Crystal structure and Hirshfeld surface analysis of 5-amino-5′-bromo-2′-oxo-2,3-dihydro-1H-spiroimidazo[1,2-a]pyridine-7,3′-indoline]-6,8-dicarbonitrile dimethyl sulfoxide disolvate

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In the title compound, C_{16}H_{11}BrN_{6}O/C_{12}C_{2}H_{6}OS, the 1,2,3,7-tetrahydroimidazo[1,2-a]pyridine ring system and the oxindole moiety are both nearly planar [maximum deviations = 0.042 (2) and 0.115 (2) Å, respectively] and their planes form a dihedral angle of 86.04 (5)° with each other. Intermolecular N—H⋯O, C—H⋯O and C—H⋯N hydrogen bonds link molecules in the crystal through the O atoms of the solvent molecules, generating a three-dimensional network. A Hirshfeld surface analysis was performed to further analyse the intermolecular interactions.

1. Chemical context

C—C and C—N bond-forming reactions represent a significant synthetic class because they play critical roles in various applications in different fields of chemistry (Yadigarov et al., 2009; Abdelhamid et al., 2011; Yin et al., 2020; Khalilov et al., 2021). Nitrogen heterocycles, particularly those including the spiroimidazo[1,2-a]pyridine moiety, play a key role in medicinal chemistry (Han et al., 2008; Mamedov et al., 2020; Samanov et al., 2021). The conjugate addition to oxindolylidenemalononitriles has been well studied in simple two-component reactions with respect to producing spiro derivatives (Lu et al., 2012; Jun et al., 2019). We have previously reported the three-component reaction of 2-(2-oxoindolin-3-ylidene)malononitrile with malononitrile and ethylenediamine which resulted in 5-amino-2′-oxo-2,3-dihydro-1H-spiroimidazo[1,2-a]pyridine-7,3′-indoline]-6,8-dicarbonitrile (Magerramov et al., 2018). In the framework of our ongoing structural studies (Naghiyev et al., 2020, 2021a,b), herein the crystal structure and Hirshfeld surface analysis of 5-amino-5′-bromo-2′-oxo-2,3-dihydro-1H-spiroimidazo[1,2-a]pyridine-7,3′-indoline]-6,8-dicarbonitrile, (1), is reported.

2. Structural commentary

In the title compound, (1) (see Scheme and Fig. 1), the 1,2,3,7-tetrahydroimidazo[1,2-a]pyridine ring system (N1/N4/C2/C3/C5–C8/C8′A) and the oxindole moiety (O1/N2/C7/C17–C16) are nearly planar, with maximum deviations of
0.042 (2) Å for C3 and 0.115 (2) Å for O1. These ring systems make a dihedral angle of 86.04 (5)° with each other. The cyano (–C≡N) and amine (NH2) groups form an intermolecular hydrogen bond with one dimethyl sulfoxide (DMSO) group, giving an S(10) motif (Bernstein et al., 1995) (Table 1).

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

| D—H···A | D—H | H···A | D···A | D—H···A |
|----------|------|-------|-------|--------|
| N1—H1···O2A1 | 0.90 | 1.98  | 2.855 (4) | 165 |
| N1—H1···O2B1 | 0.90 | 2.00  | 2.87 (4) | 160 |
| N2—H2···O2A2 | 0.90 | 1.91  | 2.793 (5) | 166 |
| N2—H2···O2B1 | 0.90 | 1.94  | 2.82 (5) | 166 |
| N5—H5A···O3A2 | 0.90 | 2.20  | 3.034 (3) | 155 |
| N5—H5B···O3A1 | 0.90 | 2.06  | 2.918 (3) | 160 |
| C19A—H19A···N9 | 0.98 | 2.41  | 3.114 (5) | 128 |
| C19A—H19C···O1 | 0.98 | 2.52  | 3.392 (4) | 148 |
| C20A—H20B···O1 | 0.98 | 2.46  | 3.359 (4) | 152 |

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

3. Supramolecular features and Hirshfeld surface analysis

In the crystal, molecules are linked through the O atoms of the DMSO solvent molecules by intermolecular N—H···O and C—H···O hydrogen bonds which, together with C—H···N hydrogen bonds, form a three-dimensional (3D) network (Table 1 and Fig. 2). The π-cloud of the C8A—N1 bond (which has some multiple-bond character) acts as an electron donor to Br1 in a kind of ‘halogen bond’, with a Br1···C8A(–x+1, –y+1, –z) distance of 3.284 (2) Å.

The Hirshfeld surfaces were calculated and the two-dimensional (2D) fingerprint plots generated using Crystal-Explorer (Version 17.5; Turner et al., 2017). Fig. 3 shows the 3D Hirshfeld surface of (1) with dnorm in the range from 0.6206 to 1.3180 a.u. The interactions given in Table 1 play a key role in the molecular packing of (1).

