

Crystal structure and Hirshfeld surface analysis of 1-(4-bromophenyl)-2-[[5-(pyridin-3-yl)-1,3,4-oxadiazol-2-yl]sulfanyl]ethan-1-one

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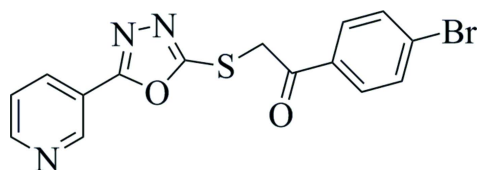
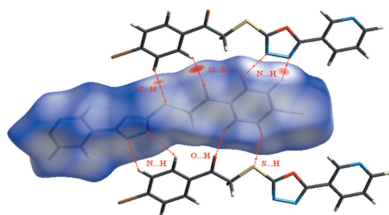
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In the title compound, C₁₅H₁₀BrN₃O₂S, the dihedral angles between the 1,3,4-oxadiazole ring and the 3-pyridinyl and bromobenzene rings are 12.17 (15) and 18.74 (15)°, respectively. In the crystal, the molecules are linked into [100] chains by way of C—H···O, C—H···N, C—H···S hydrogen bonds. The Hirshfeld surface analysis indicates that the most important contributions to the packing are H···H (19.5%), N···H (17.3%), C···H (15.5%), Br···H (11.7%), and O···H (11.0%) interactions.

1. Chemical context

Substituted 1,3,4-oxadiazoles exhibit numerous biological activities such as antibacterial and antifungal (Prakash *et al.*, 2010, Chandrakantha *et al.*, 2010), anticancer (Abu-Zaied *et al.*, 2011), anti-inflammatory, analgesic (Husain *et al.*, 2009, Omar *et al.*, 1996), anticonvulsant and neurotoxic activities (Rajak *et al.*, 2010, Zarghi *et al.*, 2005). Chemical compounds having a 1,3,4-oxadiazole moiety are also important contributors towards the synthesis of biologically active heterocyclic compounds having antibacterial activity against resistant strains (Bharti *et al.*, 2010). As part of our studies in this area, we now describe the synthesis and structure of the title compound (I), a product of the condensation reaction between alcoholic solutions of 5-(3-pyridyl)-1,3,4-oxadiazole-2-thiol and 2,4-dibromoacetophenone in the presence triethyl amine (Kashtoh *et al.*, 2014).



2. Structural commentary

The structure of (I) (Fig. 1) is composed of three near-planar aromatic rings [bromophenyl (A), 3-pyridinyl (B) and 1,3,4-oxadiazol (C)]. The inter-ring dihedral angles are A/B = 6.93 (15), A/C = 18.74 (15) and B/C = 12.17 (15)°. The C7—C8—S2—C9 torsion angle of 172.56 (17)° indicates approx-

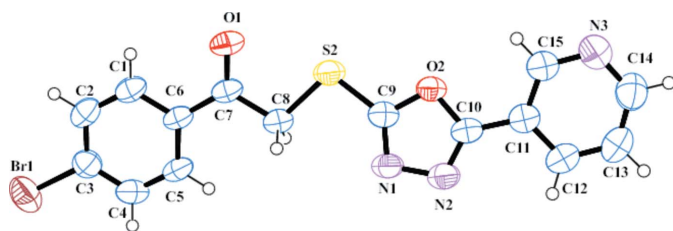


Figure 1
The molecular structure of (I) with displacement ellipsoids drawn at the 30% probability level.

imate coplanarity of these atoms. Otherwise, geometrical data for (I) are similar to those found in structurally related compounds (Xia *et al.*, 2011; Xu *et al.*, 2005).

3. Hydrogen bonding and Hirshfeld surface analysis

The packing of (I) is consolidated by C1—H1B···O1, C1—H2B···S2 and C4—H4A···N2 hydrogen bonds, which form chains running along *a*-axis direction (Fig. 2, Table 1). The Hirshfeld surface analysis (Hirshfeld, 1977) of the crystal structure indicates that the contribution of the H···H intermolecular interactions to the crystal packing amounts to 19.5%, N···H = 17.3%, Br···H = 11.7% and O···H = 11.0%. Minor intermolecular contacts for the cohesion of the structure are: C···O = 4.7%, C···C = 3.6% and others (Br···C, C···S, C···N, Br···S, N···N, Br···N, O···N) = 10.4%. These contacts are represented by conventional mapping of d_{norm} on the molecular Hirshfeld surface, as shown in Fig. 3. The H···H contribution to the crystal packing is shown as a Hirshfeld surface two-dimensional fingerprint plot with red dots (Wolff *et al.*, 2012). The d_e (*y* axis) and d_i (*x* axis) values are the closest external and internal distances (Å) from given points on the Hirshfeld surface (Fig. 4).

