IUCrData

ISSN 2414-3146

6′-(3-Bromophenyl)-7′-nitro-1′,6′,7′,7a′-tetrahydro-3′*H*-spiro[indeno[1,2-*b*]quinoxaline-11,5′-pyrrolo-[1,2-*c*]thiazole]

C. Muthuselvi,[a] M. Muthu,[b] S. Athimoolam,[c*] B. Ravikumar,[a] S. Pandiarajan[a] and R. V. Krishnakumar[d]

[a]Department of Physics, Devanga Arts College, Aruppukottai 626 101, Tamilnadu, India, [b]School of Chemistry, Madurai Kamaraj University, Madurai, Tamilnadu, India, [c]Department of Physics, University College of Engineering, Anna University, Nagercoil 629 004, Tamilnadu, India, and [d]Department of Physics, Thiagarajar College, Madurai 625 009, Tamilnadu, India. *Correspondence e-mail: athi81s@yahoo.co.in

Received 21 January 2018
Accepted 9 February 2018

Edited by J. Simpson, University of Otago, New Zealand

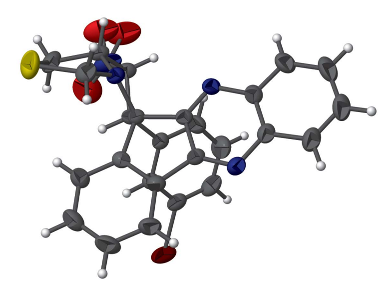
Keywords: crystal structure; spiro compound; quinoxaline; thiazole; bromophenyl.

CCDC reference: 1823122

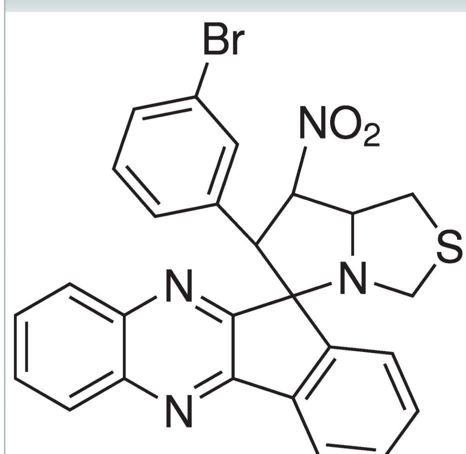
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{26}H_{19}BrN_4O_2S$, crystallizes in a monoclinic *C*-centred lattice with eight molecules in the unit cell. The five-membered thiazole and pyrrolidine rings adopt envelope conformations and the bromophenyl and indenoquinoxaline planes are oriented at a dihedral angle of 61.6 (1)° to each other. The molecular structure features an intramolecular C—H⋯N interaction leading to an *S*(6) ring motif. *C*(9) and *C*(10) chains along the *c*- and *b*-axis directions form through C—H⋯Br and C—H⋯S contacts, respectively. In addition, C—H⋯O and C—H⋯N hydrogen bonds form inversion dimers with $R_2^2(10)$ and $R_2^2(14)$ motifs, respectively. One O atom is disordered over two positions (occupancy ratio 0.63:0.37).

3D view



Chemical scheme



Structure description

Heterocyclic compounds, such as thiazoles, pyrrolidines and quinoxalines are important in many pharmaceutical applications (Bozdağ-Dündar *et al.*, 2008; Swarnkar *et al.*, 2007; Verma & Saraf, 2008; He *et al.*, 2003; Campeau *et al.*, 2008; Muralikrishnan *et al.*, 2013). The addition of bromine to these classes of compounds can offer valuable synthetic intermediates and provide additional medicinal benefits. Its introduction can also result in a more rigid conformation for the newly synthesized molecule (Wermuth, 2003). A small number of drugs containing spiro-fused rings have been investigated over several decades (Knox *et al.*, 2011). Naturally occurring spiropyrrolidine derivatives show highly pronounced biological properties and have potential pharmaceutical applications (Arun

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D$$\cdots$$A$	D—H$\cdots$$A$
C17—H17$\cdots$N2	0.98	2.78	3.345 (4)	117
C20—H20$\cdots$S1^{i}	0.93	2.94	3.775 (4)	151
C26—H26$A$$\cdots$Br1^{ii}	0.97	3.14	3.725 (3)	120
C26—H26$B$$\cdots$N1^{iii}	0.97	2.63	3.547 (4)	158
C16—H16$\cdots$O2^{iv}	0.98	2.69	3.660 (4)	172
C25—H25$A$$\cdots$O2^{iv}	0.97	2.91	3.867 (5)	170

Symmetry codes: (i) $x, -y+1, z-\frac{1}{2}$; (ii) $x, y+1, z$; (iii) $-x+\frac{3}{2}, -y+\frac{3}{2}, -z+1$; (iv) $-x+1, -y+1, -z+1$.

et al., 2014). The development of new synthetic routes to spiro scaffolds will result in more pharmaceutically active molecules (Zheng *et al.*, 2014). Recently, we have reported the synthesis of the first compound in a series of molecules, containing bromophenyl, spiropyrrolidine and thiazole groups (Muthuselvi *et al.*, 2017) and we report here the structure of the closely related title compound.