The overall 2D fingerprint plot for (1) is given in Fig. 4(a), and those delineated into H···H, N···H/H···N, O···H/H···O, C···H/H···C and Br···H/H···Br contacts are shown in Figs. 4(b)–(f). The percentage contributions to the Hirshfeld surfaces from the various interatomic contacts are as follows: H···H [Fig. 4(b); 27.1%], N···H/H···N [Fig. 4(e); 23.8%], O···H/H···O [Fig. 4(d); 15.7%], C···H/H···C [Fig. 4(e); 13.2%] and Br···H/H···Br [Fig. 4(f); 10.2%]. Other minor contributions to the Hirshfeld surface are from Br···C/C···Br.
(3.9%), Br··N/N··Br (2.0%), C··C (1.5%), S··C/C··S (0.8%), S··H/H··S (0.6%), S··N/N··S (0.4%), O··N/N··O (0.4%) and Br··O/O··Br (0.3%).

4. Database survey
A search of the Cambridge Structural Database (CSD, Version 5.42, update of September 2021; Groom et al., 2016) for the 5-bromo-1,3-dihydro-2H-indol-2-one unit of (1) gave 87 hits. The three compounds most resembling (1) are (I) (COGQAS; Nagalakshmi et al., 2014a), (II) (WOPKAP; Nagalakshmi et al., 2014b) and (III) (XODQQY; Nagalakshmi et al., 2014c), showing very similar conformation of the molecular core.

In the crystal of (I), N—H··O hydrogen bonds lead to the formation of chains along the c-axis direction. Within the chains there are further N—H··O and C—H··O hydrogen bonds enclosing $R_2^2(14)$ ring motifs. The chains are linked via N—H··O and C—H··O hydrogen bonds involving the dimethyl sulfoxide solvent molecule which acts as both an acceptor and a donor.

In (II), the asymmetric unit contains two independent molecules (A and B) having similar conformations. In the crystal, molecules are linked by N—H··O hydrogen bonds, forming chains along the a axis which enclose $R_2^2(16)$ ring motifs. The rings are linked by weak N—H··O and C—H··O hydrogen bonds, and C—H··π interactions, forming sheets lying parallel to the (001) plane.

In (III), two intramolecular N—H··O hydrogen bonds are formed, each closing an $S(6)$ loop. In the crystal, strong N—H··O hydrogen bonds lead to the formation of zigzag chains along the c axis. These are consolidated in the 3D crystal packing by weak N—H··O hydrogen bonding, as well as by C—H··O, C—H··Br and C—H··π interactions.

5. Synthesis and crystallization
To a solution of 2-(5-bromo-2-oxoindolin-3-ylidene)malononitrile (1.4 g, 5.1 mmol), which was previously prepared by a known procedure (Negar et al., 2012), and malononitrile (0.34 g, 5.2 mmol) in methanol (25 ml), ethylenediamine (0.31 g, 5.2 mmol) was added and the mixture was stirred at room temperature for 72 h (Fig. 5). Methanol (15 ml) was removed from the reaction mixture, which was left overnight. The precipitated crystals were separated by filtration and recrystallized from an ethanol–water (1:1 v/v) solution (yield 69%; m.p. 479–480 K). Single crystals of (1) were grown from DMSO solution.

Figure 4
The full 2D fingerprint plots for (1), showing (a) all interactions, and delineated into (b) H··H, (c) N··H··N, (d) O··H··O, (e) C··H··C and (f) Br··H··Br interactions. The $d_i$ and $d_e$ values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface contacts.

Figure 5
The synthesis of 5-amino-5′-bromo-2′-oxo-2,3-dihydro-1′H-spiro[imidazo[1,2-a]pyridine-7,3′-indoline]-6,8-dicarbonitrile by a reported procedure (Magerramov et al., 2018).
$^1$H NMR (300 MHz, DMSO-$d_6$, ppm): $\delta$ 3.50 (t, 4H, 2CH$_2$N), 6.61 (s, 2H, NH$_2$), 6.78 (d, 1H, Ar-H), $^3$J$_{HH} = 7.8$ Hz, 7.35 (s, 1H, Ar-H), 7.37 (d, 1H, Ar-H), $^3$J$_{HH} = 7.8$ Hz, 7.73 (s, H, NH), 10.44 (s, H, NH). $^1$C NMR (75 MHz, DMSO-$d_6$, ppm): $\delta$ 42.46 (CH$_2$N), 45.15 (CH$_3$N), 51.24 (C$_{quat}$), 51.71 (==C$_{quat}$), 54.69 (==C$_{quat}$), 112.02 (CH$_{arom}$), 114.43 (Br—C$_{arom}$), 119.63 (CN), 120.15 (CN), 128.02 (CH$_{arom}$), 131.90 (CH$_{arom}$), 137.83 (C$_{arom}$), 140.80 (C$_{arom}$), 152.19 (==C$_{quat}$), 154.76 (==C$_{quat}$), 179.67 (O==C).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms were included in calculated positions and treated as riding atoms; \( N-H = 0.90 \) Å with \( U_{iso}(H) = 1.2U_{eq}(N) \), and \( C-H = 0.95-0.99 \) Å with \( U_{iso}(H) = 1.2 \) or 1.5 \( U_{eq}(C) \). Both DMSO solvent molecules are disordered over two positions, with final occupancies of 0.90:0.10 for the first and 0.95:0.05 for the second molecule. In the first disordered DMSO molecule, the C17B and C18B atoms of the minor component were refined isotropically. The disordered atoms O2A/O2B, O3A/O3B, C19A/C19B and C20A/C20B were refined with anisotropic displacement parameters, constrained to be the same for both components. The S—C and S—O bond lengths in both disordered DMSO molecules were restrained to similarity.