4. Comparison with reported literature

A database search disclosed a long list of compounds containing the 1,3,4-oxadiazole moiety; however, only two examples of sulfanylethanone-substituted 1,3,4-oxadiazole

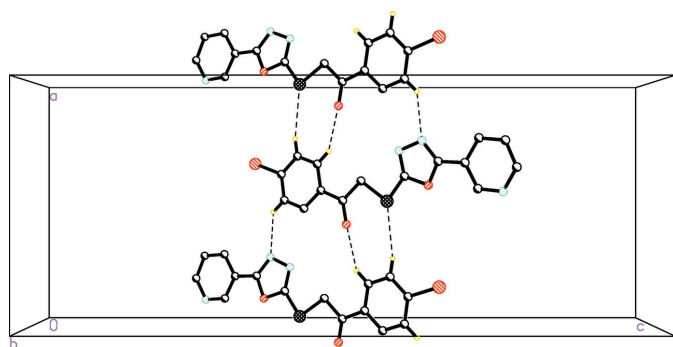


Figure 2
The crystal packing of the title compound (I). Only hydrogen atoms involved in hydrogen bonding (dashed lines) are shown.

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>
C1—H1B···O1 ⁱ	0.93	2.42	3.260 (3)	150
C2—H2B···S2 ⁱ	0.93	2.86	3.716 (3)	153
C4—H4A···N2 ⁱⁱ	0.93	2.58	3.372 (4)	144

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

derivatives were found, *viz.* 1,3-bis[[5-(pyridin-2-yl)-1,3,4-oxadiazol-2-yl]sulfanyl]propan-2-one (II) (Xia *et al.*, 2011) and 2-[5-[(1*H*-1,2,4-triazol-1-yl)-methyl]-1,3,4-oxadiazol-2-ylthio]-1-(2,4-dichlorophenyl)ethanone (III) (Xu *et al.*, 2005). H···N interactions were found to be the most relevant intermolecular interactions to form hydrogen bonds with neighboring molecules. Therefore, *D*—H···N interactions were considered in a comparison with reported structures. In the crystal of (II), the molecules are linked into a three-dimensional network *via* weak C—H···N hydrogen bonds (H···N distances = 2.51 and 2.54 Å). In (III), the C—H···N hydrogen bonds are found to be slightly weaker in comparison with the first structure (H···N distances = 2.41 Å). The change in substituents also changes the packing pattern towards zigzag chains extending along the *b*-axis direction. In addition, both (II) and (III) feature aromatic π — π stacking interactions, which are not observed in (I).

5. Synthesis and crystallization

5-(3-Pyridyl)-1,3,4-oxadiazole-2-thiol (179 mg, 1 mmol) and triethyl amine (0.1 ml) were added in ethanol (10 ml) and stirred for 10 min in a round-bottomed flask. After 10 min, to the reaction mixture was slowly added 2 4-dibromacetophenone (278 mg, 1 mmol). The mixture was refluxed until complete consumption of starting materials, the progress of reaction being monitored by TLC. After 2 h, the precipitate that had formed was separated, washed with ethanol and recrystallized from methanol solution to afford colourless blocks (346 mg, 92% yield).

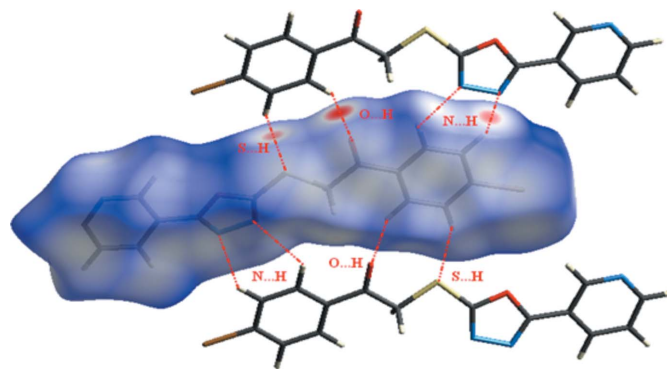


Figure 3
 d_{norm} mapped on the Hirshfeld surface illustrating the intermolecular contacts of the title compound. Dotted lines indicate hydrogen bonds.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were positioned geometrically with C–H = 0.93 Å (CH) or 0.97 Å (CH₂) and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Acknowledgements

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Table 2

Experimental details.