The structure of title compound is shown in Fig. 1. The envelope conformations of the five-membered rings are confirmed by the puckering analyses with the values of q_2 = 0.356 (3) Å; φ_2 = 75.4 (4)° for the S1/N3/C24–C26 thiazole ring and q_2 = 0.420 (3) Å; φ_2 = 105.3 (4)° for the N3/C8/C16/C17/C24 pyrroline ring. The mean planes of the bromophenyl ring and the indenoquinoxaline ring system are inclined to one another at an angle of 61.6 (1)°. The molecular conformation is in part determined by a weak intramolecular C17—H17$\cdots$N2 hydrogen bond that encloses an S(6) ring.

No classical hydrogen bonds are found but the crystal structure features a number of C—H$\cdots$Br, C—H$\cdots$S, C—H$\cdots$O and C—H$\cdots$N hydrogen bonds, Table 1. C(10) and C(9) chains form through C20—H20$\cdots$S1 and C26—H26$A$$\cdots$Br1 contacts along the c- and b-axis directions, respectively, Figs. 2 and 3. In addition, C16—H16$\cdots$O2 and C26—H26$B$$\cdots$N1 hydrogen bonds form inversion dimers with $R_2^2(10)$ and $R_2^2(14)$ motifs, respectively. The latter are shown in Fig. 4. These contacts combine to stack molecules along the b-axis direction, Fig. 5.

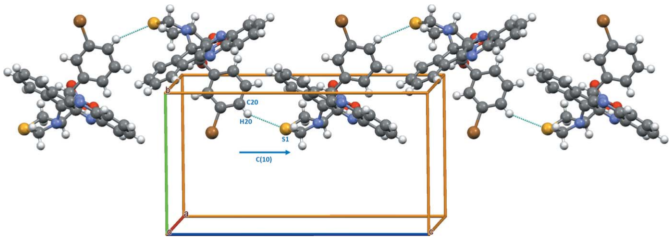


Figure 2
A C(10) chain motif formed through C—H$\cdots$S interactions extending along the c-axis direction. Hydrogen bonds are shown as dashed lines.

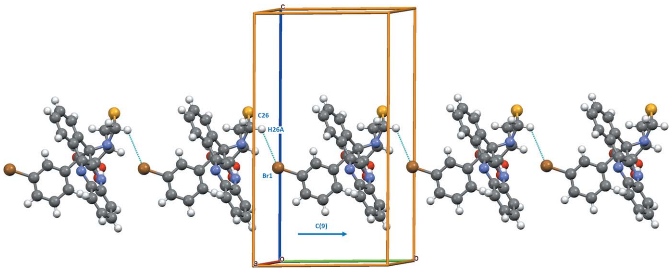


Figure 3
A C(9) chain motif formed through C—H$\cdots$Br interactions extending along the b-axis direction. Hydrogen bonds are shown as dashed lines.

Synthesis and crystallization

Equimolar quantities of benzene-1,2-diamine, 1H-indene-1,2,3-trione and thiazolidine-4-carboxylic acid were added to 20 ml of methanol and the refluxed on a water bath for 5 min.

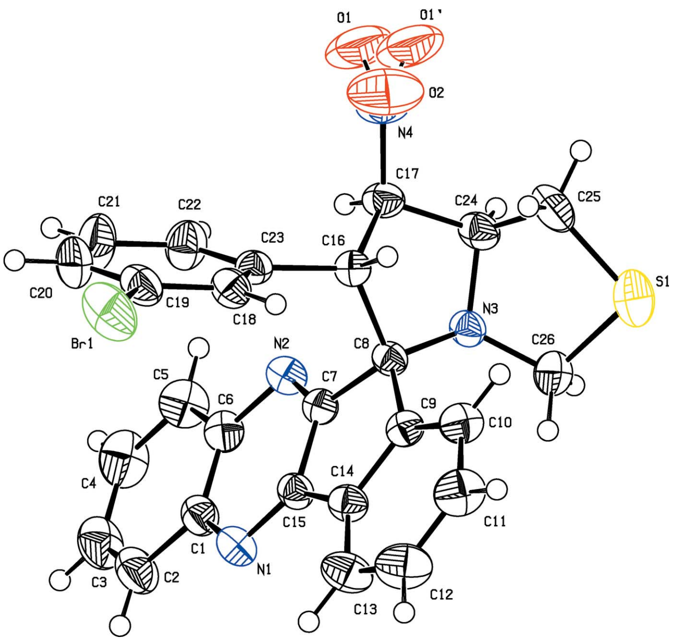


Figure 1
The structure of the title compound with the atom numbering. Displacement ellipsoids are shown at the 50% probability level.

