Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

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

Farid N. Naghiyev,[a] Victor N. Khrustalev,[b,c] Anton P. Novikov,[b] Mehmet Akkurt,[d] Rovnag M. Rzayev,[e] Anzurat A. Akobirshoeva[f]* and Ibrahim G. Mamedov[a]

[a]Department of Chemistry, Baku State University, Z. Khalilov str. 23, Az 1148, Baku, Azerbaijan, [b]Peoples' Friendship University of Russia (RUDN University), Miklukho-Maklay St. 6, Moscow 117198, Russian Federation, [c]N. D. Zelinsky Institute of Organic Chemistry RAS, Leninsky Prosp. 47, Moscow 119991, Russian Federation, [d]Department of Physics, Faculty of Sciences, Erciyes University, 38039 Kayseri, Turkey, [e]Composite Materials' Scientific Research Center, Azerbaijan State Economic University (UNEC), H. Aliyev str. 135, Az 1063, Baku, Azerbaijan, and [f]Academy of Sciences of the Republic of Tajikistan, Kh Yu Yusufbekov Pamir Biological Institute, 1 Kholdorova St, Khorog 736002, Gbao, Tajikistan. *Correspondence e-mail: anzurat2003@mail.ru

Received 12 January 2022
Accepted 3 May 2022

Edited by A. S. Batsanov, University of Durham, United Kingdom

Keywords: crystal structure; spiro[imidazo[1,2-a]pyridine; hydrogen bonds; dimethyl sulfoxide; disorder; Hirshfeld surface analysis.

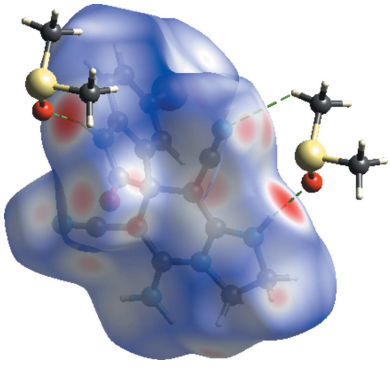
CCDC reference: 2170241

Supporting information: this article has supporting information at journals.iucr.org/e

In the title compound, $C_{16}H_{11}BrN_6O\cdot 2C_2H_6OS$, 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 spiro[imidazo[1,2-*a*]pyridine] moiety, play a key role in medicinal chemistry (Han *et al.*, 2008; Mamedov *et al.*, 2020; Samaneh *et al.*, 2021). The conjugate addition to oxoindolinylidenemalononitriles 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-1*H*-spiro[imidazo[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, 2021*a*,*b*), herein the crystal structure and Hirshfeld surface analysis of 5-amino-5′-bromo-2′-oxo-2,3-dihydro-1*H*-spiro[imidazo[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/C1/C7/C11–C16) are nearly planar, with maximum deviations of

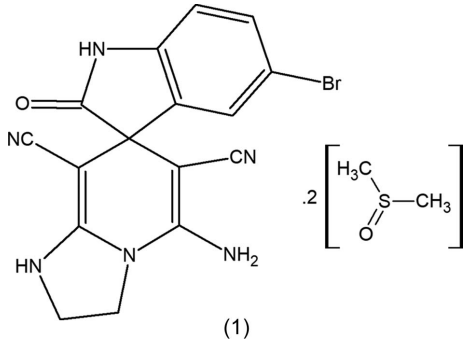
OPEN ACCESS
Published under a CC BY 4.0 licence

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2A^{i}	0.90	1.98	2.855 (4)	165
N1—H1···O2B^{i}	0.90	2.00	2.87 (4)	160
N2—H2···O2A^{ii}	0.90	1.91	2.793 (5)	166
N2—H2···O2B^{ii}	0.90	1.94	2.82 (5)	166
N5—H5A···O3A^{iii}	0.90	2.20	3.034 (3)	155
N5—H5B···O3A	0.90	2.06	2.918 (3)	160
C2—H2B···N9^{iv}	0.99	2.59	3.469 (4)	148
C19A—H19A···N9	0.98	2.41	3.114 (5)	128
C19A—H19C···O1^{v}	0.98	2.52	3.392 (4)	148
C20A—H20B···O1^{v}	0.98	2.46	3.359 (4)	152

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

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 (NH_2) groups form an intermolecular hydrogen bond with one dimethyl sulfoxide (DMSO) group, giving an $S(10)$ motif (Bernstein *et al.*, 1995) (Table 1).



