Crystal structure of 4-bromo-\(N\)-(propylcarbamoyl)benzenesulfonamide

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The title compound, \(\text{C}_{10}\text{H}_{13}\text{BrN}_{2}\text{O}_{3}\text{S}\), \(\text{I}\), contains a sulfonyl urea moiety, which possesses potential therapeutic functions (e.g., anti-diabetic and herbicidal). The geometry of \(\text{I}\) is similar to its closely related analogues, chlorpropamide and tolbutamide. This compound crystallizes in the monoclinic space group \(\text{C}2/c\), having one molecule in its asymmetric unit. The crystal structure of \(\text{I}\), recorded at 296 K, shows intermolecular \(\text{N}—\text{H}—\text{C}1—\text{O}\) and \(\text{C}—\text{H}—\text{C}1—\text{O}\)-type infinite hydrogen-bonded chains involving the sulfonyl urea moiety. Hirshfeld surface analysis and the two-dimensional fingerprint plots confirmed hydrogen bonding as the dominant feature in the crystal packing.

1. Chemical context

The title compound, \(\text{I}\), also known as bromopropamide, is a sulfonyl urea structural analogue, whose chemical structure is shown in the scheme. Compounds containing sulfonyl urea as the structural core have been used extensively for the treatment of Type II diabetes (McLamore et al., 1959), by stimulating insulin secretion from pancreatic \(\beta\)-cells by binding to the ATP-sensitive potassium channel (Proks et al., 2002). Additionally, sulfonyl urea structural analogues have shown therapeutic action as herbicides and diuretic agents (Tanwar et al., 2017). Thus, the title compound was synthesized in order to perform biological characterization. The crystal structures of several sulfonyl urea compounds have been reported, especially molecules closely related to \(\text{I}\) that contain the \(\text{N}\)-carbamoylbenzenesulfonamide substructure, all of which have multiple polymorphic forms (Kimura et al., 1999; Drebushchak et al., 2006; Fedorov et al., 2017). Subtle changes to the molecule have shown drastic effects on its biological activity and also the arrangement of molecules in the crystal structure (Bieszczad et al., 2020). Thus, it is of interest to not only confirm the molecular structure of bromopropamide, but to also identify its crystal packing relative to other structural analogues.
2. Structural commentary

Bromopropamide crystallizes in the centrosymmetric and achiral monoclinic space group $C\overline{2}/c$, having one molecule in the asymmetric unit (Fig. 1). The Br1—C1 bond length [1.887 (2) Å] is in good agreement with other structures containing a bromophenyl moiety (Khamees et al., 2019; Arif Tawfeeq et al., 2019). The bond length between C1—C2 [1.363 (4) Å], is the shortest among all the bond lengths in the phenyl group, possibly due to the inductive effect of bromine. The brominated phenyl ring is almost perpendicular [C4—S1—N1 = 105.65 (11)°] to the sulfonyl urea n-propyl group, resulting in an L-shaped molecular structure. This is similar to chloropropamide, a structural analogue of 1 [Cambridge Structural Database (CSD; Groom et al., 2016) refcode: BEDMIG10; 105.87°; Drebushchak et al., 2009]. The sum of the bond angles around N1 and N2 is 360°, indicating $sp^2$ hybridization, caused by the delocalization of the lone electron pair of N1 and N2 into the π bond of the carbonyl group. This is also supported by the trigonal-planar molecular geometry of C7—N1—S1 [123.94 (17)°], C7—N1—H1 (118°), S1—N1—H1 (118°), C7—N2—C8 [123.5 (2)°], C7—N2—H2 (118.3°), and C8—N2—H2 (118.3°). The C7—N2 bond length is 1.319 (3) Å, which is lower than the typical range; however, the values are similar to those in the crystal structures of bromopropamide analogues, chloropropamide (1.315 Å; CSD refcode: BEDMIG14; Drebushchak et al., 2009) and tolbutamide (1.319 Å; CSD refcode: ZZZPUS13; Drebushchak et al., 2011). The propyl chain takes the stable trans conformation so as to have a maximum distance of 3.794 Å between N2 and C10, while C10 exhibits rotational disorder, possibly due to the X-ray diffraction experiments being conducted at 296 K. Overall, the crystal structure of 1 showcases bond lengths (Allen et al., 1987) and angles typical of the expected ranges.