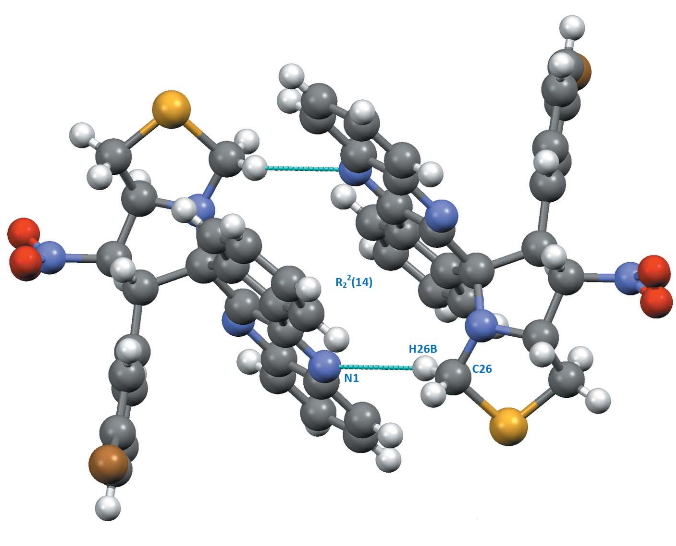


Figure 4
A centrosymmetrically related $R_2^2(14)$ ring motif formed through C—H$\cdots$N hydrogen bonds, shown as dashed lines.

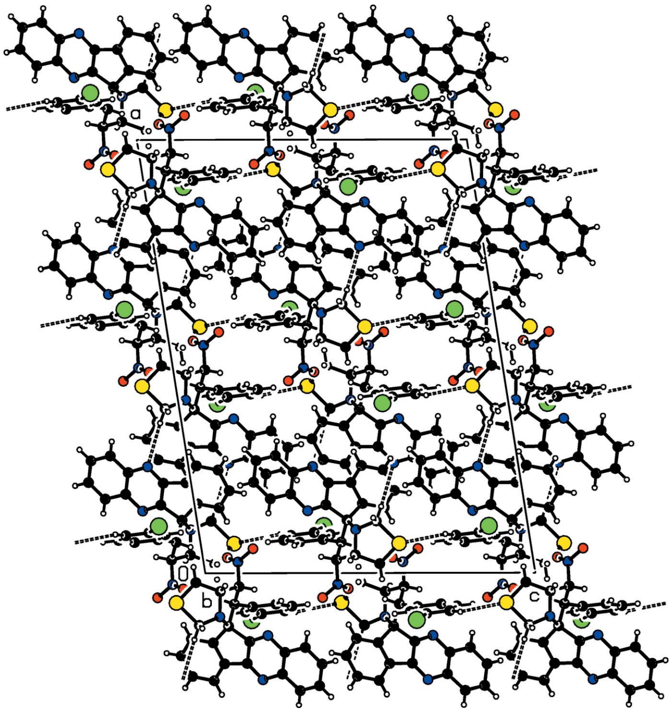


Figure 5
Overall packing of the title compound viewed along the *b* axis. Hydrogen bonds are shown as dashed lines.

An equivalent amount of substituted *trans*-bromo β-nitrostyrene was added to the reaction mixture and refluxing continued for 5 h until TLC analysis indicated that the reaction was complete. The precipitated solid was filtered and washed with methanol to obtain the title compound in good yield (92–96%). Good quality block-shaped crystals were obtained by recrystallization from an ethanolic solution.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Atom O1 is disordered over two positions and, in the final refinement cycles, the site occupancies were fixed at 0.63 and 0.37.

Acknowledgements

The authors CM, BR and SP thank the management of Devanga Arts College, Aruppukkottai for their constant support and encouragement.

References

Arun, Y., Saranraj, K., Balachandran, C. & Perumal, P. T. (2014). *Eur. J. Med. Chem.* **74**, 50–64.
Bozdağ-Dündar, O., Verspohl, E. J., Daş-Evcimen, N., Kaup, R. M., Bauer, K., Sarıkaya, M., Evranos, B. & Ertan, R. (2008). *Bioorg. Med. Chem.* **16**, 6747–6751.
Bruker (2001). *SAINT*, *SMART* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{26}H_{19}BrN_4O_2S$
M_r	531.42
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	293
a, *b*, *c* (Å)	25.289 (5), 10.076 (2), 19.050 (4)
β (°)	98.89 (3)
V (Å^3)	4795.9 (17)
Z	8
Radiation type	Mo *K*α
μ (mm^{-1})	1.83
Crystal size (mm)	0.24 × 0.22 × 0.19
Data collection	
Diffractometer	Bruker SMART APEX CCD area-detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2001)
T_{min}, T_{max}	0.517, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	40628, 4218, 3656
R_{int}	0.038
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.045, 0.121, 1.05
No. of reflections	4218
No. of parameters	310
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.89, −0.63

Computer programs: *SMART* and *SAINT* (Bruker, 2001), *SHELXS2014* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009).

