Crystal structure and Hirshfeld surface analysis of 2-(2-hydroxyphenyl)quinoline-6-sulfonamide

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In the title compound, C₁₅H₁₂N₂O₃S, there are two molecules (A and B) in the asymmetric unit. The attached phenol and quinoline moieties of each molecule are almost coplanar with a dihedral angle of 6.05 (15)° for molecule A and 1.89 (13)° for molecule B. The crystal structure features N—H···O and C—H···O hydrogen bonds, C—H···π interactions and π···π stacking interactions. Hirshfeld surface analysis indicates that the most significant contacts in the crystal packing are C···H/H···C (29.2%), O···H/H···O (28.6%) and H···H (28.5%).

1. Chemical context

Quinolines are well-known heterocyclic compounds and have been used successfully in many pharmacological and medical fields, exhibiting biological properties including anti-cancer, antimalarial, antibacterial, antiasthmatic and anti-hypertensive activities (Chi et al., 2018; Ferreira et al., 2020; Elgawad et al., 2019; Mulakayala et al., 2012; Lavanya et al., 2021; Yadav & Shah, 2021; Shishkina et al., 2018). In addition, quinolines and/or their metal complexes have a wide range of physical and chemical applications. They have been used in fields such as coordination chemistry (Twaróg et al., 2020), metal-organic frameworks (MOFs) (Wu et al., 2015), catalysis (Redshaw & Tang, 2012), textile printing (Hassan et al., 2022), food additives (Al-Shabib et al., 2020), anti-corrosion (Galai et al., 2021), photoluminescence (Twaróg et al., 2020), magnetism (Yu et al., 2019) and non-linear optics (Goel et al., 2018).

We report here the synthesis, structural characterization and Hirshfeld surface analysis of a new quinoline derivative, 2-(2-hydroxyphenyl)quinoline-6-sulfonamide. This compound was prepared in a two-step reaction, viz. reflux and solvothermal (see Synthesis and crystallization section).
2. Structural commentary

The asymmetric unit of title compound (I), illustrated in Fig. 1, contains two crystallographically independent molecules (A and B). The C6A—C7A and C6B—C7B bond lengths of 1.472 (5) and 1.470 (5) Å, respectively, are notably shorter than the normal C—C single bond due to conjugation but are comparable to those observed in related structures (Shrungesh Kumar et al., 2015; Mague et al., 2016).

The hydroxyl group in the ortho-position of each independent molecule in (I) allows the formation of an intramolecular O—H···N hydrogen bond, generating an S(6) ring motif (Fig. 1, Table 1), which stabilize the molecules and also affect the overall molecular conformation. The conformational differences between molecules A and B are highlighted in an overlay diagram shown in Fig. 2a. The two rings of the quinoline system are fused almost coaxially (r.m.s. deviation = 0.004 Å), with a dihedral angle between their planes of 4.0 (2)° for molecule A and 1.49 (17)° for molecule B.

The attached quinoline and phenol moieties are almost coplanar with a dihedral angle of 6.05 (15)° for molecule A and 1.89 (13)° for molecule B (Fig. 2b), indicating a significant electron delocalization within the molecules. The sulfonamide groups are twisted away from the attached quinoline fragment with an C11A—C12A—S1A—N2A torsion angle of 91.8 (4)° for molecule A and C11B—C12B—S1B—N2B torsion angle of −79.9 (3)° for molecule B. The sulfonamide atoms S1A and S1B deviate by 0.228 (1) and 0.054 (1) Å from the planes of the quinoline fragment in molecules A and B respectively.

3. Supramolecular features

In the crystal of (I), the presence of sulfonamide group leads indeed to the formation of strong intermolecular N—H···O hydrogen bonds (Table 1), generating supramolecular hydrogen-bonded layers parallel to the (010) plane (Fig. 3a).

The packing diagram of the title compound viewed down the a axis (Fig. 3b) shows that the layers are stacked perpendicular to the b axis at (0,1/4,0) and (0,3/4,0). These layers are formed by aggregation of R(2)(14) ring motifs (Fig. 3c). In addition, the hydroxyl group of each molecule is involved in a C—H···O hydrogen bond, forming an inversion dimer with an R(2)(16) graph-set motif. The dimers are linked by a further C—H···π interactions are also observed in the crystal packing, forming a chain along the a-axis direction (Fig. 3e).