3. Supramolecular features

The crystal packing of the title compound is dominated by hydrogen bonding, which is shown in Fig. 2. Geometric details of the hydrogen bonds are listed in Table 1. Intermolecular...
N—H···O-type hydrogen bonds link the molecules into infinite chains, which stretch along the b-axis direction (Fig. 2). Hydrogen bonding between the H1 and O3 atoms of neighboring molecules have distances of H1···O3 = 1.94 Å, N1···O3 = 2.791 (3) Å. The strongest of these is N1—H1···O3, with an angle of 171.9°, followed in rank-order of strength by the hydrogen-bonds between H2···O2 = 2.24 Å, N2···O2 = 2.998 (3) Å (angle of 146.8° between N2—H2···O2) and H2···O3 = 2.642 Å, N2···O3 = 3.351 (3) Å (angle of 140.6° between N2—H2···O3). Additionally, weak C—H···O type hydrogen bonds also help, to some extent, with the molecular packing. The intermolecular distance between H10···O1 is 2.61 Å; C10···O1 is 4.028 Å with an angle of 173.7° between C10···H10···O1. The distances and angles of the C—H···O-type hydrogen bond observed in the present structure are within the reported ranges (Desiraju, 1991; Gumireddy et al., 2021). Overall, the atoms involved in hydrogen bonding for bromopropamide are identical to those in the crystal structure for its analogue chloropropamide (CSD refcode: BEDMIG10; Drebushchak et al., 2009). Fig. 3 shows the unit cell of the title compound along the b-axis. It appears that the anti-parallely flanked phenyl rings are stacked. However, a centroid-to-centroid distance of 4.213 (2) Å, which is outside the range of π···π stacking interactions (Chulvi et al., 2015; Ahmed et al., 2019), supports its absence.

4. Hirshfeld surface analysis

Hirshfeld surface analysis was carried out using CrystalExplorer17.5 (Turner et al., 2017; Spackman et al., 2021) mapped over d\text{norm}, which was estimated by the calculations of the external and internal distances to the nearest nucleus and built over a volume of 322.24 Å³ having an area of 304.35 Å², with scaled color of −0.6347 a.u. (red) to 1.2043 a.u. (blue). The Hirshfeld surface of 1, shown in Fig. 4, displays close contacts between N1—H1···O3, N2—H2···O2, N2—H2···O3, and C10—H10C···O1, supporting the conclusions about hydrogen-bonding interactions. Hirshfeld surfaces and their associated two-dimensional fingerprint plots were used to quantify the various intermolecular interactions. The overall two-dimensional fingerprint plot for bromopropamide (Fig. 5a) and those delineated into major contacts: H···H, O···H/H···O, Br···H/H···Br, and C···H/H···C are shown in Fig. 5b–e. The other contacts have lower contributions, with individual contributions <4.3% and a sum <12.8%. The H···H interatomic contacts, which appear as a single spike in the center at d\text{c} = d\text{i} = 1.1 Å (Fig. 5b), generated 39.4% of the Hirshfeld surface, denoting these contacts have a significant effect on the molecular packing. The O···H/H···O interatomic contacts, which appear as a pair of spikes with tips at d\text{c} + d\text{e} ~1.75 Å (Fig. 5c), represent 25.8% of the total surface and confirms the prominent role of multiple hydrogen bonds in the molecular arrangement within the crystal structure. Br···H/H···Br and C···H/H···C contribute 12.2% and 9.8%, respectively, to the Hirshfeld surface. The placement of molecules in the crystal structure of the title compound results in efficient packing, as seen in the Hirshfeld surface analysis, which is further supported by the crystallographic density of

![Figure 4](image-url)

Figure 4
Hirshfeld surface of 4-bromo-N-(propylcarbamoyl)benzenesulfonamide mapped over d\text{norm} displays close contacts in the crystal. The non-covalent interactions indicated by the red spots are labeled.

![Figure 5](image-url)

Figure 5
The two-dimensional fingerprint plots of 4-bromo-N-(propylcarbamoyl)benzenesulfonamide with their relative contribution to the Hirshfeld surface. The units of d\text{c} and d\text{i} are Å.
1.626 g cm$^{-3}$, which is relatively higher than other small molecule organic compounds (Bookwala et al., 2020, 2022).