Campeau, L. C., Bertrand-Laperle, M., Leclerc, J. P., Villemure, E., Gorelsky, S. & Fagnou, K. (2008). *J. Am. Chem. Soc.* **130**, 3276–3277.
He, W., Myers, M. R., Hanney, B., Spada, A. P., Bilder, G., Galzcinski, H., Amin, D., Needle, S., Page, K., Jayyosi, Z. & Perrone, M. H. (2003). *Bioorg. Med. Chem. Lett.* **13**, 3097–3100.
Knox, C., Law, V., Jewison, T., Liu, P., Ly, S., Frolkis, A., Pon, A., Banco, K., Mak, C., Neveu, V., Djoumbou, Y., Eisner, R., Guo, A. C. & Wishart, D. S. (2011). *Nucleic Acids Res.* **39**, D1035–D1041.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Muralikrishnan, S., Raveendrareddy, P., Ravindranath, L. K., Harikrishna, S. & Jagadeeswara, R. P. (2013). *Der Pharm. Chem.* **5**, 87–93.
Muthuselvi, C., Muthu, M., Athimoolam, S., Ravikumar, B., Pandiarajan, S. & Krishnakumar, R. V. (2017). *IUCrData*, **2**, x171305.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Swarnkar, P. K., Kriplani, P., Gupta, G. N. & Ojha, K. G. (2007). *E-J. Chem.* **4**, 14–20.
Verma, A. & Saraf, S. K. (2008). *Eur. J. Med. Chem.* **43**, 897–905.
Wermuth, C. G. (2003). In *The Practice of Medicinal Chemistry*. San Diego: Elsevier Academic Press.
Zheng, Y., Tice, C. M. & Singh, S. B. (2014). *Bioorg. Med. Chem. Lett.* **24**, 3673–3682.

full crystallographic data

IUCrData (2018). **3**, x180238 [https://doi.org/10.1107/S2414314618002389]

6′-(3-Bromophenyl)-7′-nitro-1′,6′,7′,7a′-tetrahydro-3′*H*-spiro[indeno[1,2-*b*]quinoxaline-11,5′-pyrrolo[1,2-*c*]thiazole]

C. Muthuselvi, M. Muthu, S. Athimoolam, B. Ravikumar, S. Pandiarajan and R. V. Krishnakumar

6′-(3-bromophenyl)-7′-nitro-1′,6′,7′,7a′-tetrahydro-3′H-spiro [indeno[1,2-b]quinoxaline-11,5′-pyrrolo[1,2-c]thiazole]

Crystal data

$C_{26}H_{19}BrN_4O_2S$
M_r = 531.42
Monoclinic, $C2/c$
a = 25.289 (5) Å
b = 10.076 (2) Å
c = 19.050 (4) Å
β = 98.89 (3)°
V = 4795.9 (17) Å^3
Z = 8
$F(000)$ = 2160
D_x = 1.472 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3142 reflections
θ = 2.2–24.8°
μ = 1.83 mm^{-1}
T = 293 K
Block, colourless
0.24 × 0.22 × 0.19 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2001)
T_{min} = 0.517, T_{max} = 0.746
40628 measured reflections
4218 independent reflections
3656 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 25.0°, θ_{min} = 2.2°
h = −30→30
k = −11→11
l = −22→22

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.121
S = 1.05
4218 reflections
310 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 11.8643P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.89 e Å^{-3}
$\Delta\rho_{min}$ = −0.63 e Å^{-3}

Special details

Experimental. The following wavelength and cell were deduced by SADABS from the direction cosines etc. They are given here for emergency use only: CELL 0.71090 25.300 10.059 19.058 90.049 98.844 90.017

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Br1	0.60837 (2)	0.10535 (3)	0.38169 (2)	0.06601 (17)	
C1	0.73278 (11)	0.7376 (3)	0.31464 (15)	0.0360 (6)	
C2	0.77113 (13)	0.7504 (4)	0.26843 (18)	0.0489 (8)	
H2	0.8042	0.7090	0.2795	0.059*	
C3	0.75987 (15)	0.8231 (4)	0.20776 (18)	0.0545 (9)	
H3	0.7856	0.8324	0.1781	0.065*	
C4	0.70981 (16)	0.8839 (4)	0.18966 (19)	0.0567 (9)	
H4	0.7025	0.9325	0.1478	0.068*	
C5	0.67163 (14)	0.8730 (3)	0.23261 (18)	0.0477 (8)	
H5	0.6384	0.9132	0.2198	0.057*	
C6	0.68267 (11)	0.8002 (3)	0.29657 (15)	0.0349 (6)	
C7	0.65759 (10)	0.7257 (3)	0.39796 (14)	0.0280 (5)	
C8	0.62255 (10)	0.7015 (3)	0.45497 (13)	0.0280 (5)	
C9	0.66049 (11)	0.6223 (3)	0.50918 (14)	0.0306 (6)	
C10	0.65111 (12)	0.5699 (3)	0.57344 (15)	0.0396 (7)	
H10	0.6191	0.5868	0.5901	0.048*	
C11	0.69021 (13)	0.4922 (4)	0.61218 (17)	0.0494 (8)	
H11	0.6842	0.4560	0.6551	0.059*	
C12	0.73811 (14)	0.4673 (4)	0.58825 (19)	0.0543 (9)	
H12	0.7640	0.4157	0.6155	0.065*	
C13	0.74790 (13)	0.5182 (3)	0.52437 (18)	0.0469 (8)	
H13	0.7800	0.5006	0.5080	0.056*	
C14	0.70894 (11)	0.5965 (3)	0.48491 (15)	0.0332 (6)	
C15	0.70813 (10)	0.6617 (3)	0.41601 (14)	0.0306 (6)	
C16	0.57141 (10)	0.6179 (2)	0.42668 (14)	0.0281 (5)	
H16	0.5603	0.5736	0.4678	0.034*	
C17	0.53081 (11)	0.7270 (3)	0.40397 (16)	0.0357 (6)	
H17	0.5376	0.7659	0.3591	0.043*	
C18	0.58926 (11)	0.3828 (3)	0.39714 (16)	0.0354 (6)	
H18	0.5941	0.3646	0.4456	0.043*	
C19	0.59367 (12)	0.2821 (3)	0.34890 (18)	0.0417 (7)	
C20	0.58702 (14)	0.3057 (4)	0.27749 (19)	0.0542 (9)	
H20	0.5898	0.2369	0.2457	0.065*	
C21	0.57613 (17)	0.4330 (4)	0.25332 (18)	0.0608 (10)	
H21	0.5719	0.4503	0.2048	0.073*	
C22	0.57142 (13)	0.5360 (3)	0.30048 (16)	0.0459 (7)	
H22	0.5641	0.6216	0.2834	0.055*	