**Table 1**

| Hydrogen-bond geometry (Å, °) |
|-----------------------------|
| D—H···A | D—H | H···A |
| O1B—H1B···N1B | 0.85 (2) | 1.82 (3) | 2.576 (3) | 146 (4) |
| O1A—H1A···N1A | 0.87 (2) | 1.76 (3) | 2.566 (4) | 153 (6) |
| N2B—H2BA···O2A | 0.87 (5) | 2.20 (5) | 2.878 (4) | 135 (4) |
| N2A—H2AA···O3B | 0.87 (5) | 2.13 (5) | 2.908 (6) | 149 (4) |
| C11B—H15BB···C15B | 0.92 (5) | 2.13 (5) | 2.742 (5) | 123 (4) |
| C13B—H13BB···O2B | 0.95 | 2.37 | 2.928 (6) | 103 |
| C7B—H7BA···C15B | 0.95 | 2.76 | 3.191 (6) | 109 |
| C8B—H8BA···C14B | 0.95 | 2.55 | 3.496 (4) | 176 |
| C14B—H14BA···O1B | 0.95 | 2.59 | 3.515 (4) | 165 |
| C14A—H14A···O1A | 0.95 | 2.48 | 3.419 (5) | 170 |
| C9A—H9A···C8A | 0.95 | 2.62 | 3.333 (3) | 132 |
| C9B—H9B···C8B | 0.95 | 2.77 | 3.333 (5) | 119 |
| C5A—H5A···C6A | 0.95 | 2.91 | 3.470 (5) | 119 |
| C5A—H5A···C6A | 0.95 | 2.89 | 3.566 (4) | 129 |

Symmetry codes: (i) x, y+1/2, z+1/2; (ii) x+1, y, z; (iii) x−1, y, z; (iv) x+1, y−1, z−1; (v) x+1, y, z−1; (vi) x−1, y, z+1; (vii) x+1, y, z−1; (viii) x−1, y+1, z−1; (ix) x+1, y+1, z+1; (x) x−1, y−1, z+1.

The packing diagram of the title compound viewed down the a axis (Fig. 3b) shows that the layers are stacked perpendicular to the b axis at (0,1/4,0) and (0,3/4,0). These layers are formed by aggregation of R(2)(14) ring motifs (Fig. 3c). In addition, the hydroxyl group of each molecule is involved in a C—H···O hydrogen bond, forming an inversion dimer with an R(2)(16) graph-set motif. The dimers are linked by a further C—H···π interactions are also observed in the crystal packing, forming a chain along the a-axis direction (Fig. 3e).
Cohesion of the crystal structure is enhanced by the presence of π–π stacking interactions, the most significant being between the 2-hydroxyphenyl and benzene rings of the quinoline groups of each molecule \[ Cg_2 \cdots Cg_3 \cdots \] (Fig. 4a) for A molecules and \[ Cg_6 \cdots Cg_7 \cdots \] (Fig. 4b) for B molecules where \( Cg_2, Cg_3, Cg_6 \) and \( Cg_7 \) are the centroids of the \( C_1A–C_6A, C_{10A–C15A, C1B–C6B} \) and \( C10B–C15B \) rings, respectively. These result in the formation of a supramolecular ribbon parallel to the \( a \) axis based on the stacked molecules (Fig. 4c).

4. Hirshfeld surface analysis

For further characterization of the intermolecular interactions in (I), we carried out a Hirshfeld surface (HS) analysis (Spackman & Jayatilaka, 2009) using CrystalExplorer (Spackman et al., 2021) and generated the associated two-dimensional fingerprint plots (McKinnon et al., 2007). The HS of (I) mapped over \( d_{	ext{norm}} \) in the range \(-0.5231 \) to \(+1.1263 \) a.u. is illustrated in Fig. 5a using color to indicate contacts that are shorter (red areas), equal to (white areas), or longer than (blue areas) the sum of the van der Waals radii. The dominant interactions between sulfonamide N—H and O atoms can be seen as the bright-red areas marked as 1, 2, 3 and 4. The light-red spots labeled as 5, 6 and 7 are due to C—H/O interactions. The weak C—H···π contacts are indicated by the red ellipse.

The presence of characteristic triangles on the shape-index surface (Fig. 5b) clearly indicate the presence of π–π interactions between neighboring molecules while the curvedness plots (Fig. 5c) show flat surface patches characteristic of planar stacking.