5. Database survey

A search in the Cambridge Structural Database (Version 5.41, update of March 2020; Groom et al., 2016) for compounds possessing the sulfonyl urea substructure resulted in 178 hits, reinforcing the importance of this scaffold as having potential as an anti-diabetic or diuretic drug, and a herbicide. Of the 178 hits, 82 were distributed among chlorpropamide (deposited structures: 20), tolazamide (deposited structures: 40), and tolbutamide (deposited structures: 22), all of which share a close structural relationship to bromopropamide. The search was then narrowed to identify compounds containing different halogen substitutions. An exact search for the title compound resulted in zero hits, further supporting the previous claim. Thus, X-ray studies were important to identify, if any, changes in the crystal structure by replacing the peripheral Cl with a Br atom.

6. Synthesis and crystallization

The synthesis of 4-bromo-N-(n-propylcarbamoyl)benzenesulfonamide used in situ formation of n-propylisocyanate from n-propylcarbamic chloride with direct capture by 4-bromobenzenesulfonamide in the presence of excess potassium carbonate in refluxing toluene (Fig. 6). This is a new methodology to generate sulfonyl ureas in an atom-efficient manner with identical chemical characterization to prior methods proceeding via carbamate (Marshall & Sigal, 1958) or carbonate (Tanwar et al., 2017) intermediates. A manuscript describing the optimization of this synthetic strategy is in preparation.

n-Propylcarbamic chloride (labeled 2 in Fig. 6): A solution of triphosgene (2.24 g, 22.62 mMol as phosgene) in 25 mL of dichloromethane (DCM) was cooled in a 100 mL round-bottom flask. A solution of triethylamine (TEA) (5.6 mL, 40 mMol), n-propylamine (labeled 1 in Fig. 6) (1.4306 g, 6.06 mMol) and 10 mL of DCM was added to the triphosgene solution with slow dropwise addition over 15 min maintaining an internal temperature between 278 and 283 K. The cooling bath was removed following addition and the reaction was permitted to stir for an additional 2 h at 296 K. The reaction mixture was cooled in an ice/water bath and then transferred to a 125 mL separatory funnel previously cooled in ice–water. The mixture was then washed with 3 × 5 mL portions of ice-cold water, 2 × 5 mL of ice-cold 0.5 N HCl, 2 × 5 mL portions of ice-cold brine, dried Na$_2$SO$_4$, decanted, and the solvent was carefully removed under reduced pressure without heating to theoretical mass. The conversion to n-propylcarbamic chloride was confirmed with IR absorbance of 1734 cm$^{-1}$ and afforded 2.5 g (98% of a light yellow oil) and stored at 253 K until use.

4-Bromobenzenesulfonamide (labeled 4 in Fig. 6): Synthesized using a variation of the published procedure (Anana et al., 2006). Concentrated NH$_2$OH (150 mL, 1.10 mol) was charged into a 500 mL three-neck round-bottom flask equipped with an overhead stirrer, thermowell, and condenser. The reaction was then cooled in an ice/water bath to an internal temperature of 283 K. Solid 4-bromobenzenesulfonfonyl chloride (49.9954 g, 0.1957 mol) was added in portions over 5 min. The ice/water bath was removed and the mixture was stirred at room temperature for 15 min and then brought to 308 K for 30 min. After this, the reaction was warmed to reflux for an additional 30 min. The reaction was followed by thin-layer chromatography (TLC) [$R_t = 0.69$ (labeled 3 in Fig. 6), $R_t = 0.54$ (labeled 4 in Fig. 6) 1/1 hexane/ethyl acetate (H/Ea), short wavelength ultra-violet (SWUV)]. The reaction was cooled to room temperature upon consumption of the starting material and then poured into 200 mL of ice-cold water. This heterogeneous mixture was brought to pH = 1 (pHyrion paper) with 6 N HCl. The precipitated white solid was collected on a filter paper, pressed dry with a rubber dam, and dried 12 h in a drying pistol (P$_2$O$_5$, 150 mTorr, 383 K) to afford 43.03 g (93.5%) of a white solid. Proton identical with literature (Richardson et al., 2007), m.p. 434–438 K (m.p. lit: 435 K).