Crystal data	
Chemical formula	C ₁₅ H ₁₀ BrN ₃ O ₂ S
M_r	376.23
Crystal system, space group	Orthorhombic, <i>Pbca</i>
Temperature (K)	273
a, b, c (Å)	11.9144 (16), 8.3755 (12), 30.382 (4)
V (Å ³)	3031.8 (7)
Z	8
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	2.86
Crystal size (mm)	0.47 × 0.39 × 0.11
Data collection	
Diffractometer	Bruker SMART APEX CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2000)
$T_{\text{min}}, T_{\text{max}}$	0.347, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16806, 2765, 2106
R_{int}	0.038
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.606
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.035, 0.114, 1.13
No. of reflections	2765
No. of parameters	199
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.40, -0.25

Computer programs: *SMART* and *SAINT* (Bruker, 2000), *SHELXS97*, *SHELXL97* and *SHELXTL* (Sheldrick, 2008), *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2009).

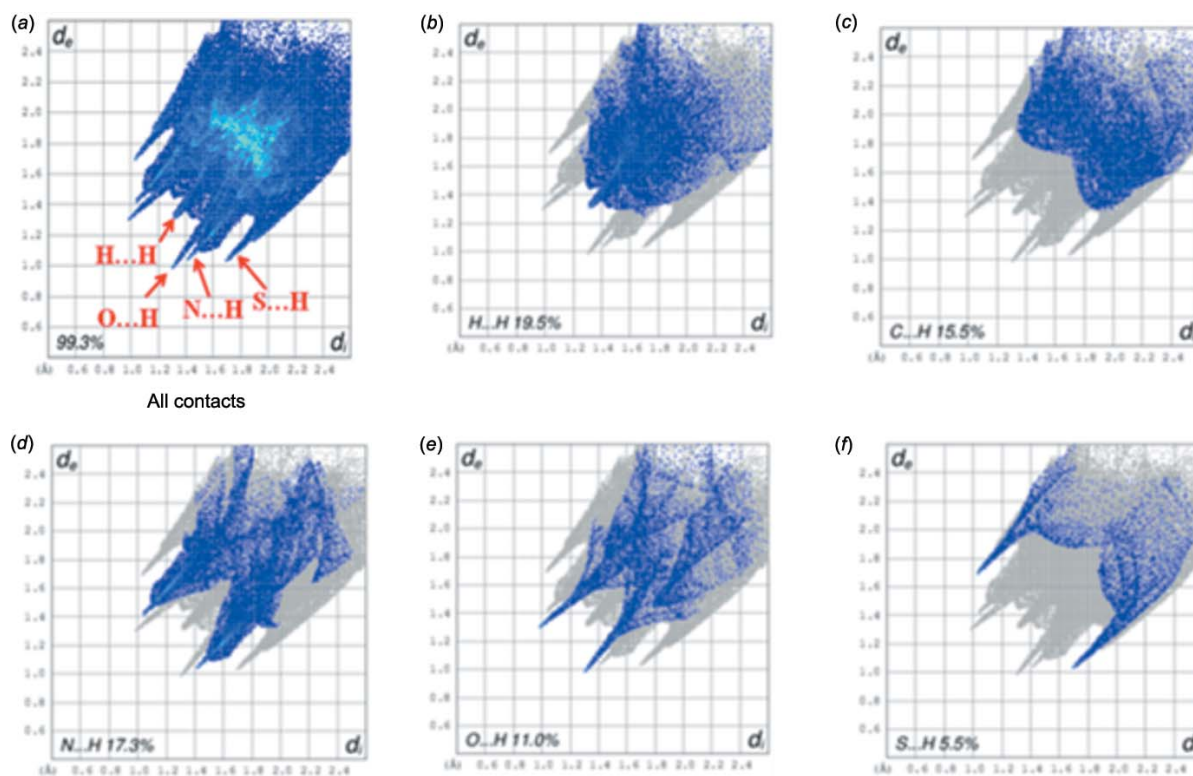


Figure 4

Fingerprint plots of the title compound, for (a) all, (b) H...H, (c) C...H, (d) N...H, (e) O...H and (f) S...H contacts. The outline of the full fingerprint plot is shown in grey. d_i is the closet internal distance from a given point on the Hirshfeld surface and d_e is the closet external contact.