The overall two-dimensional fingerprint plot and those delineated into C···H/H···C, O···H/H···O, H···H, C···C and N···H/H···N contacts are illustrated in Fig. 6 together with their relative contributions to the Hirshfeld surface. The fingerprint plots show that the C···H/H···C contacts (29.2%) actions.
make the largest contribution to the overall packing of the crystal (Table 2, Fig. 7), which are related to the presence of C—H⋯π interactions in the structure of (I) (Fig. 8c–d).

The second most important interactions are O⋯H/H⋯O

contributing by 28.6% to the overall crystal packing (Table 2, Fig. 6), and are related to the presence of N⋯H⋯O and C—H⋯O interactions in the structure of (I) (Fig. 8a,b). In addition, van der Waals interactions (H⋯H) are one of the major (28.5%) interactions in this structure. The presence of weak π⋯π stacking interactions are reflected in the 5.2 and 1.2% contributions from C⋯C and C⋯N/N⋯C contacts to the Hirshfeld surface. Other contacts make a contribution of 3.5% in total and are not discussed in this work.

5. Database survey

A search for 2-hydroxyphenylquinoline in the Cambridge Structural Database (CSD; Version 2021.3.0, last update November 2021; Groom et al., 2016) gave 29 hits, which exhibit structural diversity with interesting properties, such as chemical (Alexandre et al., 2020; Han et al., 2017; Yao et al., 2012; Guo et al., 2006), physical (Zheng et al., 2013; Elbert et al., 2017) and biological (Mulakayala et al., 2012).

6. Synthesis and crystallization

The title compound was prepared by a two-step reaction. First, an ethanol solution (5 mL) of 4-aminobenzensulfonamide (0.33 g, 1.9 mmol) was added dropwise under stirring to an ethanol solution (5 mL) of 2-hydroxybenzaldehyde (0.2 mL, 0.234 g, 1.9 mmol) and refluxed for 2 h. After that, an acetone (0.33 g, 1.9 mmol) was added dropwise under stirring for 1 h. The yellow mixture was then transferred to a 25 mL Teflon-lined stainless-steel autoclave and sealed to heat at 393 K. After reaction for 48 h, the autoclave was cooled down to room temperature. Yellow block-like crystals suitable for X-ray diffraction analysis were obtained, isolated by filtration, washed with water and dried in air. Yield: 0.25 g, 43.44%.

7. Refinement

Crystal data, details of data collection, and results of structure refinement are summarized in Table 3. The hydrogen atoms of the sulfonamide NH2 and hydroxyl groups were localized in a difference-Fourier map and refined with O—H = 0.84 ± 0.01 A, and with Uiso(H) set to 1.5Ueq(O) or 1.2Ueq(N). All other hydrogen atoms were placed in calculated positions with C—H = 0.95 Å and refined using a riding model with fixed isotropic displacement parameters [Uiso(H) = 1.2Ueq(C)].
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Computing details

Data collection: APEX2 (Bruker, 2012); cell refinement: SAINT (Bruker, 2012); data reduction: SAINT (Bruker, 2012); program(s) used to solve structure: SHELXT2018/2 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009) and PLATON (Spek, 2020).

2-(2-Hydroxyphenyl)quinoline-6-sulfonamide

Crystal data

C15H12N2O3S

Mr = 300.33

Monoclinic, $P_2_1/c$

$\alpha = 5.7667 (2)$ Å

$\beta = 28.4129 (7)$ Å

$\gamma = 15.5339 (5)$ Å

$\beta = 91.728 (3)^\circ$

$V = 2544.05 (14)$ Å$^3$

Z = 8

$F(000) = 1248$

$D_x = 1.568$ Mg m$^{-3}$

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

Cell parameters from 81539 reflections

$\theta = 3.4-25.0^\circ$

$\mu = 0.27$ mm$^{-1}$

$T = 100$ K

Block, yellow

0.18 × 0.11 × 0.05 mm

Data collection

Nonius KappaCCD
diffractometer

Radiation source: fine-focus sealed tube

$\omega$ scans

81539 measured reflections

4473 independent reflections

3058 reflections with $I > 2\sigma(I)$

$R_{int} = 0.103$

$\theta_{max} = 25.0^\circ$, $\theta_{min} = 3.4^\circ$

$h = -6\rightarrow6$

$k = -33\rightarrow33$

$l = -18\rightarrow18$

Refinement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.060$

$wR(F^2) = 0.184$

$S = 1.05$

4473 reflections

397 parameters

2 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_c^2) + (0.1002P)^2 + 1.3957P]$

where $P = (F_c^2 + 2F_s^2)/3$

$(\Delta\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.36$ e Å$^{-3}$

$\Delta\rho_{min} = -0.58$ 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.

