
H22B	0.4902	0.3889	0.2938	0.051*
C23	0.6501 (4)	0.2623 (3)	0.2390 (2)	0.0398 (9)
C24	0.5805 (4)	0.1577 (3)	0.2609 (2)	0.0443 (9)
H24A	0.6180	0.0975	0.2221	0.053*
H24B	0.4823	0.1933	0.2526	0.053*
C25	0.3683 (4)	0.2620 (3)	0.4236 (2)	0.0408 (9)
C26	0.2755 (4)	0.1958 (5)	0.4163 (3)	0.0689 (13)
H26	0.3076	0.1095	0.4150	0.083*
C27	0.1370 (5)	0.2559 (7)	0.4112 (4)	0.0916 (18)
H27	0.0770	0.2102	0.4041	0.110*
C28	0.0860 (5)	0.3791 (7)	0.4159 (3)	0.0851 (18)
H28	−0.0087	0.4178	0.4135	0.102*
C29	0.1746 (5)	0.4483 (5)	0.4245 (3)	0.0760 (15)
H29	0.1402	0.5342	0.4271	0.091*
C30	0.3149 (4)	0.3891 (4)	0.4292 (3)	0.0558 (11)
H30	0.3743	0.4353	0.4362	0.067*
C31	0.6767 (4)	0.2524 (3)	0.5174 (2)	0.0451 (10)
C32	0.5996 (5)	0.2989 (5)	0.5868 (3)	0.0657 (13)
H32	0.5071	0.3449	0.5820	0.079*
C33	0.6601 (6)	0.2772 (6)	0.6635 (3)	0.0850 (16)
H33	0.6089	0.3094	0.7103	0.102*
C34	0.7943 (7)	0.2088 (6)	0.6703 (4)	0.0921 (18)
H34	0.8343	0.1936	0.7222	0.111*
C35	0.8720 (6)	0.1616 (5)	0.6019 (4)	0.0887 (17)
H35	0.9642	0.1150	0.6072	0.106*
C36	0.8122 (4)	0.1838 (4)	0.5243 (3)	0.0695 (13)
H36	0.8641	0.1521	0.4774	0.083*
C37	0.8030 (4)	0.2257 (4)	0.2163 (3)	0.0552 (11)
H37A	0.8570	0.2756	0.2322	0.066*

H37B	0.8505	0.1364	0.2190	0.066*
C38	0.7043 (4)	0.2870 (4)	0.1474 (2)	0.0568 (11)
H38A	0.6921	0.2347	0.1088	0.068*
H38B	0.6985	0.3738	0.1219	0.068*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0446 (6)	0.0385 (5)	0.0399 (6)	−0.0138 (4)	0.0059 (4)	−0.0100 (4)
S2	0.0508 (6)	0.0347 (5)	0.0426 (6)	−0.0130 (4)	0.0093 (4)	−0.0068 (4)
O1	0.0448 (16)	0.0613 (17)	0.0607 (19)	−0.0246 (13)	−0.0016 (13)	−0.0066 (14)
O2	0.0698 (18)	0.0385 (14)	0.0496 (17)	−0.0175 (13)	0.0096 (14)	−0.0138 (12)
O3	0.0642 (18)	0.0405 (15)	0.0470 (17)	0.0023 (13)	−0.0024 (13)	−0.0137 (12)
O4	0.0458 (16)	0.0501 (16)	0.0580 (18)	−0.0007 (13)	0.0026 (13)	−0.0042 (13)
O5	0.086 (2)	0.0417 (15)	0.0595 (19)	−0.0386 (15)	0.0152 (15)	−0.0067 (13)
O6	0.083 (2)	0.0677 (19)	0.0467 (18)	−0.0488 (17)	0.0014 (15)	−0.0049 (14)
N1	0.0386 (16)	0.0349 (15)	0.0309 (17)	−0.0068 (13)	0.0009 (13)	−0.0114 (13)