C23	0.57758 (10)	0.5114 (3)	0.37270 (14)	0.0309 (6)	
C24	0.54224 (11)	0.8299 (3)	0.46335 (16)	0.0360 (6)	
H24	0.5291	0.9173	0.4460	0.043*	
C25	0.52148 (13)	0.7969 (3)	0.53309 (18)	0.0494 (8)	
H25A	0.5205	0.7016	0.5402	0.059*	
H25B	0.4858	0.8324	0.5327	0.059*	
C26	0.62012 (13)	0.8918 (3)	0.54297 (16)	0.0429 (7)	
H26A	0.6272	0.9849	0.5355	0.052*	
H26B	0.6532	0.8500	0.5647	0.052*	
N1	0.74585 (9)	0.6656 (2)	0.37613 (13)	0.0369 (5)	
N2	0.64390 (9)	0.7938 (2)	0.34013 (12)	0.0332 (5)	
N3	0.60047 (9)	0.8291 (2)	0.47670 (12)	0.0309 (5)	
N4	0.47412 (11)	0.6778 (3)	0.39594 (19)	0.0595 (8)	
O2	0.46398 (11)	0.5783 (4)	0.4257 (2)	0.0885 (10)	
S1	0.56825 (4)	0.87389 (12)	0.60150 (5)	0.0656 (3)	
O1	0.4436 (3)	0.7341 (7)	0.3438 (3)	0.0871 (19)	0.63
O1′	0.4388 (5)	0.7516 (14)	0.3830 (6)	0.0871 (19)	0.37

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0729 (3)	0.0307 (2)	0.0999 (4)	0.01279 (16)	0.0308 (2)	−0.00099 (17)
C1	0.0364 (14)	0.0336 (15)	0.0399 (15)	−0.0029 (12)	0.0125 (12)	−0.0037 (12)
C2	0.0461 (18)	0.054 (2)	0.0518 (19)	−0.0017 (15)	0.0229 (14)	−0.0027 (16)
C3	0.061 (2)	0.058 (2)	0.0514 (19)	−0.0125 (18)	0.0288 (16)	0.0005 (17)
C4	0.076 (2)	0.052 (2)	0.0448 (19)	−0.0111 (18)	0.0203 (17)	0.0126 (15)
C5	0.0533 (19)	0.0428 (18)	0.0481 (18)	−0.0018 (15)	0.0111 (15)	0.0136 (14)
C6	0.0394 (15)	0.0288 (14)	0.0379 (15)	−0.0062 (12)	0.0098 (12)	0.0009 (12)
C7	0.0294 (13)	0.0216 (12)	0.0329 (13)	−0.0010 (10)	0.0051 (10)	−0.0005 (10)
C8	0.0270 (12)	0.0258 (13)	0.0316 (13)	0.0017 (10)	0.0058 (10)	0.0004 (10)
C9	0.0310 (13)	0.0275 (14)	0.0326 (14)	−0.0010 (11)	0.0025 (11)	0.0006 (11)
C10	0.0379 (15)	0.0422 (17)	0.0386 (15)	−0.0029 (13)	0.0054 (12)	0.0058 (13)
C11	0.0531 (19)	0.053 (2)	0.0414 (17)	−0.0022 (16)	0.0037 (14)	0.0171 (15)
C12	0.0491 (19)	0.052 (2)	0.058 (2)	0.0110 (16)	−0.0018 (16)	0.0212 (17)
C13	0.0373 (16)	0.0461 (18)	0.0571 (19)	0.0124 (14)	0.0071 (14)	0.0129 (15)
C14	0.0318 (14)	0.0295 (14)	0.0379 (15)	0.0026 (11)	0.0045 (11)	0.0020 (11)
C15	0.0297 (13)	0.0265 (13)	0.0360 (14)	0.0019 (11)	0.0065 (11)	−0.0023 (11)
C16	0.0298 (13)	0.0237 (13)	0.0307 (13)	0.0000 (10)	0.0044 (10)	0.0023 (10)
C17	0.0291 (14)	0.0316 (15)	0.0451 (16)	0.0025 (11)	0.0015 (11)	−0.0001 (12)
C18	0.0361 (14)	0.0311 (15)	0.0404 (15)	0.0021 (11)	0.0097 (12)	0.0016 (12)
C19	0.0369 (15)	0.0327 (16)	0.0579 (19)	0.0016 (12)	0.0152 (13)	−0.0056 (14)
C20	0.060 (2)	0.050 (2)	0.054 (2)	0.0043 (16)	0.0139 (16)	−0.0216 (16)
C21	0.081 (3)	0.066 (2)	0.0343 (17)	0.009 (2)	0.0065 (17)	−0.0098 (17)
C22	0.0584 (19)	0.0426 (18)	0.0356 (15)	0.0057 (15)	0.0043 (14)	0.0024 (13)
C23	0.0259 (13)	0.0307 (14)	0.0366 (14)	−0.0025 (11)	0.0062 (11)	−0.0029 (11)
C24	0.0321 (14)	0.0270 (14)	0.0487 (17)	0.0054 (11)	0.0062 (12)	−0.0006 (12)
C25	0.0454 (17)	0.0428 (18)	0.066 (2)	0.0001 (14)	0.0292 (16)	−0.0091 (16)
C26	0.0458 (17)	0.0398 (17)	0.0431 (17)	0.0004 (13)	0.0066 (13)	−0.0086 (13)