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

| Atom | x   | y   | z   | Uiso* / Ueq |
|------|-----|-----|-----|-------------|
| S1B  | 0.43707 (17) | 0.26762 (3) | 0.54873 (6) | 0.0427 (3) |
| S1A  | 0.0621 (2) | 0.22144 (3) | 0.29850 (7) | 0.0542 (4) |
| O1B  | 0.8560 (4) | 0.54324 (8) | 0.56908 (17) | 0.0415 (6) |
| H1B  | 0.793 (7) | 0.5165 (9) | 0.559 (3) | 0.062* |
| O2B  | 0.5936 (4) | 0.25170 (9) | 0.48546 (17) | 0.0472 (7) |
| O1A  | 0.3524 (4) | −0.04503 (9) | 0.4612 (2) | 0.0510 (7) |
| O3B  | 0.1941 (5) | 0.26115 (10) | 0.5344 (2) | 0.0608 (9) |
| N1B  | 0.5920 (5) | 0.47193 (9) | 0.59665 (18) | 0.0334 (7) |
| O2A  | 0.3019 (6) | 0.23513 (9) | 0.29823 (19) | 0.0604 (9) |
| O3A  | −0.0705 (6) | 0.22426 (10) | 0.22008 (19) | 0.0656 (9) |
| N1A  | 0.0991 (5) | 0.02087 (10) | 0.39571 (19) | 0.0382 (7) |
| N2B  | 0.5049 (8) | 0.24069 (11) | 0.6371 (2) | 0.0552 (10) |
| H2BA | 0.380 (8) | 0.2476 (17) | 0.664 (3) | 0.066* |
| H2BB | 0.653 (9) | 0.2448 (17) | 0.646 (3) | 0.066* |
| C15B | 0.5513 (6) | 0.42388 (11) | 0.5876 (2) | 0.0320 (8) |
| C7B  | 0.4401 (5) | 0.49941 (11) | 0.6335 (2) | 0.0328 (8) |
| C10B | 0.3518 (6) | 0.40222 (11) | 0.6190 (2) | 0.0316 (8) |
| C11B | 0.3197 (6) | 0.35382 (11) | 0.6058 (2) | 0.0316 (8) |
| H11B | 0.184184 | 0.338807 | 0.625647 | 0.038* |
| C12B | 0.4831 (6) | 0.32827 (12) | 0.5646 (2) | 0.0323 (8) |
| C7A  | −0.0617 (6) | −0.00943 (12) | 0.3720 (2) | 0.0344 (8) |
| C6B  | 0.4950 (6) | 0.54968 (11) | 0.6434 (2) | 0.0318 (8) |
| C1B  | 0.7007 (6) | 0.56924 (12) | 0.6119 (2) | 0.0329 (8) |
| C6A  | −0.0177 (6) | −0.05960 (11) | 0.3894 (2) | 0.0332 (8) |
| C5B  | 0.3413 (6) | 0.57959 (12) | 0.6855 (2) | 0.0349 (8) |
| H5B  | 0.201567 | 0.567044 | 0.706798 | 0.042* |
| C13B | 0.6843 (6) | 0.34967 (12) | 0.5342 (2) | 0.0355 (8) |
| H13B | 0.797853 | 0.331376 | 0.506364 | 0.043* |
| C14B | 0.7158 (6) | 0.39730 (12) | 0.5450 (2) | 0.0339 (8) |
| H14B | 0.849790 | 0.412131 | 0.523458 | 0.041* |
| N2A  | −0.0595 (10) | 0.25402 (12) | 0.3687 (3) | 0.0700 (14) |
| H2AA | 0.030 (9) | 0.258 (2) | 0.416 (3) | 0.084* |
| H2AB | −0.215 (9) | 0.2471 (19) | 0.371 (3) | 0.084* |
| C1A  | 0.1874 (6) | −0.07528 (12) | 0.4322 (2) | 0.0369 (8) |
| C2B  | 0.7453 (6) | 0.61686 (12) | 0.6239 (2) | 0.0381 (8) |
| H2B  | 0.884080 | 0.629988 | 0.602850 | 0.046* |
| C3B  | 0.5928 (6) | 0.64522 (12) | 0.6654 (2) | 0.0397 (9) |
| H3B  | 0.626395 | 0.677708 | 0.673074 | 0.048* |
| C15A | 0.0715 (6) | 0.06803 (12) | 0.3764 (2) | 0.0402 (9) |
| Atomic displacement parameters (Å²) | \( U^{11} \) | \( U^{22} \) | \( U^{33} \) | \( U^{12} \) | \( U^{13} \) | \( U^{23} \) |
|-----------------------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| S1B                               | 0.0467 (6)  | 0.0297 (5)  | 0.0529 (6)  | −0.0118 (4) | 0.0204 (4)  | −0.0139 (4) |
| S1A                               | 0.0887 (9)  | 0.0228 (5)  | 0.0533 (7)  | −0.0071 (5) | 0.0400 (6)  | 0.0043 (4)  |
| O1B                               | 0.0353 (13) | 0.0271 (13) | 0.0627 (17) | −0.0064 (11)| 0.0140 (12) | −0.0010 (12)|
| O2B                               | 0.0527 (16) | 0.0352 (15) | 0.0547 (17) | −0.0069 (12)| 0.0198 (13) | −0.0160 (12)|
| O1A                               | 0.0411 (15) | 0.0271 (14) | 0.084 (2)   | −0.0025 (12)| −0.0145 (14)| 0.0052 (13) |
| O3B                               | 0.0464 (17) | 0.0471 (17) | 0.090 (2)   | −0.0215 (13)| 0.0276 (15) | −0.0315 (15)|
| N1B                               | 0.0345 (15) | 0.0240 (15) | 0.0421 (17) | −0.0030 (12)| 0.0061 (13) | 0.0014 (12) |
| O2A                               | 0.092 (2)   | 0.0278 (14) | 0.0642 (19) | −0.0076 (14)| 0.0472 (17) | −0.0009 (12)|
| O3A                               | 0.103 (2)   | 0.0396 (17) | 0.0556 (19) | 0.0231 (16) | 0.0297 (17) | 0.0169 (13) |
| N1A                               | 0.0396 (17) | 0.0273 (16) | 0.0475 (18) | −0.0027 (13)| −0.0012 (13)| 0.0015 (13) |
| N2B                               | 0.079 (3)   | 0.0261 (17) | 0.062 (2)   | −0.0065 (18)| 0.033 (2)   | −0.0044 (15)|
| C15B                              | 0.0348 (18) | 0.0239 (17) | 0.0372 (19) | −0.0069 (14)| 0.0014 (15) | −0.0002 (14)|
| C7B                               | 0.0320 (18) | 0.0282 (18) | 0.039 (2)   | −0.0035 (14)| 0.0089 (15) | 0.0015 (15) |
| C10B                              | 0.0305 (18) | 0.0278 (18) | 0.0371 (19) | −0.0003 (14)| 0.0072 (15) | −0.0017 (14)|
| C11B                              | 0.0317 (18) | 0.0296 (18) | 0.0339 (18) | −0.0100 (14)| 0.0048 (14) | 0.0000 (14) |
| C12B                              | 0.0367 (19) | 0.0264 (18) | 0.0340 (18) | −0.0050 (14)| 0.0077 (15) | −0.0045 (14)|
| C7A                               | 0.0365 (19) | 0.0290 (19) | 0.037 (2)   | −0.0016 (15)| −0.0010 (15)| 0.0036 (15) |
Geometric parameters (Å, º)