N2	0.0402 (17)	0.0414 (16)	0.0325 (17)	−0.0170 (14)	0.0031 (13)	−0.0034 (13)
C1	0.0384 (19)	0.0368 (18)	0.030 (2)	−0.0057 (15)	0.0036 (15)	−0.0106 (15)
C2	0.041 (2)	0.0339 (19)	0.037 (2)	−0.0116 (16)	0.0045 (16)	−0.0075 (16)
C3	0.050 (2)	0.042 (2)	0.032 (2)	−0.0127 (17)	0.0017 (17)	−0.0114 (16)
C4	0.048 (2)	0.041 (2)	0.030 (2)	−0.0103 (17)	0.0073 (16)	−0.0085 (15)
C5	0.054 (2)	0.044 (2)	0.036 (2)	−0.0131 (18)	0.0092 (17)	−0.0057 (16)
C6	0.0347 (19)	0.047 (2)	0.030 (2)	−0.0073 (17)	0.0036 (15)	−0.0074 (16)
C7	0.043 (2)	0.051 (2)	0.069 (3)	−0.0045 (19)	0.002 (2)	−0.003 (2)
C8	0.037 (2)	0.078 (3)	0.087 (4)	0.002 (2)	−0.001 (2)	0.003 (3)
C9	0.041 (3)	0.106 (4)	0.067 (3)	−0.025 (3)	−0.008 (2)	−0.006 (3)
C10	0.051 (3)	0.077 (3)	0.062 (3)	−0.030 (2)	0.006 (2)	−0.016 (2)
C11	0.042 (2)	0.052 (2)	0.051 (3)	−0.0154 (19)	0.0060 (18)	−0.0138 (19)
C12	0.037 (2)	0.0368 (19)	0.037 (2)	−0.0070 (16)	−0.0044 (16)	−0.0085 (15)
C13	0.046 (2)	0.061 (3)	0.043 (2)	−0.0164 (19)	−0.0015 (19)	−0.0106 (19)
C14	0.051 (3)	0.075 (3)	0.061 (3)	−0.013 (2)	−0.017 (2)	−0.017 (2)
C15	0.072 (3)	0.069 (3)	0.046 (3)	−0.008 (2)	−0.023 (2)	−0.006 (2)
C16	0.065 (3)	0.078 (3)	0.034 (2)	−0.009 (2)	0.001 (2)	0.001 (2)
C17	0.043 (2)	0.065 (3)	0.043 (3)	−0.0073 (19)	0.0023 (19)	−0.004 (2)
C18	0.097 (4)	0.050 (2)	0.040 (3)	−0.011 (2)	0.021 (2)	−0.0082 (19)
C19	0.056 (3)	0.052 (2)	0.067 (3)	−0.015 (2)	0.023 (2)	−0.015 (2)
C20	0.042 (2)	0.042 (2)	0.031 (2)	−0.0195 (16)	0.0059 (16)	−0.0013 (15)
C21	0.050 (2)	0.041 (2)	0.037 (2)	−0.0187 (18)	0.0144 (18)	−0.0101 (16)
C22	0.055 (2)	0.038 (2)	0.033 (2)	−0.0156 (17)	0.0106 (17)	−0.0046 (16)
C23	0.046 (2)	0.044 (2)	0.028 (2)	−0.0161 (17)	0.0114 (16)	−0.0050 (15)
C24	0.050 (2)	0.047 (2)	0.035 (2)	−0.0156 (18)	0.0091 (17)	−0.0108 (17)
C25	0.039 (2)	0.053 (2)	0.027 (2)	−0.0134 (18)	0.0067 (15)	−0.0030 (16)
C26	0.047 (3)	0.085 (3)	0.080 (4)	−0.024 (2)	0.007 (2)	−0.023 (3)
C27	0.047 (3)	0.142 (6)	0.094 (4)	−0.036 (3)	0.002 (3)	−0.029 (4)
C28	0.041 (3)	0.140 (5)	0.053 (3)	−0.003 (3)	0.001 (2)	−0.002 (3)