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References

Abdelhamid, A. A., Mohamed, S. K., Khalilov, A. N., Gurbanov, A. V. & Ng, S. W. (2011). Acta Cryst. E67, o744.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). Angew. Chem. Int. Ed. Engl. 34, 1555–1573.
Farrugia, L. J. (2012). ORTEP-3 for Windows (Farrugia, 2012) and PLATON (Spek, 2020).

Table 2

| Experimental details. |
|-----------------------|
| **Crystal data**      |
| Chemical formula      | C$_4$H$_7$BrN$_6$O·2C$_2$H$_6$OS |
| Crystal system, space group | Monoclinic, P2$_1$/c |
| Temperature (K)       | 100 |
| No. of measured, independent and observed \([I > 2\sigma(I)]\) reflections | 7151 |
| \(R_{1} = \sum w(|F_{o}|-|F_{c}|) / \sum w|F_{o}|\) | 0.029 |
| \(wR_{2} = \sum w(|F_{o}^{2}| - |F_{c}^{2}|)^{2} / \sum w|F_{o}^{2}|^{2}\) | 0.039, 0.094, 1.17 |
| No. of reflections    | 5062 |
| No. of parameters     | 331 |
| No. of restraints     | 6 |
| H-atom treatment      | H-atom parameters constrained |

Naghiyev, F. N., Cisterna, J., Khalilov, A. N., Maharramov, A. M., Askerov, R. K., Asadov, K. A., Mamedov, I. G., Akkurt, M., Akobirshoeva, A. A. & Mamedov, I. G. (2021). Acta Cryst. E77, 512–515.
Naghiyev, F. N., Cisterna, J., Khalilov, A. N., Maharramov, A. M., Askerov, R. K., Asadov, K. A., Mamedov, I. G., Salmanli, K. S., Cárdenas, A. & Brito, I. (2020). Molecules, 25, 2235–2248.

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References

Abdelhamid, A. A., Mohamed, S. K., Khalilov, A. N., Gurbanov, A. V. & Ng, S. W. (2011). Acta Cryst. E67, o744.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). Angew. Chem. Int. Ed. Engl. 34, 1555–1573.

Farrugia, L. J. (2012). ORTEP-3 for Windows (Farrugia, 2012) and PLATON (Spek, 2020).

Khalilov, A. N., Tüzün, B., Taslimi, P., Tas, A., Tuncbilek, Z. & Cakmak, N. K. (2021). J. Mol. Liq. 344, 117761.

Lu, L., Deyan, W., Xianglin, M., Sinan, W., Hao, L., Jian, L. & Wei, W. (2012). Chem. Commun. 48, 1692–1694.

Magerramov, A. M., Nagiev, F. N., Mamedova, G. Z. Kh., Asadov, K. A. & Mamedov, I. G. (2018). Russ. J. Organ. Chem. 54, 1713–1717.

Mamedov, I., Naghiyev, F., Maharramov, A., Uswangue, O., Farewell, A., Sunnerhagen, P. & Erdelyi, M. (2020). Mendeleev Commun. 30, 498–499.

Nagalakshmi, R. A., Suresh, J., Sivakumar, S., Kumar, R. R. & Lakshman, P. L. N. (2014a). Acta Cryst. E70, o604–o605.

Nagalakshmi, R. A., Suresh, J., Sivakumar, S., Kumar, R. R. & Lakshman, P. L. N. (2014b). Acta Cryst. E70, o971–o972.

Nagalakshmi, R. A., Suresh, J., Sivakumar, S., Kumar, R. R. & Lakshman, P. L. N. (2014c). Acta Cryst. E70, o816–o817.

Naghiyev, F. N., Cisterna, J., Khalilov, A. N., Maharramov, A. M., Askerov, R. K., Asadov, K. A., Mamedov, I. G., Salmanli, K. S., Cárdenas, A. & Brito, I. (2020). Molecules, 25, 2235–2248.

Naghiyev, F. N., Grishina, M. M., Khurstaleva, V. N., Khalilov, A. N., Akkurtt, M., Akobirhoeva, A. A. & Mamedov, I. G. (2021a). Acta Cryst. E77, 195–199.

Naghiyev, F. N., Grishina, M. M., Khurstaleva, V. N., Akkurtt, M., Khalilov, A. N., Akobirhoeva, A. A. & Mamedov, I. G. (2021b). Acta Cryst. E77, 512–515.