|     | S1B—O2B | 1.428 (2) | C5B—C4B | 1.371 (5) |
|-----|----------|-----------|----------|-----------|
|     | S1B—O3B | 1.424 (3) | C13B—H13B | 0.9500 |
|     | S1B—N2B | 1.610 (4) | C13B—C14B | 1.375 (5) |
|     | S1B—C12B | 1.760 (3) | C14B—H14B | 0.9500 |
|     | S1A—O2A | 1.437 (3) | N2A—H2AA | 0.89 (5) |
|     | S1A—O3A | 1.421 (4) | N2A—H2AB | 0.92 (5) |
|     | S1A—N2A | 1.607 (4) | C1A—C2A | 1.390 (5) |
|     | S1A—C12A | 1.764 (4) | C2B—H2B | 0.9500 |
|     | O1B—H1B | 0.854 (19) | C2B—C3B | 1.369 (5) |
|     | O1B—C1B | 1.351 (4) | C3B—H3B | 0.9500 |
|     | O1A—C1A | 1.350 (4) | C3B—C4B | 1.390 (5) |
|     | O1A—H1A | 0.87 (2) | C15A—C14A | 1.387 (5) |
|     | N1B—C15B | 1.392 (4) | C15A—C10A | 1.393 (5) |
|     | N1B—C7B | 1.317 (4) | C4B—H4B | 0.9500 |
|     | N1A—C7A | 1.310 (4) | C3A—H3A | 0.9500 |
|     | N1A—C15A | 1.381 (4) | C3A—C2A | 1.373 (5) |
|     | N2B—H2BA | 0.87 (5) | C3A—C4A | 1.392 (5) |
|     | N2B—H2BB | 0.87 (5) | C5A—H5A | 0.9500 |
|     | C15B—C10B | 1.405 (4) | C5A—C4A | 1.372 (5) |
|     | C15B—C14B | 1.394 (5) | C12A—C13A | 1.398 (5) |
| Bond                  | Length (Å) | Bond                  | Length (Å) | Bond                  | Length (Å) |
|----------------------|------------|----------------------|------------|----------------------|------------|
| C7B—C6B              | 1.470 (5)  | C12A—C11A            | 1.367 (5)  |
| C7B—C8B              | 1.398 (6)  | C14A—H14A            | 0.9500     |
| C10B—C11B            | 1.401 (5)  | C14A—C13A            | 1.368 (5)  |
| C10B—C9B             | 1.369 (6)  | C2A—H2A              | 0.9500     |
| C11B—H11B            | 0.9500     | C13A—H13A            | 0.9500     |
| C11B—C12B            | 1.365 (4)  | C4A—H4A              | 0.9500     |
| C12B—C13B            | 1.404 (4)  | C11A—H11A            | 0.9500     |
| C7A—C6A              | 1.472 (5)  | C11A—C10A            | 1.411 (5)  |
| C7A—C8A              | 1.380 (6)  | C10A—C9A             | 1.359 (6)  |
| C6B—C1B              | 1.411 (5)  | C8B—H8B              | 0.9500     |
| C6B—C5B              | 1.403 (5)  | C8B—C9B              | 1.385 (7)  |
| C1B—C2B              | 1.389 (5)  | C9B—H9B              | 0.9500     |
| C6A—C1A              | 1.411 (5)  | C8A—H8A              | 0.9500     |
| C6A—C5A              | 1.394 (5)  | C8A—C9A              | 1.392 (7)  |