C29	0.065 (3)	0.077 (3)	0.056 (3)	0.009 (3)	0.014 (2)	0.003 (2)
C30	0.050 (2)	0.057 (3)	0.047 (3)	−0.004 (2)	0.0110 (19)	−0.0030 (19)

C31	0.051 (2)	0.050 (2)	0.040 (2)	−0.0262 (19)	−0.0021 (19)	−0.0022 (18)
C32	0.063 (3)	0.103 (4)	0.039 (3)	−0.036 (3)	−0.001 (2)	−0.012 (2)
C33	0.092 (4)	0.142 (5)	0.040 (3)	−0.062 (4)	0.003 (3)	−0.019 (3)
C34	0.104 (5)	0.128 (5)	0.061 (4)	−0.069 (4)	−0.027 (4)	0.016 (3)
C35	0.067 (3)	0.108 (4)	0.090 (5)	−0.025 (3)	−0.035 (3)	0.004 (4)
C36	0.056 (3)	0.075 (3)	0.073 (4)	−0.014 (2)	−0.008 (2)	−0.006 (3)
C37	0.052 (2)	0.053 (2)	0.057 (3)	−0.016 (2)	0.018 (2)	−0.012 (2)
C38	0.077 (3)	0.057 (2)	0.036 (2)	−0.028 (2)	0.019 (2)	−0.0075 (19)

Geometric parameters (Å, º)

S1—O1	1.423 (3)	C16—H16	0.9300
S1—O2	1.434 (3)	C16—C17	1.381 (5)
S1—C1	1.833 (4)	C17—H17	0.9300
S1—C5	1.759 (4)	C18—H18A	0.9700
S2—O4	1.426 (3)	C18—H18B	0.9700
S2—O5	1.441 (3)	C18—C19	1.486 (6)
S2—C20	1.830 (4)	C19—H19A	0.9700
S2—C24	1.752 (4)	C19—H19B	0.9700
O3—C2	1.209 (4)	C20—H20	0.9800
O6—C21	1.217 (4)	C20—C25	1.513 (5)
N1—C1	1.451 (4)	C21—C22	1.499 (5)
N1—C2	1.378 (4)	C22—H22A	0.9700
N1—C12	1.442 (4)	C22—H22B	0.9700
N2—C20	1.458 (4)	C22—C23	1.520 (5)
N2—C21	1.377 (4)	C23—C24	1.508 (5)
N2—C31	1.442 (5)	C23—C37	1.501 (5)
C1—H1	0.9800	C23—C38	1.509 (5)
C1—C6	1.526 (5)	C24—H24A	0.9700
C2—C3	1.517 (5)	C24—H24B	0.9700
C3—H3A	0.9700	C25—C26	1.385 (5)
C3—H3B	0.9700	C25—C30	1.384 (5)
C3—C4	1.520 (5)	C26—H26	0.9300
C4—C5	1.499 (5)	C26—C27	1.370 (6)
C4—C18	1.505 (5)	C27—H27	0.9300
C4—C19	1.495 (5)	C27—C28	1.338 (7)
C5—H5A	0.9700	C28—H28	0.9300
C5—H5B	0.9700	C28—C29	1.382 (7)
C6—C7	1.376 (5)	C29—H29	0.9300
C6—C11	1.394 (5)	C29—C30	1.383 (6)
C7—H7	0.9300	C30—H30	0.9300
C7—C8	1.399 (6)	C31—C32	1.376 (6)
C8—H8	0.9300	C31—C36	1.365 (5)
C8—C9	1.358 (6)	C32—H32	0.9300
C9—H9	0.9300	C32—C33	1.383 (6)
C9—C10	1.350 (6)	C33—H33	0.9300
C10—H10	0.9300	C33—C34	1.354 (7)
C10—C11	1.375 (5)	C34—H34	0.9300

C11—H11	0.9300	C34—C35	1.369 (8)
C12—C13	1.364 (5)	C35—H35	0.9300
C12—C17	1.374 (5)	C35—C36	1.391 (7)
C13—H13	0.9300	C36—H36	0.9300
C13—C14	1.379 (5)	C37—H37A	0.9700