Negar, L., Ghodsi Mohammadi, Z., Alireza, B. & Parisa, G. (2012). Eur. J. Chem. 3, 310–313.

Rigaku OD (2021). CrysAlis PRO. Rigaku Oxford Diffraction Ltd, Yarnton, England.

Samaneh, A., Homa, A. & Javad, A. (2021). J. Chin. Chem. Soc. 68, 1090–1103.

Sheldrick, G. M. (2015a). Acta Cryst. A71, 3–8.

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Sheldrick, G. M. (2015b). *Acta Cryst.* C71, 3–8.
Spek, A. L. (2020). *Acta Cryst.* E76, 1–11.
Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17*. The University of Western Australia.

Yadigarov, R. R., Khalilov, A. N., Mamedov, I. G., Nagiev, F. N., Magerramov, A. M. & Allakhverdiev, M. A. (2009). *Russ. J. Org. Chem.* 45, 1856–1858.
Yin, J., Khalilov, A. N., Muthupandi, P., Ladd, R. & Birman, V. B. (2020). *J. Am. Chem. Soc.* 142, 60–65.
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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2021); cell refinement: *CrysAlis PRO* (Rigaku OD, 2021); data reduction: *CrysAlis PRO* (Rigaku OD, 2021); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2020).

5-Amino-5′-bromo-2′-oxo-2,3-dihydro-1H-spiro[imidazo[1,2-a]pyridine-7,3′-indoline]-6,8-dicarbonitrile dimethyl sulfoxide disolvate

**Crystal data**

\[
\begin{align*}
C_{16}H_{11}BrN_{6}O_2\cdot2C_{2}H_{6}OS & \quad F(000) = 1104 \\
M_r & = 539.47 \\
	ext{Monoclinic, } P_{2_1}/c & \quad D_\lambda = 1.538 \text{ Mg m}^{-3} \\
a & = 10.3940 (1) \text{ Å} & \quad \text{Cu } K\alpha \text{ radiation, } \lambda = 1.54184 \text{ Å} \\
b & = 26.2421 (2) \text{ Å} & \quad \text{Cell parameters from 27880 reflections} \\
c & = 8.9860 (1) \text{ Å} & \quad \theta = 3.4-79.2^\circ \\
\beta & = 108.056 (1)^\circ & \quad \mu = 4.38 \text{ mm}^{-1} \\
V & = 2330.32 (4) \text{ Å}^3 & \quad T = 100 \text{ K} \\
Z & = 4 & \quad \text{Prism, colourless} \\
\end{align*}
\]

**Data collection**

Rigaku XtaLAB Synergy Dualflex HyPix  
Radiation source: micro-focus sealed X-ray tube  
Detector resolution: 0 pixels mm\(^{-1}\)  
\(\varphi\) and \(\omega\) scans  
Absorption correction: multi-scan  
\(T_{\text{min}} = 0.793, T_{\text{max}} = 0.899\)

**Refinement**

Refinement on \(F^2\)  
Least-squares matrix: full  
\(R(F^2 > 2\sigma(F^2)) = 0.039\)  
\(wR(F^2) = 0.094\)  
\(S = 1.17\)  
5062 reflections  
331 parameters  
6 restraints
Hydrogen site location: mixed
H-atom parameters constrained
\( w = \frac{1}{\sigma^2(F_o^2) + (0.0287P)^2 + 4.5523P} \)
where \( P = (F_o^2 + 2F_c^2)/3 \)
\( (\Delta/\sigma)_{max} = 0.003 \)
\( \Delta \rho_{max} = 0.63 \text{ e Å}^{-3} \)
\( \Delta \rho_{min} = -0.41 \text{ e Å}^{-3} \)
Extinction correction: SHELXL (Sheldrick, 2015b), \( F_c^\ast=kF_c[1+0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4} \)
Extinction coefficient: 0.00068 (7)

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)