| C5B—H5B              | 0.9500     | C9A—H9A              | 0.9500     |
| O2B—S1B—N2B          | 107.10 (19)| S1A—N2A—H2AB         | 110 (3)    |
| O2B—S1B—C12B         | 108.09 (15)| H2AA—N2A—H2AB        | 122 (5)    |
| O3B—S1B—O2B          | 119.39 (17)| O1A—C1A—C6A          | 121.9 (3)  |
| O3B—S1B—N2B          | 106.6 (2)  | O1A—C1A—C2A          | 118.0 (3)  |
| O3B—S1B—C12B         | 106.96 (16)| C2A—C1A—C6A          | 120.0 (3)  |
| N2B—S1B—C12B         | 108.33 (17)| C1B—C2B—H2B          | 119.4      |
| O2A—S1A—N2A          | 106.6 (2)  | C3B—C2B—C1B          | 121.2 (3)  |
| O2A—S1A—C12A         | 106.65 (18)| C3B—C2B—H2B          | 119.4      |
| O3A—S1A—O2A          | 118.37 (18)| C2B—C3B—H3B          | 120.0      |
| O3A—S1A—N2A          | 108.3 (2)  | C2B—C3B—C4B          | 120.1 (3)  |
| O3A—S1A—C12A         | 107.01 (19)| C4B—C3B—H3B          | 120.0      |
| N2A—S1A—C12A         | 109.67 (18)| N1A—C15A—C14A        | 117.0 (3)  |
| C1B—O1B—H1B          | 107 (3)    | N1A—C15A—C10A        | 123.3 (3)  |
| C1A—O1A—H1A          | 105 (4)    | C14A—C15A—C10A       | 119.7 (3)  |
| C7B—N1B—C15B         | 120.9 (3)  | C5B—C4B—C3B          | 119.7 (3)  |
| C7A—N1A—C15A         | 120.0 (3)  | C5B—C4B—H4B          | 120.1      |
| S1B—N2B—H2BA         | 97 (3)     | C3B—C4B—H4B          | 120.1      |
| S1B—N2B—H2BB         | 106 (3)    | C2A—C3A—H3A          | 120.2      |
| H2BA—N2B—H2BB        | 136 (4)    | C2A—C3A—C4A          | 119.5 (3)  |
| N1B—C15B—C10B        | 122.1 (3)  | C4A—C3A—H3A          | 120.2      |
| N1B—C15B—C14B        | 117.7 (3)  | C6A—C5A—H5A          | 119.1      |
| C14B—C15B—C10B       | 120.2 (3)  | C4A—C5A—C6A          | 121.7 (4)  |
| N1B—C7B—C6B          | 118.5 (3)  | C4A—C5A—H5A          | 119.1      |
| N1B—C7B—C8B          | 119.3 (3)  | C13A—C12A—S1A        | 118.7 (3)  |
| C8B—C7B—C6B          | 122.1 (3)  | C11A—C12A—S1A        | 119.9 (3)  |
| C11B—C10B—C15B       | 119.0 (3)  | C11A—C12A—C13A       | 121.4 (3)  |
| C9B—C10B—C15B        | 115.4 (3)  | C15A—C14A—H14A       | 119.6      |
| C9B—C10B—C11B        | 125.5 (3)  | C13A—C14A—C15A       | 120.8 (4)  |
| C10B—C11B—H11B       | 120.0      | C13A—C14A—H14A       | 119.6      |
| C12B—C11B—C10B       | 120.0 (3)  | C1A—C2A—H2A          | 119.5      |
| C12B—C11B—H11B       | 120.0      | C3A—C2A—C1A          | 120.9 (3)  |