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Huma Bano, Shafqat Hussain, Khalid M. Khan, Shahnaz Perveen and Sammer Yousuf

Computing details

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008), *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2009).

1-(4-Bromophenyl)-2-[[5-(pyridin-3-yl)-1,3,4-oxadiazol-2-yl]sulfanyl]-ethan-1-one

Crystal data

$C_{15}H_{10}BrN_3O_2S$
 $M_r = 376.23$
 Orthorhombic, *Pbca*
 $a = 11.9144$ (16) Å
 $b = 8.3755$ (12) Å
 $c = 30.382$ (4) Å
 $V = 3031.8$ (7) Å³
 $Z = 8$
 $F(000) = 1504$

$D_x = 1.648$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 3887 reflections
 $\theta = 2.7$ – 22.9°
 $\mu = 2.86$ mm⁻¹
 $T = 273$ K
 Block, colorless
 $0.47 \times 0.39 \times 0.11$ mm

Data collection

Bruker SMART APEX CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 ω scan
 Absorption correction: multi-scan
 (SADABS; Bruker, 2000)
 $T_{\min} = 0.347$, $T_{\max} = 0.746$

16806 measured reflections
 2765 independent reflections
 2106 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$
 $\theta_{\max} = 25.5^\circ$, $\theta_{\min} = 1.3^\circ$
 $h = -14 \rightarrow 13$
 $k = -10 \rightarrow 10$
 $l = -36 \rightarrow 36$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.114$
 $S = 1.13$
 2765 reflections
 199 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 atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0639P)^2 + 0.238P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.40$ e Å⁻³
 $\Delta\rho_{\min} = -0.25$ e Å⁻³

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.