|     | x     | y     | z     | Uiso*/Ueq | Occ. (<1) |
|-----|-------|-------|-------|-----------|-----------|
| Br1 | 0.43785 (3) | 0.56355 (2) | 0.19141 (3) | 0.02651 (10) | 0.0262 (4) |
| O1  | 0.84018 (19) | 0.31921 (7) | 0.4894 (2) | 0.0262 (4) | 0.0262 (4) |
| N1  | 0.7688 (2) | 0.33596 (8) | -0.0737 (2) | 0.0236 (4) | 0.0236 (4) |
| H1  | 0.846974 | 0.349380 | -0.079035 | 0.028* | 0.028* |
| C1  | 0.7948 (2) | 0.36248 (9) | 0.4575 (3) | 0.0195 (5) | 0.0195 (5) |
| N2  | 0.8234 (2) | 0.40340 (8) | 0.5544 (2) | 0.0223 (4) | 0.0223 (4) |
| H2  | 0.883850 | 0.403189 | 0.650976 | 0.027* | 0.027* |
| C2  | 0.6818 (3) | 0.30219 (12) | -0.1925 (3) | 0.0311 (6) | 0.0311 (6) |
| H2A | 0.730367 | 0.270499 | -0.201996 | 0.037* | 0.037* |
| H2B | 0.651308 | 0.319271 | -0.295753 | 0.037* | 0.037* |
| C3  | 0.5622 (3) | 0.29063 (10) | -0.1340 (3) | 0.0269 (6) | 0.0269 (6) |
| H3A | 0.476650 | 0.303812 | -0.207158 | 0.032* | 0.032* |
| H3B | 0.553120 | 0.253560 | -0.119462 | 0.032* | 0.032* |
| N4  | 0.5981 (2) | 0.31762 (8) | 0.0156 (2) | 0.0181 (4) | 0.0181 (4) |
| C5  | 0.5237 (2) | 0.31827 (8) | 0.1184 (3) | 0.0162 (4) | 0.0162 (4) |
| N5  | 0.4101 (2) | 0.28990 (8) | 0.0779 (2) | 0.0206 (4) | 0.0206 (4) |
| H5A | 0.387282 | 0.271975 | -0.011822 | 0.025* | 0.025* |
| H5B | 0.357158 | 0.288865 | 0.140338 | 0.025* | 0.025* |
| C6  | 0.5691 (2) | 0.34678 (9) | 0.2534 (3) | 0.0175 (4) | 0.0175 (4) |
| C7  | 0.6955 (2) | 0.37927 (9) | 0.2964 (3) | 0.0164 (4) | 0.0164 (4) |
| C8  | 0.7672 (2) | 0.37480 (9) | 0.1734 (3) | 0.0170 (4) | 0.0170 (4) |
| C8A | 0.7175 (2) | 0.34454 (9) | 0.0441 (3) | 0.0169 (4) | 0.0169 (4) |
| C9  | 0.4989 (3) | 0.34610 (9) | 0.3650 (3) | 0.0227 (5) | 0.0227 (5) |
| N9  | 0.4511 (3) | 0.34703 (10) | 0.4650 (3) | 0.0313 (5) | 0.0313 (5) |
| C10 | 0.8877 (3) | 0.40296 (9) | 0.1953 (3) | 0.0219 (5) | 0.0219 (5) |
| N10 | 0.9860 (3) | 0.42647 (10) | 0.2186 (3) | 0.0321 (5) | 0.0321 (5) |
| C11 | 0.7468 (2) | 0.44627 (9) | 0.4847 (3) | 0.0198 (5) | 0.0198 (5) |
| C12 | 0.6681 (2) | 0.43415 (9) | 0.3327 (3) | 0.0173 (4) | 0.0173 (4) |
| C13 | 0.5776 (2) | 0.46901 (9) | 0.2424 (3) | 0.0187 (5) | 0.0187 (5) |
| H13 | 0.523468 | 0.461160 | 0.138649 | 0.022* | 0.022* |
| C14 | 0.5690 (2) | 0.51605 (9) | 0.3097 (3) | 0.0208 (5) | 0.0208 (5) |
| C15 | 0.6498 (3) | 0.52928 (10) | 0.4587 (3) | 0.0244 (5) | 0.0244 (5) |
| H15 | 0.642919 | 0.562266 | 0.499107 | 0.029* | 0.029* |
| C16 | 0.7414 (3) | 0.49383 (10) | 0.5490 (3) | 0.0243 (5) | 0.0243 (5) |
### Atomic displacement parameters (Å²)

|    | U^11  | U^22  | U^33  | U^12  | U^13  | U^23  |
|----|------|------|------|------|------|------|
| Br1 | 0.02864 (16) | 0.01708 (14) | 0.03326 (17) | 0.00539 (10) | 0.00878 (11) | 0.00476 (10) |
| O1  | 0.0292 (10) | 0.0233 (9) | 0.0252 (9) | 0.0092 (7) | 0.0069 (8) | 0.0058 (7) |
| N1  | 0.0255 (11) | 0.0263 (11) | 0.0216 (10) | −0.0070 (9) | 0.0111 (9) | −0.0061 (8) |
sup-4

Geometric parameters (Å, °)