| C11B—C12B—S1B        | 118.9 (2)  | C3A—C2A—H2A          | 119.5      |
C11B—C12B—C13B 121.1 (3) C12A—C13A—H13A 120.4
C13B—C12B—S1B 120.0 (2) C14A—C13A—C12A 119.3 (3)
N1A—C7A—C6A 117.9 (3) C14A—C13A—H13A 120.4
N1A—C7A—C8A 119.3 (4) C3A—C4A—H4A 120.0
C8A—C7A—C6A 122.7 (4) C5A—C4A—C3A 120.0 (3)
C1B—C6B—C7B 121.8 (3) C5A—C4A—H4A 120.0
C5B—C6B—C7B 120.0 (3) C12A—C11A—H11A 120.5
C5B—C6B—C1B 118.2 (3) C12A—C11A—C10A 119.0 (4)
O1B—C1B—C6B 122.1 (3) C10A—C11A—H11A 120.5
O1B—C1B—C2B 118.4 (3) C15A—C10A—C11A 119.6 (4)
C2B—C1B—C6B 119.4 (3) C9A—C10A—C15A 115.4 (4)
C1A—C6A—C7A 122.0 (3) C9A—C10A—C11A 125.0 (4)
C5A—C6A—C7A 120.3 (3) C7B—C8B—H8B 120.1
C5A—C6A—C1A 117.7 (3) C9B—C8B—C7B 119.8 (4)
C6B—C5B—H5B 119.3 C9B—C8B—H8B 120.1
C4B—C5B—C6B 121.4 (3) C10B—C9B—C8B 122.5 (4)
C4B—C5B—H5B 119.3 C10B—C9B—H9B 118.8
C12B—C13B—H13B 120.3 C8B—C9B—H9B 118.8
C14B—C13B—C12B 119.5 (3) C7A—C8A—H8A 119.6
C14B—C13B—H13B 120.3 C7A—C8A—C9A 120.8 (5)
C15B—C14B—H14B 119.9 C9A—C8A—H8A 119.6
C13B—C14B—C15B 120.1 (3) C10A—C9A—C8A 121.1 (5)
C13B—C14B—H14B 119.9 C10A—C9A—H9A 119.5
S1A—N2A—H2AA 112 (4) C8A—C9A—H9A 119.5
S1B—C12B—C13B—C14B 178.4 (3) C7A—N1A—C15A—C14A 179.1 (3)
S1A—C12A—C13A—C14A −175.7 (3) C7A—N1A—C15A—C10A −1.9 (5)
S1A—C12A—C11A—C10A 176.4 (3) C7A—C6A—C1A—O1A 1.4 (5)
O1B—C1B—C2B—C3B 178.9 (3) C7A—C6A—C1A—C2A −178.9 (3)
O2B—S1B—C12B—C11B 164.4 (3) C7A—C6A—C5A—C4A −179.9 (3)
O2B—S1B—C12B—C13B −15.0 (3) C7A—C8A—C9A 2.4 (8)
O1A—C1A—C2A—C3A 178.5 (3) C6B—C7B—C8B—C9B −177.9 (4)
O3B—S1B—C12B—C11B 34.7 (3) C6B—C1B—C2B—C3B −0.2 (5)
O3B—S1B—C12B—C13B −144.7 (3) C6B—C5B—C4B—C3B 0.0 (5)
N1B—C15B—C10B—C11B 178.6 (3) C1B—C6B—C5B—C4B −0.3 (5)
N1B—C15B—C10B—C9B 1.4 (5) C1B—C2B—C3B—C4B −0.1 (5)
N1B—C15B—C14B—C13B −180.0 (3) C6A—C7A—C8A—C9A −176.4 (4)
N1B—C7B—C6B—C1B 2.3 (5) C6A—C1A—C2A—C3A −1.2 (5)
N1B—C7B—C6B—C5B −177.4 (3) C6A—C5A—C4A—C3A −1.2 (6)
N1B—C7B—C8B—C9B −1.2 (7) C5B—C6B—C1B—O1B −178.6 (3)
O2A—S1A—C12A—C13A 25.1 (3) C5B—C6B—C1B—C2B 0.4 (5)
O2A—S1A—C12A—C11A −153.1 (3) C14B—C15B—C10B—C11B −0.8 (5)
O3A—S1A—C12A—C13A 152.7 (3) C14B—C15B—C10B—C9B −178.0 (4)
O3A—S1A—C12A—C11A −25.5 (4) N2A—S1A—C12A—C13A −90.0 (4)
N1A—C7A—C6A—C1A 1.7 (5) N2A—S1A—C12A—C11A 91.8 (4)
N1A—C7A—C6A—C5A −177.7 (3) C1A—C6A—C5A—C4A 0.8 (5)
N1A—C7A—C8A—C9A 0.4 (7) C2B—C3B—C4B—C5B 0.2 (5)
N1A—C15A—C14A—C13A 175.2 (3) C15A—N1A—C7A—C6A 176.3 (3)
**Hydrogen-bond geometry (Å, °)**