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 $F^2 > 2\sigma(F^2)$ 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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.32966 (4)	1.17413 (5)	0.651655 (12)	0.0855 (2)
S2	0.48889 (6)	0.57198 (9)	0.42780 (3)	0.0573 (2)
O1	0.58756 (16)	0.7313 (2)	0.49352 (7)	0.0627 (6)
O2	0.42221 (15)	0.3878 (2)	0.36429 (6)	0.0519 (5)
N1	0.2823 (2)	0.4393 (3)	0.40960 (8)	0.0593 (6)
N2	0.2436 (2)	0.3373 (3)	0.37529 (9)	0.0632 (7)
N3	0.4463 (3)	0.0865 (4)	0.25578 (10)	0.0847 (9)
C1	0.3327 (2)	0.8827 (4)	0.54232 (11)	0.0561 (7)
H1B	0.2798	0.8391	0.5233	0.067*
C2	0.2986 (3)	0.9787 (4)	0.57656 (11)	0.0642 (8)
H2B	0.2227	1.0005	0.5806	0.077*
C3	0.3762 (3)	1.0418 (3)	0.60463 (9)	0.0561 (7)
C4	0.4894 (2)	1.0117 (3)	0.59921 (10)	0.0572 (8)
H4A	0.5416	1.0550	0.6186	0.069*
C5	0.5238 (2)	0.9178 (3)	0.56513 (10)	0.0528 (7)
H5A	0.5999	0.8979	0.5612	0.063*
C6	0.4458 (2)	0.8510 (3)	0.53610 (9)	0.0450 (6)
C7	0.4875 (2)	0.7497 (3)	0.49968 (9)	0.0468 (6)
C8	0.4052 (2)	0.6676 (3)	0.46970 (10)	0.0495 (7)
H8A	0.3543	0.7445	0.4566	0.059*
H8B	0.3617	0.5892	0.4858	0.059*
C9	0.3863 (2)	0.4642 (3)	0.40109 (9)	0.0501 (7)
C10	0.3272 (2)	0.3106 (3)	0.35029 (10)	0.0514 (7)
C11	0.3335 (2)	0.2139 (3)	0.31076 (11)	0.0541 (7)
C12	0.2370 (3)	0.1585 (3)	0.29051 (11)	0.0621 (8)
H12A	0.1665	0.1820	0.3020	0.075*
C13	0.2476 (3)	0.0681 (4)	0.25307 (11)	0.0717 (10)
H13A	0.1842	0.0287	0.2389	0.086*
C14	0.3520 (3)	0.0365 (4)	0.23684 (12)	0.0779 (10)
H14A	0.3575	-0.0232	0.2111	0.093*
C15	0.4355 (3)	0.1747 (4)	0.29175 (12)	0.0702 (9)
H15A	0.5005	0.2127	0.3051	0.084*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.1083 (4)	0.0886 (3)	0.0597 (3)	-0.00727 (19)	0.02208 (18)	-0.00144 (17)
S2	0.0409 (4)	0.0600 (4)	0.0711 (5)	-0.0033 (3)	0.0054 (3)	-0.0031 (4)
O1	0.0357 (14)	0.0716 (13)	0.0808 (15)	0.0013 (10)	-0.0025 (10)	0.0025 (11)
O2	0.0407 (11)	0.0572 (10)	0.0578 (12)	-0.0024 (9)	0.0065 (9)	0.0010 (9)
N1	0.0405 (14)	0.0658 (15)	0.0716 (17)	-0.0039 (11)	0.0083 (12)	-0.0052 (12)
N2	0.0454 (16)	0.0682 (16)	0.0759 (18)	-0.0064 (11)	0.0074 (14)	-0.0062 (13)
N3	0.075 (2)	0.103 (2)	0.076 (2)	0.0034 (17)	0.0039 (16)	-0.0197 (17)
C1	0.0354 (17)	0.0653 (17)	0.068 (2)	-0.0096 (13)	-0.0067 (13)	0.0019 (15)
C2	0.0432 (18)	0.075 (2)	0.074 (2)	-0.0041 (15)	0.0102 (15)	0.0014 (17)
C3	0.059 (2)	0.0566 (16)	0.0527 (17)	-0.0062 (14)	0.0036 (14)	0.0095 (13)
C4	0.055 (2)	0.0570 (17)	0.0592 (19)	-0.0102 (13)	-0.0151 (14)	0.0116 (14)
C5	0.0409 (16)	0.0536 (16)	0.0638 (18)	-0.0013 (12)	-0.0102 (13)	0.0114 (14)
C6	0.0343 (15)	0.0450 (13)	0.0558 (16)	-0.0031 (11)	-0.0059 (12)	0.0128 (12)
C7	0.0350 (18)	0.0455 (14)	0.0600 (17)	-0.0014 (11)	-0.0046 (12)	0.0130 (12)
C8	0.0381 (16)	0.0504 (15)	0.0601 (17)	-0.0002 (11)	0.0001 (12)	0.0039 (12)
C9	0.0451 (18)	0.0450 (14)	0.0600 (18)	0.0018 (12)	0.0039 (13)	0.0057 (13)
C10	0.0409 (18)	0.0515 (16)	0.0619 (19)	-0.0025 (12)	0.0015 (13)	0.0096 (13)
C11	0.053 (2)	0.0515 (15)	0.0580 (18)	0.0001 (12)	-0.0009 (13)	0.0075 (13)
C12	0.053 (2)	0.0605 (18)	0.073 (2)	-0.0053 (14)	-0.0073 (16)	0.0071 (15)
C13	0.074 (3)	0.069 (2)	0.072 (2)	-0.0099 (18)	-0.0188 (18)	-0.0001 (17)
C14	0.085 (3)	0.079 (2)	0.070 (2)	0.002 (2)	-0.010 (2)	-0.0093 (18)
C15	0.055 (2)	0.087 (2)	0.069 (2)	-0.0046 (16)	0.0017 (16)	-0.0092 (17)

Geometric parameters (\AA , $^\circ$)

Br1—C3	1.891 (3)	C4—C5	1.363 (4)
S2—C9	1.722 (3)	C4—H4A	0.9300
S2—C8	1.804 (3)	C5—C6	1.398 (4)
O1—C7	1.217 (3)	C5—H5A	0.9300
O2—C9	1.357 (3)	C6—C7	1.480 (4)
O2—C10	1.372 (3)	C7—C8	1.504 (4)
N1—C9	1.283 (4)	C8—H8A	0.9700
N1—N2	1.424 (3)	C8—H8B	0.9700
N2—C10	1.272 (4)	C10—C11	1.451 (4)
N3—C15	1.326 (4)	C11—C12	1.384 (4)
N3—C14	1.330 (5)	C11—C15	1.385 (4)
C1—C2	1.376 (4)	C12—C13	1.372 (4)
C1—C6	1.387 (4)	C12—H12A	0.9300
C1—H1B	0.9300	C13—C14	1.364 (4)
C2—C3	1.365 (4)	C13—H13A	0.9300
C2—H2B	0.9300	C14—H14A	0.9300
C3—C4	1.382 (4)	C15—H15A	0.9300
C9—S2—C8	99.97 (13)	C7—C8—H8A	110.6
C9—O2—C10	102.6 (2)	S2—C8—H8A	110.6