4-Bromo-N-(n-propylcarbamoyl)benzenesulfonamide (labeled 5 in Fig. 6): n-Propylcarbamic chloride (labeled 2 in Fig. 6), (2.0 g, 15.9 mMol), toluene (15 mL), K$_2$CO$_3$, (2.019 g, 14.6 mMol), and 4-bromobenzenesulfonamide (labeled 4 in Fig. 6), (1.4306 g, 6.06 mMol) were added to a dry 100 mL round-bottom flask fitted with a straight condenser and brought to reflux for 30 min. Upon loss of the sulfonamide (TLC: $R_t = 0.86$, 1/1: H/Ea, SWUV, I$_2$), the heating was stopped, the oil bath was removed, and the reaction was permitted to cool to room temperature. The resulting white suspension was cooled in an ice/water bath and brought to a pH = 1 (pHyrion paper: red) with 6 N HCl. This mixture was extracted with 3 × 10 mL portions of EA, washed [3 × 5 mL 1 N HCl, then 2 × 5 mL NaCl (sat. aq.)], dried MgSO$_4$, filtered under vacuum through #1 Whatman filter paper, and then the solvent was removed under reduced pressure to give 2.2 g of a white solid. This material was purified on a SiO$_2$ column (1/1: H/Ea SiO$_2$, $R_t = 0.66$) then recrystallized from toluene to yield, after drying in a drying pistol at 383 K (P$_2$O$_5$,
treated as riding atoms during refinement, with 
\[ U \]
they were dissolved in methanol to obtain a supersaturated solution (37.5 mg mL\(^{-1}\)). This was placed in a 20 mL scintillation vial, which was covered with Parafilm\(^{\text{R}}\) and punched with 5 pin holes to allow slow evaporation of methanol at room temperature over several days, until larger single crystals appeared.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were positioned geometrically (aromatic C—H = 0.93 Å, amide N—H = 0.86 Å) and treated as riding groups during refinement, with \( U_{eq}(\text{H}) \) = 1.2\( U_{eq}(\text{aromatic C, amide N, and methylene C}) \) or 1.5\( U_{eq}(\text{methyl C}) \). The methyl groups were allowed to rotate about their local threefold axes.

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Computing details
Data collection: SMART and SAINT (Bruker, 1998); cell refinement: SMART and SAINT (Bruker, 1998); data reduction: SMART and SAINT (Bruker, 1998); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015); molecular graphics: CrystalMaker (Palmer, 2014); software used to prepare material for publication: SHELXL2018/3 (Sheldrick, 2015).

4-Bromo-N-(propylcarbamoyl)benzenesulfonamide

Crystal data
C₁₀H₁₃BrN₂O₃S
Mr = 321.19
Monoclinic, C2/c
a = 21.0939 (12) Å
b = 9.2520 (6) Å
c = 15.0283 (10) Å
β = 116.211 (4)°
V = 2631.4 (3) Å³
Z = 8
F(000) = 1296

Data collection
Bruker SMART APEXII
diffractometer
Radiation source: Fine-focus Sealed Tube
φ and ω Scans scans
Absorption correction: multi-scans
(SADABS; Krause et al., 2015)
Tmin = 0.522, Tmax = 0.746
2918 independent reflections
15567 measured reflections

Refinement
Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.036
wR(F²) = 0.095
S = 1.01
2918 reflections
155 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/[σ²(Fo²) + (0.0397P)² + 0.7765P]
where P = (Fo² + 2Fc²)/3
(Δ/σ)max = 0.001
Δρmax = 0.26 e Å⁻³
Δρmin = -0.26 e Å⁻³

Melting point: 411 K
Mo Kα radiation, λ = 0.71073 Å
Cell parameters from 2918 reflections
θmax = 27.2°, θmin = 2.2°
h = -26→27
k = -11→11
l = -19→19

Crystal data
Dₐ = 1.622 Mg m⁻³
2918 independent reflections

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 (Å²)