C14—H14	0.9300	C37—H37B	0.9700
C14—C15	1.378 (6)	C37—C38	1.497 (6)
C15—H15	0.9300	C38—H38A	0.9700
C15—C16	1.356 (6)	C38—H38B	0.9700

O1—S1—O2	118.34 (17)	C19—C18—C4	60.0 (3)
O1—S1—C1	106.13 (15)	C19—C18—H18A	117.8
O1—S1—C5	109.40 (18)	C19—C18—H18B	117.8
O2—S1—C1	107.56 (16)	C4—C19—H19A	117.7
O2—S1—C5	108.30 (16)	C4—C19—H19B	117.7
C5—S1—C1	106.48 (17)	C18—C19—C4	60.7 (3)
O4—S2—O5	117.82 (16)	C18—C19—H19A	117.7
O4—S2—C20	106.93 (17)	C18—C19—H19B	117.7
O4—S2—C24	109.41 (17)	H19A—C19—H19B	114.8
O5—S2—C20	107.33 (17)	S2—C20—H20	104.0
O5—S2—C24	108.42 (18)	N2—C20—S2	110.3 (2)
C24—S2—C20	106.33 (17)	N2—C20—H20	104.0
C2—N1—C1	125.4 (3)	N2—C20—C25	117.1 (3)
C2—N1—C12	119.0 (3)	C25—C20—S2	115.8 (3)
C12—N1—C1	115.4 (3)	C25—C20—H20	104.0
C21—N2—C20	125.6 (3)	O6—C21—N2	119.5 (4)
C21—N2—C31	118.1 (3)	O6—C21—C22	120.5 (3)
C31—N2—C20	116.0 (3)	N2—C21—C22	120.0 (3)
S1—C1—H1	104.4	C21—C22—H22A	108.7
N1—C1—S1	109.4 (2)	C21—C22—H22B	108.7
N1—C1—H1	104.4	C21—C22—C23	114.2 (3)
N1—C1—C6	116.7 (3)	H22A—C22—H22B	107.6
C6—C1—S1	116.0 (2)	C23—C22—H22A	108.7
C6—C1—H1	104.4	C23—C22—H22B	108.7
O3—C2—N1	120.5 (3)	C24—C23—C22	115.7 (3)
O3—C2—C3	120.3 (3)	C24—C23—C38	115.9 (3)
N1—C2—C3	119.1 (3)	C37—C23—C22	118.0 (3)
C2—C3—H3A	108.7	C37—C23—C24	117.5 (3)
C2—C3—H3B	108.7	C37—C23—C38	59.7 (2)
C2—C3—C4	114.3 (3)	C38—C23—C22	118.5 (3)
H3A—C3—H3B	107.6	S2—C24—H24A	108.9
C4—C3—H3A	108.7	S2—C24—H24B	108.9
C4—C3—H3B	108.7	C23—C24—S2	113.3 (3)
C5—C4—C3	115.7 (3)	C23—C24—H24A	108.9
C5—C4—C18	116.0 (3)	C23—C24—H24B	108.9
C18—C4—C3	117.8 (3)	H24A—C24—H24B	107.7
C19—C4—C3	118.0 (3)	C26—C25—C20	121.3 (3)
C19—C4—C5	118.3 (3)	C30—C25—C20	120.8 (4)

C19—C4—C18	59.4 (3)	C30—C25—C26	117.5 (4)
S1—C5—H5A	108.9	C25—C26—H26	119.6
S1—C5—H5B	108.9	C27—C26—C25	120.8 (5)
C4—C5—S1	113.5 (3)	C27—C26—H26	119.6
C4—C5—H5A	108.9	C26—C27—H27	119.3
C4—C5—H5B	108.9	C28—C27—C26	121.4 (5)
H5A—C5—H5B	107.7	C28—C27—H27	119.3
C7—C6—C1	121.4 (4)	C27—C28—H28	120.2
C7—C6—C11	117.8 (4)	C27—C28—C29	119.7 (5)
C11—C6—C1	120.4 (3)	C29—C28—H28	120.2
C6—C7—H7	119.9	C28—C29—H29	120.2