|        |        |        |        |        |        |        |        |        |        |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Br1—C14 | 1.909 (2) | C16—H16 | 0.9500 |        |        |        |        |        |        |
| O1—C1  | 1.229 (3) | S1A—O2A | 1.497 (3) |        |        |        |        |        |        |
| N1—C8A | 1.344 (3) | S1A—C18A | 1.778 (4) |        |        |        |        |        |        |
| N1—C2  | 1.464 (3) | S1A—C17A | 1.787 (3) |        |        |        |        |        |        |
| N1—H1  | 0.9000 | C17A—H17A | 0.9800 |        |        |        |        |        |        |
| C1—N2  | 1.356 (3) | C17A—H17B | 0.9800 |        |        |        |        |        |        |
| C1—C7  | 1.559 (3) | C17A—H17C | 0.9800 |        |        |        |        |        |        |
| N2—C11 | 1.408 (3) | C18A—H18A | 0.9800 |        |        |        |        |        |        |
| N2—H2  | 0.8999 | C18A—H18B | 0.9800 |        |        |        |        |        |        |
| C2—C3  | 1.523 (4) | C18A—H18C | 0.9800 |        |        |        |        |        |        |
| Bond                  | Length/Angle          | Bond                  | Length/Angle          |
|-----------------------|-----------------------|-----------------------|-----------------------|
| C2—H2A                | 0.9900                | S1B—O2B               | 1.497 (4)             |
| C2—H2B                | 0.9900                | S1B—C18B              | 1.777 (5)             |
| C3—N4                 | 1.462 (3)             | S1B—C17B              | 1.787 (5)             |
| C3—H3A                | 0.9900                | C17B—H17D             | 0.9800                |
| C3—H3B                | 0.9900                | C17B—H17E             | 0.9800                |
| N4—C5                 | 1.377 (3)             | C17B—H17F             | 0.9800                |
| N4—C8A                | 1.381 (3)             | C18B—H18D             | 0.9800                |
| C5—N5                 | 1.347 (3)             | C18B—H18E             | 0.9800                |
| C5—C6                 | 1.378 (3)             | C18B—H18F             | 0.9800                |
| N5—H5A                | 0.8996                | S2A—O3A               | 1.521 (2)             |
| N5—H5B                | 0.8999                | S2A—C20A              | 1.782 (3)             |
| C6—C9                 | 1.412 (3)             | S2A—C19A              | 1.790 (3)             |
| C6—C7                 | 1.513 (3)             | C19A—H19A             | 0.9800                |
| C7—C8                 | 1.517 (3)             | C19A—H19B             | 0.9800                |
| C7—C12                | 1.523 (3)             | C19A—H19C             | 0.9800                |
| C8—C8A                | 1.369 (3)             | C20A—H20A             | 0.9800                |
| C8—C10                | 1.414 (3)             | C20A—H20B             | 0.9800                |
| C9—N9                 | 1.154 (4)             | C20A—H20C             | 0.9800                |
| C10—N10               | 1.156 (4)             | S2B—O3B               | 1.522 (4)             |
| C11—C16               | 1.384 (4)             | S2B—C20B              | 1.782 (5)             |
| C11—C12               | 1.394 (3)             | S2B—C19B              | 1.790 (4)             |
| C12—C13               | 1.381 (3)             | C19B—H19D             | 0.9800                |
| C13—C14               | 1.390 (3)             | C19B—H19E             | 0.9800                |
| C13—H13               | 0.9500                | C19B—H19F             | 0.9800                |
| C14—C15               | 1.386 (4)             | C20B—H20D             | 0.9800                |
| C15—C16               | 1.397 (4)             | C20B—H20E             | 0.9800                |
| C15—H15               | 0.9500                | C20B—H20F             | 0.9800                |
| C8A—N1—C2             | 111.7 (2)             | C11—C16—H16          | 121.1                 |
| C8A—N1—H1             | 124.1                 | C15—C16—H16          | 121.1                 |
| C2—N1—H1              | 124.2                 | O2A—S1A—C18A         | 106.15 (19)           |
| O1—C1—N2              | 126.2 (2)             | O2A—S1A—C17A         | 105.0 (2)             |
| O1—C1—C7              | 125.0 (2)             | C18A—S1A—C17A        | 98.23 (18)            |
| N2—C1—C7              | 108.8 (2)             | S1A—C17A—H17A        | 109.5                 |
| C1—N2—C11             | 111.5 (2)             | S1A—C17A—H17B        | 109.5                 |
| C1—N2—H2              | 124.2                 | H17A—C17A—H17B       | 109.5                 |
| C11—N2—H2             | 124.3                 | S1A—C17A—H17C        | 109.5                 |
| N1—C2—C3              | 104.8 (2)             | H17A—C17A—H17C       | 109.5                 |
| N1—C2—H2A             | 110.8                 | H17B—C17A—H17C       | 109.5                 |
| C3—C2—H2A             | 110.8                 | S1A—C18A—H18A        | 109.5                 |
| N4—C3—C2              | 111.3                 | O2B—S1B—C18B         | 107 (2)               |
| N4—C3—H3A             | 111.3                 | O2B—S1B—C17B         | 108 (2)               |
| C2—C3—H3B             | 111.3                 | C18B—S1B—C17B        | 101.7 (16)            |