N1	0.0342 (12)	0.0369 (13)	0.0413 (13)	0.0048 (10)	0.0112 (10)	0.0008 (11)
N2	0.0329 (12)	0.0281 (12)	0.0393 (13)	0.0013 (9)	0.0079 (10)	0.0040 (10)
N3	0.0301 (11)	0.0257 (11)	0.0375 (12)	0.0010 (9)	0.0067 (9)	−0.0030 (9)
N4	0.0336 (15)	0.0543 (19)	0.085 (2)	0.0073 (14)	−0.0081 (15)	−0.0152 (17)
O2	0.0485 (16)	0.099 (3)	0.117 (3)	−0.0275 (16)	0.0089 (16)	0.019 (2)
S1	0.0733 (6)	0.0839 (7)	0.0438 (5)	0.0019 (5)	0.0223 (4)	−0.0113 (5)
O1	0.052 (2)	0.087 (3)	0.107 (5)	0.014 (2)	−0.036 (4)	−0.020 (4)
O1′	0.052 (2)	0.087 (3)	0.107 (5)	0.014 (2)	−0.036 (4)	−0.020 (4)

Geometric parameters (Å, º)

Br1—C19	1.905 (3)	C15—N1	1.309 (4)
C1—N1	1.374 (4)	C16—C23	1.511 (4)
C1—C6	1.410 (4)	C16—C17	1.520 (4)
C1—C2	1.413 (4)	C16—H16	0.9800
C2—C3	1.360 (5)	C17—N4	1.502 (4)
C2—H2	0.9300	C17—C24	1.529 (4)
C3—C4	1.401 (5)	C17—H17	0.9800
C3—H3	0.9300	C18—C19	1.385 (4)
C4—C5	1.363 (5)	C18—C23	1.393 (4)
C4—H4	0.9300	C18—H18	0.9300
C5—C6	1.412 (4)	C19—C20	1.366 (5)
C5—H5	0.9300	C20—C21	1.376 (5)
C6—N2	1.380 (4)	C20—H20	0.9300
C7—N2	1.299 (4)	C21—C22	1.390 (5)
C7—C15	1.425 (4)	C21—H21	0.9300
C7—C8	1.524 (4)	C22—C23	1.383 (4)
C8—N3	1.486 (3)	C22—H22	0.9300
C8—C9	1.523 (4)	C24—N3	1.455 (3)
C8—C16	1.568 (4)	C24—C25	1.539 (4)
C9—C10	1.387 (4)	C24—H24	0.9800
C9—C14	1.399 (4)	C25—S1	1.795 (4)
C10—C11	1.382 (4)	C25—H25A	0.9700
C10—H10	0.9300	C25—H25B	0.9700
C11—C12	1.382 (5)	C26—N3	1.430 (4)
C11—H11	0.9300	C26—S1	1.857 (3)
C12—C13	1.378 (5)	C26—H26A	0.9700
C12—H12	0.9300	C26—H26B	0.9700
C13—C14	1.389 (4)	N4—O1′	1.158 (13)
C13—H13	0.9300	N4—O2	1.199 (4)
C14—C15	1.465 (4)	N4—O1	1.290 (7)
N1—C1—C6	122.2 (2)	N4—C17—C16	112.5 (2)
N1—C1—C2	118.8 (3)	N4—C17—C24	111.6 (2)
C6—C1—C2	119.0 (3)	C16—C17—C24	103.7 (2)
C3—C2—C1	120.3 (3)	N4—C17—H17	109.6
C3—C2—H2	119.8	C16—C17—H17	109.6
C1—C2—H2	119.8	C24—C17—H17	109.6