C6—C7—C8	120.2 (4)	C28—C29—C30	119.5 (5)
C8—C7—H7	119.9	C30—C29—H29	120.2
C7—C8—H8	119.7	C25—C30—H30	119.5
C9—C8—C7	120.6 (4)	C29—C30—C25	121.0 (5)
C9—C8—H8	119.7	C29—C30—H30	119.5
C8—C9—H9	120.3	C32—C31—N2	118.6 (4)
C10—C9—C8	119.4 (4)	C36—C31—N2	121.0 (4)
C10—C9—H9	120.3	C36—C31—C32	120.4 (4)
C9—C10—H10	119.3	C31—C32—H32	120.1
C9—C10—C11	121.3 (4)	C31—C32—C33	119.7 (4)
C11—C10—H10	119.3	C33—C32—H32	120.1
C6—C11—H11	119.8	C32—C33—H33	120.1
C10—C11—C6	120.5 (4)	C34—C33—C32	119.8 (5)
C10—C11—H11	119.8	C34—C33—H33	120.1
C13—C12—N1	121.1 (3)	C33—C34—H34	119.5
C13—C12—C17	119.7 (3)	C33—C34—C35	121.0 (5)
C17—C12—N1	119.3 (3)	C35—C34—H34	119.5
C12—C13—H13	119.8	C34—C35—H35	120.2
C12—C13—C14	120.4 (4)	C34—C35—C36	119.6 (5)
C14—C13—H13	119.8	C36—C35—H35	120.2
C13—C14—H14	120.1	C31—C36—C35	119.5 (5)
C15—C14—C13	119.9 (4)	C31—C36—H36	120.3
C15—C14—H14	120.1	C35—C36—H36	120.3
C14—C15—H15	120.2	C23—C37—H37A	117.7
C16—C15—C14	119.7 (4)	C23—C37—H37B	117.7
C16—C15—H15	120.2	H37A—C37—H37B	114.8
C15—C16—H16	119.7	C38—C37—C23	60.4 (2)
C15—C16—C17	120.6 (4)	C38—C37—H37A	117.7
C17—C16—H16	119.7	C38—C37—H37B	117.7
C12—C17—C16	119.8 (4)	C23—C38—H38A	117.8
C12—C17—H17	120.1	C23—C38—H38B	117.8
C16—C17—H17	120.1	C37—C38—C23	59.9 (3)
C4—C18—H18A	117.8	C37—C38—H38A	117.8
C4—C18—H18B	117.8	C37—C38—H38B	117.8
H18A—C18—H18B	114.9	H38A—C38—H38B	114.9
S1—C1—C6—C7	43.2 (4)	C9—C10—C11—C6	1.5 (6)

S1—C1—C6—C11	−143.7 (3)	C11—C6—C7—C8	2.6 (6)
S2—C20—C25—C26	44.9 (4)	C12—N1—C1—S1	−105.8 (3)
S2—C20—C25—C30	−142.2 (3)	C12—N1—C1—C6	120.0 (3)
O1—S1—C1—N1	38.4 (3)	C12—N1—C2—O3	−5.1 (5)
O1—S1—C1—C6	173.0 (2)	C12—N1—C2—C3	172.5 (3)
O1—S1—C5—C4	−53.8 (3)	C12—C13—C14—C15	−0.3 (6)
O2—S1—C1—N1	166.0 (2)	C13—C12—C17—C16	−1.7 (6)
O2—S1—C1—C6	−59.4 (3)	C13—C14—C15—C16	1.4 (7)
O2—S1—C5—C4	175.9 (3)	C14—C15—C16—C17	−2.7 (7)
O3—C2—C3—C4	106.8 (4)	C15—C16—C17—C12	2.8 (7)
O4—S2—C20—N2	39.2 (3)	C17—C12—C13—C14	0.4 (6)
O4—S2—C20—C25	175.0 (2)	C18—C4—C5—S1	150.0 (3)
O4—S2—C24—C23	−53.5 (3)	C19—C4—C5—S1	82.4 (4)
O5—S2—C20—N2	166.5 (2)	C20—S2—C24—C23	61.7 (3)
O5—S2—C20—C25	−57.7 (3)	C20—N2—C21—O6	−178.5 (3)