Cg3, Cg4, Cg5 and Cg6 are the centroids of the C10A–C15A, N1A/C7A–C15A, N1B/C7B–C10B/C15B and C1B–C6B rings, respectively.

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| O1B—H1B···N1B | 0.85 (2) | 1.82 (3) | 2.578 (3) | 146 (4) |
| O1A—H1A···N1A | 0.87 (2) | 1.76 (3) | 2.566 (4) | 153 (6) |
| N2B—H2BA···O2A | 0.87 (5) | 2.20 (5) | 2.878 (4) | 135 (4) |
| N2B—H2BB···O3A | 0.87 (5) | 2.13 (5) | 2.908 (6) | 149 (4) |
| N2A—H2AA···O3B | 0.89 (5) | 2.05 (5) | 2.929 (6) | 171 (5) |
| N2A—H2AB···O2B | 0.92 (5) | 2.13 (5) | 2.742 (5) | 124 (4) |
| C13B—H13B···O2B | 0.95 | 2.57 | 2.928 (4) | 103 |
| C8B—H8B···O1B | 0.95 | 2.76 | 3.191 (6) | 109 |
| C3B—H3B···O2A | 0.95 | 2.55 | 3.496 (4) | 176 |
| C14B—H14B···O1B | 0.95 | 2.59 | 3.515 (4) | 165 |
| C14A—H14A···O1A | 0.95 | 2.48 | 3.419 (5) | 170 |
| C9A—H9A···Cg5 | 0.95 | 2.62 | 3.331 (3) | 132 |
| C9B—H9B···Cg4 | 0.95 | 2.77 | 3.331 (5) | 119 |
| C9B—H9B···Cg3 | 0.95 | 2.91 | 3.470 (5) | 119 |
| C5A—H5A···Cg6 | 0.95 | 2.89 | 3.566 (4) | 129 |

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