*Acta Cryst. (2022). E78, 554-558*
| Bond/Angle/Distance | Value 1 | Value 2 |
|--------------------|---------|---------|
| \( \text{H3A—C3—H3B} \) | 109.2   | \( \text{S1B—C17B—H17D} \) | 109.5 |
| \( \text{C5—N4—C8A} \) | 121.9 (2) | \( \text{S1B—C17B—H17E} \) | 109.5 |
| \( \text{C5—N4—C3} \) | 125.9 (2) | \( \text{H17D—C17B—H17F} \) | 109.5 |
| \( \text{C8A—N4—C3} \) | 112.2 (2) | \( \text{S1B—C17B—H17F} \) | 109.5 |
| \( \text{N5—C5—N4} \) | 116.1 (2) | \( \text{H17D—C17B—H17F} \) | 109.5 |
| \( \text{N5—C5—C6} \) | 124.8 (2) | \( \text{H17E—C17B—H17F} \) | 109.5 |
| \( \text{N4—C5—C6} \) | 119.1 (2) | \( \text{S1B—C18B—H18D} \) | 109.5 |
| \( \text{C5—N5—H5A} \) | 119.8   | \( \text{S1B—C18B—H18E} \) | 109.5 |
| \( \text{C5—N5—H5B} \) | 120.2   | \( \text{H18D—C18B—H18E} \) | 109.5 |
| \( \text{H5A—N5—H5B} \) | 120.0   | \( \text{S1B—C18B—H18F} \) | 109.5 |
| \( \text{C5—C6—C9} \) | 120.5 (2) | \( \text{H18D—C18B—H18F} \) | 109.5 |
| \( \text{C5—C6—C7} \) | 124.4 (2) | \( \text{H18E—C18B—H18F} \) | 109.5 |
| \( \text{C9—C6—C7} \) | 115.1 (2) | \( \text{O3A—S2A—C20A} \) | 105.94 (15) |
| \( \text{C6—C7—C8} \) | 110.72 (19) | \( \text{O3A—S2A—C19A} \) | 107.28 (13) |
| \( \text{C6—C7—C12} \) | 112.51 (19) | \( \text{C20A—S2A—C19A} \) | 96.65 (19) |
| \( \text{C8—C7—C12} \) | 113.31 (19) | \( \text{S2A—C19A—H19A} \) | 109.5 |
| \( \text{C6—C7—C1} \) | 110.56 (19) | \( \text{S2A—C19A—H19B} \) | 109.5 |
| \( \text{C8—C7—C1} \) | 108.74 (19) | \( \text{H19A—C19A—H19B} \) | 109.5 |
| \( \text{C12—C7—C1} \) | 100.51 (18) | \( \text{S2A—C19A—H19C} \) | 109.5 |
| \( \text{C8A—C8—C10} \) | 120.4 (2) | \( \text{H19A—C19A—H19C} \) | 109.5 |
| \( \text{C8A—C8—C7} \) | 121.5 (2) | \( \text{H19B—C19A—H19C} \) | 109.5 |
| \( \text{C10—C8—C7} \) | 118.2 (2) | \( \text{S2A—C20A—H20A} \) | 109.5 |
| \( \text{N1—C8A—C8} \) | 128.9 (2) | \( \text{S2A—C20A—H20B} \) | 109.5 |
| \( \text{N1—C8A—N4} \) | 108.7 (2) | \( \text{H20A—C20A—H20B} \) | 109.5 |
| \( \text{C8A—C8—N4} \) | 122.3 (2) | \( \text{S2A—C20A—H20C} \) | 109.5 |
| \( \text{N9—C9—C6} \) | 174.4 (3) | \( \text{H20A—C20A—H20C} \) | 109.5 |
| \( \text{N10—C10—C8} \) | 177.5 (3) | \( \text{H20B—C20A—H20C} \) | 109.5 |
| \( \text{C16—C11—C12} \) | 121.8 (2) | \( \text{O3B—S2B—C20B} \) | 97 (4) |
| \( \text{C16—C11—N2} \) | 128.7 (2) | \( \text{O3B—S2B—C19B} \) | 93 (3) |
| \( \text{C12—C11—N2} \) | 109.4 (2) | \( \text{C20B—S2B—C19B} \) | 72 (4) |
| \( \text{C13—C12—C11} \) | 120.7 (2) | \( \text{S2B—C19B—H19D} \) | 109.5 |
| \( \text{C13—C12—C7} \) | 129.7 (2) | \( \text{S2B—C19B—H19E} \) | 109.5 |
| \( \text{C11—C12—C7} \) | 109.5 (2) | \( \text{H19D—C19B—H19E} \) | 109.5 |
| \( \text{C12—C13—C14} \) | 117.1 (2) | \( \text{S2B—C19B—H19F} \) | 109.5 |
| \( \text{C12—C13—H13} \) | 121.4 | \( \text{H19D—C19B—H19F} \) | 109.5 |