| Atom | x    | y    | z    | Uiso* Ueq |
|------|------|------|------|-----------|
| Br1  | 0.62045 (2) | 0.74137 (4) | 0.56073 (3) | 0.0982 (2) |
| S1   | 0.33290 (3)  | 0.91269 (7)  | 0.18667 (5)  | 0.0519 (2)  |
| O1   | 0.34641 (11) | 1.0325 (2)   | 0.13838 (14) | 0.0677 (5)  |
| N1   | 0.28060 (11) | 0.9785 (2)   | 0.23075 (16) | 0.0525 (6)  |
| H1   | 0.267634     | 1.067206     | 0.217972     | 0.063*      |
| C1   | 0.53543 (14) | 0.7926 (3)   | 0.4505 (2)   | 0.0576 (7)  |
| O2   | 0.30317 (11) | 0.7841 (2)   | 0.13234 (14) | 0.0629 (5)  |
| N2   | 0.22679 (11) | 0.9777 (2)   | 0.33323 (17) | 0.0579 (6)  |
| H2   | 0.223806     | 1.069690     | 0.323849     | 0.069*      |
| C7   | 0.25586 (12) | 0.8997 (3)   | 0.2876 (2)   | 0.0486 (6)  |
| C2   | 0.52538 (15) | 0.9312 (3)   | 0.4162 (2)   | 0.0664 (8)  |
| H2A  | 0.560352     | 1.000298     | 0.446974     | 0.080*      |
| O3   | 0.26161 (11) | 0.76750 (17) | 0.29256 (16) | 0.0612 (5)  |
| C3   | 0.46344 (14) | 0.9687 (3)   | 0.3360 (2)   | 0.0599 (7)  |
| H3   | 0.456463     | 1.062947     | 0.312127     | 0.072*      |
| C4   | 0.41168 (13) | 0.8659 (3)   | 0.29115 (18) | 0.0460 (6)  |
| C5   | 0.42201 (15) | 0.7269 (3)   | 0.3267 (2)   | 0.0608 (8)  |
| H5   | 0.386886     | 0.657922     | 0.296706     | 0.073*      |
| C6   | 0.48436 (15) | 0.6894 (3)   | 0.4068 (2)   | 0.0658 (8)  |
| H6   | 0.491670     | 0.595259     | 0.430921     | 0.079*      |
| C8   | 0.19943 (17) | 0.9163 (4)   | 0.3988 (2)   | 0.0726 (9)  |
| H8A  | 0.215639     | 0.974924     | 0.458349     | 0.087*      |
| H8B  | 0.218898     | 0.820113     | 0.418427     | 0.087*      |
| C9   | 0.12066 (19) | 0.9070 (4)   | 0.3534 (3)   | 0.0960 (12) |
| H9A  | 0.103998     | 0.849364     | 0.293370     | 0.115*      |
| H9B  | 0.100819     | 1.003157     | 0.335194     | 0.115*      |
| C10  | 0.0955 (3)   | 0.8407 (5)   | 0.4230 (4)   | 0.1239 (17) |
| H10A | 0.044787     | 0.836946     | 0.391608     | 0.186*      |
| H10B | 0.111388     | 0.898207     | 0.482141     | 0.186*      |
| H10C | 0.114123     | 0.744633     | 0.439896     | 0.186*      |

Atomic displacement parameters (Å²)

| Atom | U11   | U22   | U33   | U12   | U13   | U23   |
|------|-------|-------|-------|-------|-------|-------|
| Br1  | 0.0584 (2) | 0.1095 (4) | 0.0856 (3) | 0.01372 (19) | −0.00560 (18) | −0.0048 (2) |
| S1   | 0.0493 (4)  | 0.0394 (4)  | 0.0605 (4)  | 0.0027 (3)  | 0.0184 (3)  | 0.0051 (3)  |
| O1   | 0.0721 (13) | 0.0571 (12) | 0.0766 (13) | 0.0052 (10) | 0.0354 (11) | 0.0223 (11) |
| N1   | 0.0505 (12) | 0.0283 (10) | 0.0788 (16) | 0.0045 (10) | 0.0285 (12) | 0.0093 (11) |
| C1   | 0.0395 (14) | 0.070 (2)   | 0.0567 (16) | 0.0047 (14) | 0.0149 (13) | −0.0058 (15) |

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O2  0.0633 (11)  0.0485 (11)  0.0599 (11)  0.0019 (10)  0.0118 (10)  −0.0062 (9)
N2  0.0567 (14)  0.0405 (12)  0.0777 (16)  0.0001 (11)  0.0308 (13)  0.0032 (12)
C7  0.0330 (12)  0.0342 (14)  0.0648 (16)  −0.0019 (11)  0.0091 (12)  0.0005 (13)
C2  0.0507 (16)  0.064 (2)  0.075 (2)  −0.0164 (15)  0.0188 (15)  −0.0123 (17)
O3  0.0663 (13)  0.0297 (10)  0.0885 (14)  −0.0019 (9)  0.0349 (11)  0.0027 (9)
C3  0.0571 (17)  0.0459 (16)  0.0736 (19)  −0.0083 (14)  0.0262 (16)  0.0022 (15)
C4  0.0442 (13)  0.0360 (14)  0.0596 (16)  0.0011 (11)  0.0245 (12)  0.0003 (12)
C5  0.0492 (16)  0.0419 (16)  0.0746 (19)  −0.0030 (13)  0.0122 (14)  0.0007 (14)
C6  0.0560 (17)  0.0503 (16)  0.0736 (19)  0.0099 (15)  0.0125 (15)  0.0091 (16)
C8  0.077 (2)  0.066 (2)  0.077 (2)  0.0027 (18)  0.0361 (18)  0.0017 (18)
C9  0.089 (3)  0.084 (3)  0.133 (3)  0.004 (2)  0.066 (3)  0.025 (2)
C10 0.153 (4)  0.078 (3)  0.201 (5)  0.008 (3)  0.133 (4)  0.013 (3)