C9—N1—N2	105.2 (2)	C7—C8—H8B	110.6
C10—N2—N1	106.8 (2)	S2—C8—H8B	110.6
C15—N3—C14	116.7 (3)	H8A—C8—H8B	108.7
C2—C1—C6	120.1 (3)	N1—C9—O2	113.2 (2)
C2—C1—H1B	119.9	N1—C9—S2	132.5 (2)
C6—C1—H1B	119.9	O2—C9—S2	114.32 (19)
C3—C2—C1	119.9 (3)	N2—C10—O2	112.2 (3)
C3—C2—H2B	120.0	N2—C10—C11	129.3 (3)
C1—C2—H2B	120.0	O2—C10—C11	118.5 (2)
C2—C3—C4	121.1 (3)	C12—C11—C15	117.7 (3)
C2—C3—Br1	120.0 (2)	C12—C11—C10	120.8 (3)
C4—C3—Br1	118.9 (2)	C15—C11—C10	121.5 (3)
C5—C4—C3	119.2 (3)	C13—C12—C11	118.5 (3)
C5—C4—H4A	120.4	C13—C12—H12A	120.8
C3—C4—H4A	120.4	C11—C12—H12A	120.8
C4—C5—C6	120.7 (3)	C14—C13—C12	119.4 (3)
C4—C5—H5A	119.6	C14—C13—H13A	120.3
C6—C5—H5A	119.6	C12—C13—H13A	120.3
C1—C6—C5	118.9 (3)	N3—C14—C13	123.6 (4)
C1—C6—C7	122.5 (3)	N3—C14—H14A	118.2
C5—C6—C7	118.6 (2)	C13—C14—H14A	118.2
O1—C7—C6	121.1 (2)	N3—C15—C11	124.1 (3)
O1—C7—C8	119.2 (3)	N3—C15—H15A	117.9
C6—C7—C8	119.7 (2)	C11—C15—H15A	117.9
C7—C8—S2	105.69 (19)		
C9—N1—N2—C10	0.6 (3)	C10—O2—C9—N1	0.1 (3)
C6—C1—C2—C3	-0.5 (5)	C10—O2—C9—S2	178.86 (18)
C1—C2—C3—C4	0.3 (5)	C8—S2—C9—N1	-7.1 (3)
C1—C2—C3—Br1	179.8 (2)	C8—S2—C9—O2	174.34 (19)
C2—C3—C4—C5	0.2 (4)	N1—N2—C10—O2	-0.6 (3)
Br1—C3—C4—C5	-179.3 (2)	N1—N2—C10—C11	179.7 (3)
C3—C4—C5—C6	-0.6 (4)	C9—O2—C10—N2	0.3 (3)
C2—C1—C6—C5	0.1 (4)	C9—O2—C10—C11	-179.9 (2)
C2—C1—C6—C7	-179.5 (3)	N2—C10—C11—C12	12.1 (5)
C4—C5—C6—C1	0.5 (4)	O2—C10—C11—C12	-167.6 (2)
C4—C5—C6—C7	-179.9 (2)	N2—C10—C11—C15	-168.4 (3)
C1—C6—C7—O1	175.7 (3)	O2—C10—C11—C15	11.9 (4)
C5—C6—C7—O1	-3.8 (4)	C15—C11—C12—C13	0.2 (4)
C1—C6—C7—C8	-4.4 (4)	C10—C11—C12—C13	179.7 (3)
C5—C6—C7—C8	176.0 (2)	C11—C12—C13—C14	-0.4 (5)
O1—C7—C8—S2	-4.8 (3)	C15—N3—C14—C13	-1.6 (6)
C6—C7—C8—S2	175.32 (19)	C12—C13—C14—N3	1.2 (6)
C9—S2—C8—C7	172.56 (17)	C14—N3—C15—C11	1.4 (5)
N2—N1—C9—O2	-0.4 (3)	C12—C11—C15—N3	-0.7 (5)
N2—N1—C9—S2	-178.9 (2)	C10—C11—C15—N3	179.8 (3)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C1—H1B \cdots O1 ⁱ	0.93	2.42	3.260 (3)	150
C2—H2B \cdots S2 ⁱ	0.93	2.86	3.716 (3)	153
C4—H4A \cdots N2 ⁱⁱ	0.93	2.58	3.372 (4)	144

Symmetry codes: (i) $x-1/2, -y+3/2, -z+1$; (ii) $x+1/2, -y+3/2, -z+1$.