| \( \text{C14—C13—H13} \) | 121.4 | \( \text{H19E—C19B—H19F} \) | 109.5 |
| \( \text{C15—C14—C13} \) | 122.8 (2) | \( \text{S2B—C20B—H20D} \) | 109.5 |
| \( \text{C15—C14—Br1} \) | 119.25 (19) | \( \text{S2B—C20B—H20E} \) | 109.5 |
| \( \text{C13—C14—Br1} \) | 117.94 (18) | \( \text{H20D—C20B—H20E} \) | 109.5 |
| \( \text{C14—C15—C16} \) | 119.6 (2) | \( \text{S2B—C20B—H20F} \) | 109.5 |
| \( \text{C14—C15—H15} \) | 120.2 | \( \text{H20D—C20B—H20F} \) | 109.5 |
| \( \text{C16—C15—H15} \) | 120.2 | \( \text{H20E—C20B—H20F} \) | 109.5 |
| \( \text{C11—C16—C15} \) | 117.8 (2) | \( \text{O1—C1—N2—C11} \) | \(-175.7 (2)\) | \( \text{C2—N1—C8A—C8} \) | \(-178.1 (3)\) |
| \( \text{C7—C1—N2—C11} \) | 5.0 (3) | \( \text{C2—N1—C8A—N4} \) | 0.9 (3) |
| \( \text{C8A—N1—C2—C3} \) | 1.0 (3) | \( \text{C10—C8—C8A—N1} \) | 0.9 (4) |
| \( \text{N1—C2—C3—N4} \) | \(-2.3 (3)\) | \( \text{C7—C8—C8A—N1} \) | \(-179.2 (2)\) |
C2—C3—N4—C5  −178.4 (2)  C10—C8—C8A—N4  −178.0 (2)
C2—C3—N4—C8A  3.0 (3)  C7—C8—C8A—N4  1.9 (3)
C8A—N4—C5—C6  −179.2 (2)  C5—N4—C8A—N1  178.8 (2)
C3—N4—C5—C6  2.4 (3)  C3—N4—C8A—N1  −2.6 (3)
C8A—N4—C5—N5  0.3 (3)  C5—N4—C8A—C8  −2.1 (3)
C3—N4—C5—N5  −178.2 (2)  C3—N4—C8A—C8  176.5 (2)
C2—C3—N4—C8A  3.0 (3)  C1—N2—C11—C16  175.8 (3)
C7—C8—C8A—N4  1.9 (3)  C1—N2—C11—C12  −2.6 (3)
C8A—N4—C5—C6  −176.6 (2)  C1—N2—C11—C12  −179.5 (2)
C3—N4—C5—C6  −178.9 (2)  C5—N4—C8A—C8  176.5 (2)
C8A—N4—C5—C6  1.7 (3)  N2—C11—C12—C13  −112.3 (2)
C3—N4—C5—C6  −176.6 (2)  N2—C11—C12—C7  −1.0 (3)
N5—C5—C6—C7  2.8 (4)  C16—C11—C12—C7  121.2 (2)
N4—C5—C6—C7  −1.8 (3)  C1—N2—C11—C12  175.8 (3)
N5—C5—C6—C7  −178.9 (2)  C16—C11—C12—C13  −2.4 (4)
N4—C5—C6—C7  1.7 (3)  N2—C11—C12—C13  176.2 (2)
C9—C6—C7—C8  176.6 (2)  C16—C11—C12—C7  0.0 (4)
C12—C7—C8—C8A  0.0 (3)  C16—C11—C12—C13  −1.0 (3)
C9—C6—C7—C8  −122.3 (2)  C16—C11—C12—C7  −175.7 (2)
C12—C7—C8—C8A  −127.5 (2)  C8—C7—C12—C7  −121.2 (2)
C1—C7—C8—C8A  121.6 (2)  C1—C7—C8—C7  3.6 (2)
C1—C7—C8—C10  179.8 (2)  C8—C7—C12—C7  −112.3 (2)
C6—C7—C8—C8A  56.6 (3)  C12—C11—C16—C15  2.5 (4)
C6—C7—C8—C10  52.4 (3)  C12—C11—C16—C15  −175.7 (2)
C1—C7—C8—C10  −58.5 (3)  C14—C15—C16—C11  −0.3 (4)

Hydrogen-bond geometry (Å, °)

| D—H···A       | D—H  | H···A | D···A   | D—H···A |
|---------------|------|-------|---------|---------|
| N1—H1···O2A   | 0.90 | 1.98  | 2.855 (4) | 165     |
| N1—H1···O2B   | 0.90 | 2.00  | 2.87 (4)  | 160     |
| N2—H2···O2A   | 0.90 | 1.91  | 2.793 (5) | 166     |
| N2—H2···O2B   | 0.90 | 1.94  | 2.82 (5)  | 166     |
| N5—H5A···O3A  | 0.90 | 2.20  | 3.034 (3) | 155     |
| N5—H5B···O3A  | 0.90 | 2.06  | 2.918 (3) | 160     |
| C2—H2···N9    | 0.99 | 2.59  | 3.469 (4) | 148     |
| C19A—H19A···N9| 0.98 | 2.41  | 3.114 (5) | 128     |
| C19A—H19C···O1| 0.98 | 2.52  | 3.392 (4) | 148     |
| C20A—H20B···O1| 0.98 | 2.46  | 3.359 (4) | 152     |

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