C2—C3—C4	120.5 (3)	C19—C18—C23	119.6 (3)
C2—C3—H3	119.8	C19—C18—H18	120.2
C4—C3—H3	119.8	C23—C18—H18	120.2
C5—C4—C3	120.9 (3)	C20—C19—C18	121.5 (3)
C5—C4—H4	119.5	C20—C19—Br1	118.5 (2)
C3—C4—H4	119.5	C18—C19—Br1	119.9 (2)
C4—C5—C6	119.7 (3)	C19—C20—C21	118.9 (3)
C4—C5—H5	120.1	C19—C20—H20	120.5
C6—C5—H5	120.1	C21—C20—H20	120.5
N2—C6—C1	121.8 (2)	C20—C21—C22	120.8 (3)
N2—C6—C5	118.6 (3)	C20—C21—H21	119.6
C1—C6—C5	119.6 (3)	C22—C21—H21	119.6
N2—C7—C15	123.7 (2)	C23—C22—C21	120.1 (3)
N2—C7—C8	125.5 (2)	C23—C22—H22	120.0
C15—C7—C8	110.8 (2)	C21—C22—H22	120.0
N3—C8—C9	119.3 (2)	C22—C23—C18	119.0 (3)
N3—C8—C7	110.2 (2)	C22—C23—C16	122.8 (3)
C9—C8—C7	101.1 (2)	C18—C23—C16	118.2 (2)
N3—C8—C16	103.60 (19)	N3—C24—C17	101.3 (2)
C9—C8—C16	110.6 (2)	N3—C24—C25	108.6 (2)
C7—C8—C16	112.4 (2)	C17—C24—C25	116.2 (3)
C10—C9—C14	119.9 (3)	N3—C24—H24	110.1
C10—C9—C8	128.5 (3)	C17—C24—H24	110.1
C14—C9—C8	111.4 (2)	C25—C24—H24	110.1
C11—C10—C9	118.8 (3)	C24—C25—S1	105.0 (2)
C11—C10—H10	120.6	C24—C25—H25A	110.7
C9—C10—H10	120.6	S1—C25—H25A	110.7
C12—C11—C10	121.2 (3)	C24—C25—H25B	110.7
C12—C11—H11	119.4	S1—C25—H25B	110.7
C10—C11—H11	119.4	H25A—C25—H25B	108.8
C13—C12—C11	120.7 (3)	N3—C26—S1	107.8 (2)
C13—C12—H12	119.7	N3—C26—H26A	110.1
C11—C12—H12	119.7	S1—C26—H26A	110.1
C12—C13—C14	118.7 (3)	N3—C26—H26B	110.1
C12—C13—H13	120.7	S1—C26—H26B	110.1
C14—C13—H13	120.7	H26A—C26—H26B	108.5
C13—C14—C9	120.7 (3)	C15—N1—C1	114.2 (2)
C13—C14—C15	130.5 (3)	C7—N2—C6	114.4 (2)
C9—C14—C15	108.7 (2)	C26—N3—C24	110.8 (2)
N1—C15—C7	123.6 (2)	C26—N3—C8	122.2 (2)
N1—C15—C14	128.5 (2)	C24—N3—C8	111.7 (2)
C7—C15—C14	107.9 (2)	O1′—N4—O2	115.1 (8)
C23—C16—C17	117.1 (2)	O2—N4—O1	125.8 (4)
C23—C16—C8	116.7 (2)	O1′—N4—C17	120.1 (8)
C17—C16—C8	101.2 (2)	O2—N4—C17	119.9 (3)
C23—C16—H16	107.0	O1—N4—C17	112.4 (5)
C17—C16—H16	107.0	C25—S1—C26	93.06 (14)
C8—C16—H16	107.0		