O5—S2—C24—C23	176.8 (2)	C20—N2—C21—C22	1.4 (5)
O6—C21—C22—C23	108.0 (4)	C20—N2—C31—C32	−76.4 (4)
N1—C1—C6—C7	174.5 (3)	C20—N2—C31—C36	101.6 (4)
N1—C1—C6—C11	−12.5 (5)	C20—C25—C26—C27	176.0 (4)
N1—C2—C3—C4	−70.8 (4)	C20—C25—C30—C29	−175.5 (4)
N1—C12—C13—C14	−178.7 (3)	C21—N2—C20—S2	65.9 (4)
N1—C12—C17—C16	177.4 (3)	C21—N2—C20—C25	−69.3 (4)
N2—C20—C25—C26	177.6 (3)	C21—N2—C31—C32	109.7 (4)
N2—C20—C25—C30	−9.5 (5)	C21—N2—C31—C36	−72.2 (5)
N2—C21—C22—C23	−71.9 (4)	C21—C22—C23—C24	85.7 (4)
N2—C31—C32—C33	178.8 (4)	C21—C22—C23—C37	−61.1 (4)
N2—C31—C36—C35	−178.3 (4)	C21—C22—C23—C38	−129.9 (4)
C1—S1—C5—C4	60.5 (3)	C22—C23—C24—S2	−66.5 (4)
C1—N1—C2—O3	179.9 (3)	C22—C23—C37—C38	−108.4 (4)
C1—N1—C2—C3	−2.5 (5)	C22—C23—C38—C37	107.6 (4)
C1—N1—C12—C13	113.9 (4)	C24—S2—C20—N2	−77.6 (3)
C1—N1—C12—C17	−65.2 (4)	C24—S2—C20—C25	58.1 (3)
C1—C6—C7—C8	175.9 (4)	C24—C23—C37—C38	105.4 (4)
C1—C6—C11—C10	−176.3 (3)	C24—C23—C38—C37	−108.1 (4)
C2—N1—C1—S1	69.3 (4)	C25—C26—C27—C28	−2.4 (8)
C2—N1—C1—C6	−64.9 (4)	C26—C25—C30—C29	−2.3 (6)
C2—N1—C12—C13	−61.5 (5)	C26—C27—C28—C29	1.4 (8)
C2—N1—C12—C17	119.3 (4)	C27—C28—C29—C30	−0.9 (7)
C2—C3—C4—C5	86.5 (4)	C28—C29—C30—C25	1.4 (6)
C2—C3—C4—C18	−130.0 (4)	C30—C25—C26—C27	2.8 (6)
C2—C3—C4—C19	−61.9 (4)	C31—N2—C20—S2	−107.4 (3)
C3—C4—C5—S1	−65.9 (4)	C31—N2—C20—C25	117.4 (3)
C3—C4—C18—C19	107.7 (4)	C31—N2—C21—O6	−5.3 (5)
C3—C4—C19—C18	−107.4 (4)	C31—N2—C21—C22	174.6 (3)
C5—S1—C1—N1	−78.1 (3)	C31—C32—C33—C34	−0.9 (8)
C5—S1—C1—C6	56.5 (3)	C32—C31—C36—C35	−0.2 (6)
C5—C4—C18—C19	−108.8 (4)	C32—C33—C34—C35	0.7 (9)
C5—C4—C19—C18	105.1 (4)	C33—C34—C35—C36	−0.2 (9)

C6—C7—C8—C9	−0.9 (7)	C34—C35—C36—C31	0.0 (8)
C7—C6—C11—C10	−2.9 (6)	C36—C31—C32—C33	0.7 (7)
C7—C8—C9—C10	−0.7 (7)	C37—C23—C24—S2	80.5 (4)
C8—C9—C10—C11	0.4 (7)	C38—C23—C24—S2	148.2 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O2^{i}	0.98	2.29	3.242 (4)	165
C5—H5*A*···O6	0.97	2.53	3.460 (5)	161
C20—H20···O5^{ii}	0.98	2.35	3.310 (4)	166
C24—H24*A*···O3^{iii}	0.97	2.47	3.413 (5)	165

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