Geometric parameters (Å, °)

| Bond          | Length (Å) | Angle (°)  |
|---------------|------------|------------|
| Br1—C1        | 1.887 (3)  | C3—C4     |
| S1—O1         | 1.4207 (19)| C3—H3     | 0.9300 |
| S1—O2         | 1.4225 (19)| C4—C5     | 1.372 (3) |
| S1—N1         | 1.634 (2)  | C5—C6     | 1.379 (4) |
| S1—C4         | 1.763 (3)  | C5—H5     | 0.9300 |
| N1—C7         | 1.388 (3)  | C6—H6     | 0.9300 |
| N1—H1         | 0.8600     | C8—C9     | 1.494 (4) |
| C1—C2         | 1.363 (4)  | C8—H8A    | 0.9700 |
| C1—C6         | 1.371 (4)  | C8—H8B    | 0.9700 |
| N2—C7         | 1.319 (3)  | C9—C10    | 1.498 (5) |
| N2—C8         | 1.460 (4)  | C9—H9A    | 0.9700 |
| N2—H2         | 0.8600     | C9—H9B    | 0.9700 |
| C7—O3         | 1.228 (3)  | C10—H10A  | 0.9600 |
| C2—C3         | 1.374 (4)  | C10—H10B  | 0.9600 |
| C2—H2A        | 0.9300     | C10—H10C  | 0.9600 |
| O1—S1—O2      | 119.76 (13)| C3—C4—S1  | 119.8 (2) |
| O1—S1—N1      | 103.90 (12)| C4—C5—C6  | 120.1 (3) |
| O2—S1—N1      | 109.80 (12)| C4—C5—H5  | 119.9 |
| O1—S1—C4      | 108.87 (12)| C6—C5—H5  | 119.9 |
| O2—S1—C4      | 108.00 (12)| C1—C6—C5  | 119.2 (3) |
| N1—S1—C4      | 105.65 (11)| C1—C6—H6  | 120.4 |
| C7—N1—S1      | 123.94 (17)| C5—C6—H6  | 120.4 |
| C7—N1—H1      | 118.0      | N2—C8—C9  | 113.9 (3) |
| S1—N1—H1      | 118.0      | N2—C8—H8A | 108.8 |
| C2—C1—C6      | 121.1 (3)  | C9—C8—H8A | 108.8 |
| C2—C1—Br1     | 119.8 (2)  | N2—C8—H8B | 108.8 |
| C6—C1—Br1     | 119.1 (2)  | C9—C8—H8B | 108.8 |
| C7—N2—C8      | 123.5 (2)  | H8A—C8—H8B| 107.7 |
| C7—N2—H2      | 118.3      | C8—C9—C10 | 111.7 (3) |
| C8—N2—H2      | 118.3      | C8—C9—H9A | 109.3 |
| O3—C7—N2      | 124.7 (3)  | C10—C9—H9A| 109.3 |
| O3—C7—N1      | 120.4 (3)  | C8—C9—H9B | 109.3 |
Hydrogen-bond geometry (Å, °)

|          | D—H  | H···A | D···A     | D—H···A |
|----------|------|------|----------|---------|
| N1—H1···O3<sup>i</sup> | 0.86 | 1.94 | 2.791 (3) | 172     |
| N2—H2···O2<sup>i</sup> | 0.86 | 2.24 | 2.998 (3) | 147     |
| N2—H2···O3<sup>i</sup> | 0.86 | 2.64 | 3.351 (3) | 141     |

Symmetry code: (i) −x+1/2, y+1/2, −z+1/2.