N1—C1—C2—C3	−178.8 (3)	C23—C16—C17—C24	−169.2 (2)
C6—C1—C2—C3	0.5 (5)	C8—C16—C17—C24	−41.2 (3)
C1—C2—C3—C4	−1.2 (5)	C23—C18—C19—C20	0.2 (5)
C2—C3—C4—C5	0.7 (6)	C23—C18—C19—Br1	−178.9 (2)
C3—C4—C5—C6	0.5 (5)	C18—C19—C20—C21	0.5 (5)
N1—C1—C6—N2	0.6 (4)	Br1—C19—C20—C21	179.7 (3)
C2—C1—C6—N2	−178.7 (3)	C19—C20—C21—C22	−0.6 (6)
N1—C1—C6—C5	180.0 (3)	C20—C21—C22—C23	−0.1 (6)
C2—C1—C6—C5	0.7 (4)	C21—C22—C23—C18	0.9 (5)
C4—C5—C6—N2	178.2 (3)	C21—C22—C23—C16	−178.2 (3)
C4—C5—C6—C1	−1.2 (5)	C19—C18—C23—C22	−0.9 (4)
N2—C7—C8—N3	−50.7 (3)	C19—C18—C23—C16	178.2 (2)
C15—C7—C8—N3	130.0 (2)	C17—C16—C23—C22	33.0 (4)
N2—C7—C8—C9	−177.8 (3)	C8—C16—C23—C22	−87.1 (3)
C15—C7—C8—C9	2.8 (3)	C17—C16—C23—C18	−146.1 (3)
N2—C7—C8—C16	64.3 (3)	C8—C16—C23—C18	93.8 (3)
C15—C7—C8—C16	−115.1 (2)	N4—C17—C24—N3	162.2 (2)
N3—C8—C9—C10	59.7 (4)	C16—C17—C24—N3	40.8 (3)
C7—C8—C9—C10	−179.4 (3)	N4—C17—C24—C25	44.7 (4)
C16—C8—C9—C10	−60.2 (4)	C16—C17—C24—C25	−76.6 (3)
N3—C8—C9—C14	−124.6 (3)	N3—C24—C25—S1	35.8 (3)
C7—C8—C9—C14	−3.6 (3)	C17—C24—C25—S1	149.1 (2)
C16—C8—C9—C14	115.6 (2)	C7—C15—N1—C1	0.2 (4)
C14—C9—C10—C11	−0.2 (4)	C14—C15—N1—C1	−178.9 (3)
C8—C9—C10—C11	175.2 (3)	C6—C1—N1—C15	−0.6 (4)
C9—C10—C11—C12	0.5 (5)	C2—C1—N1—C15	178.7 (3)
C10—C11—C12—C13	−0.8 (6)	C15—C7—N2—C6	−0.2 (4)
C11—C12—C13—C14	0.8 (5)	C8—C7—N2—C6	−179.5 (2)
C12—C13—C14—C9	−0.5 (5)	C1—C6—N2—C7	−0.2 (4)
C12—C13—C14—C15	−179.4 (3)	C5—C6—N2—C7	−179.6 (3)
C10—C9—C14—C13	0.2 (4)	S1—C26—N3—C24	26.9 (3)
C8—C9—C14—C13	−175.9 (3)	S1—C26—N3—C8	−108.2 (2)
C10—C9—C14—C15	179.3 (3)	C17—C24—N3—C26	−164.5 (2)
C8—C9—C14—C15	3.2 (3)	C25—C24—N3—C26	−41.6 (3)
N2—C7—C15—N1	0.2 (4)	C17—C24—N3—C8	−24.4 (3)
C8—C7—C15—N1	179.6 (2)	C25—C24—N3—C8	98.4 (3)
N2—C7—C15—C14	179.5 (3)	C9—C8—N3—C26	10.6 (4)
C8—C7—C15—C14	−1.2 (3)	C7—C8—N3—C26	−105.6 (3)
C13—C14—C15—N1	−3.1 (5)	C16—C8—N3—C26	134.0 (3)
C9—C14—C15—N1	178.0 (3)	C9—C8—N3—C24	−124.2 (3)
C13—C14—C15—C7	177.8 (3)	C7—C8—N3—C24	119.6 (2)
C9—C14—C15—C7	−1.2 (3)	C16—C8—N3—C24	−0.8 (3)
N3—C8—C16—C23	154.1 (2)	C16—C17—N4—O1′	175.5 (7)
C9—C8—C16—C23	−76.9 (3)	C24—C17—N4—O1′	59.3 (8)
C7—C8—C16—C23	35.2 (3)	C16—C17—N4—O2	21.6 (5)
N3—C8—C16—C17	25.8 (2)	C24—C17—N4—O2	−94.6 (4)
C9—C8—C16—C17	154.8 (2)	C16—C17—N4—O1	−143.6 (4)

C7—C8—C16—C17	−93.1 (2)	C24—C17—N4—O1	100.3 (4)
C23—C16—C17—N4	70.0 (3)	C24—C25—S1—C26	−17.4 (2)
C8—C16—C17—N4	−161.9 (2)	N3—C26—S1—C25	−4.4 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C17—H17···N2	0.98	2.78	3.345 (4)	117
C20—H20···S1^{i}	0.93	2.94	3.775 (4)	151
C26—H26*A*···Br1^{ii}	0.97	3.14	3.725 (3)	120
C26—H26*B*···N1^{iii}	0.97	2.63	3.547 (4)	158
C16—H16···O2^{iv}	0.98	2.69	3.660 (4)	172
C25—H25*A*···O2^{iv}	0.97	2.91	3.867 (5)	170

Symmetry codes: (i) *x*, −*y*+1, *z*−1/2; (ii) *x*, *y*+1, *z*; (iii) −*x*+3/2, −*y*+3/2, −*z*+1; (iv) −*x*+1, −*y*+1, −*z*+1.