(1)

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.

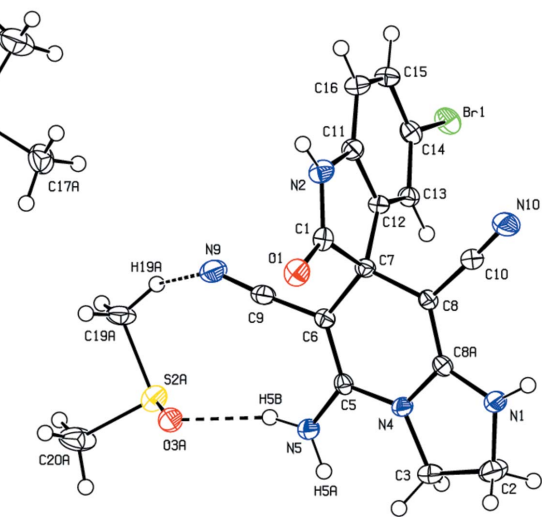


Figure 1
The title molecule with the labelling scheme and displacement ellipsoids drawn at the 50% probability level. The minor components of the disorder are not shown.

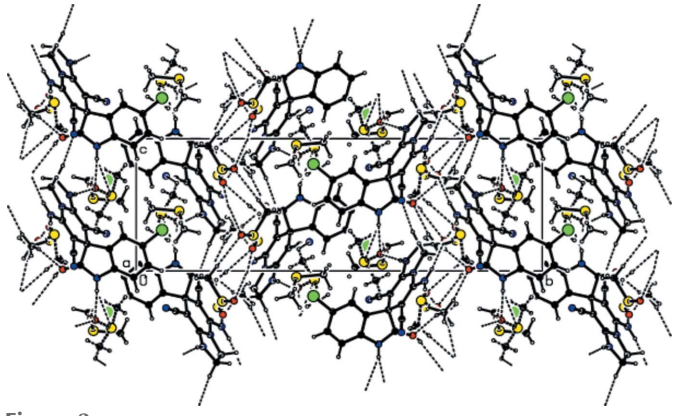


Figure 2
A view of the molecular packing of (1) along the a-axis direction.

The Hirshfeld surfaces were calculated and the two-dimensional (2D) fingerprint plots generated using *CrystalExplorer* (Version 17.5; Turner *et al.*, 2017). Fig. 3 shows the 3D Hirshfeld surface of (1) with d_{norm} (normalized contact distance) plotted over 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(c); 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

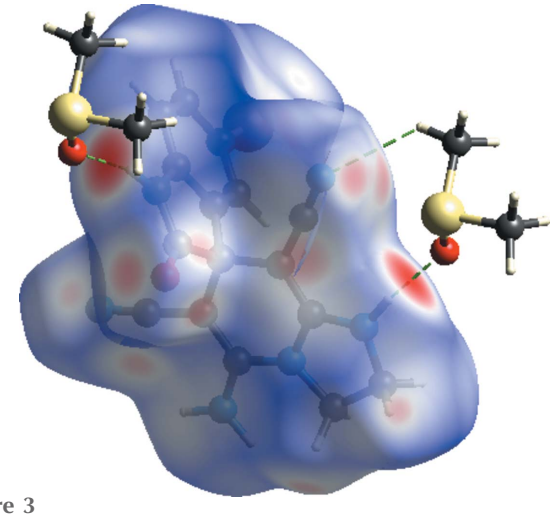


Figure 3
View of the 3D Hirshfeld surface of (1) plotted over d_{norm} in the range from −0.6206 to 1.3180 a.u.

(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-2*H*-indol-2-one unit of (1) gave 87 hits. The three compounds most resembling (1) are (**I**) (COGQAS; Nagalakshmi *et al.*, 2014*a*), (**II**) (WOPKAP; Nagalakshmi *et al.*, 2014*b*) and (**III**) (XODQOY; Nagalakshmi *et al.*, 2014*c*), 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.

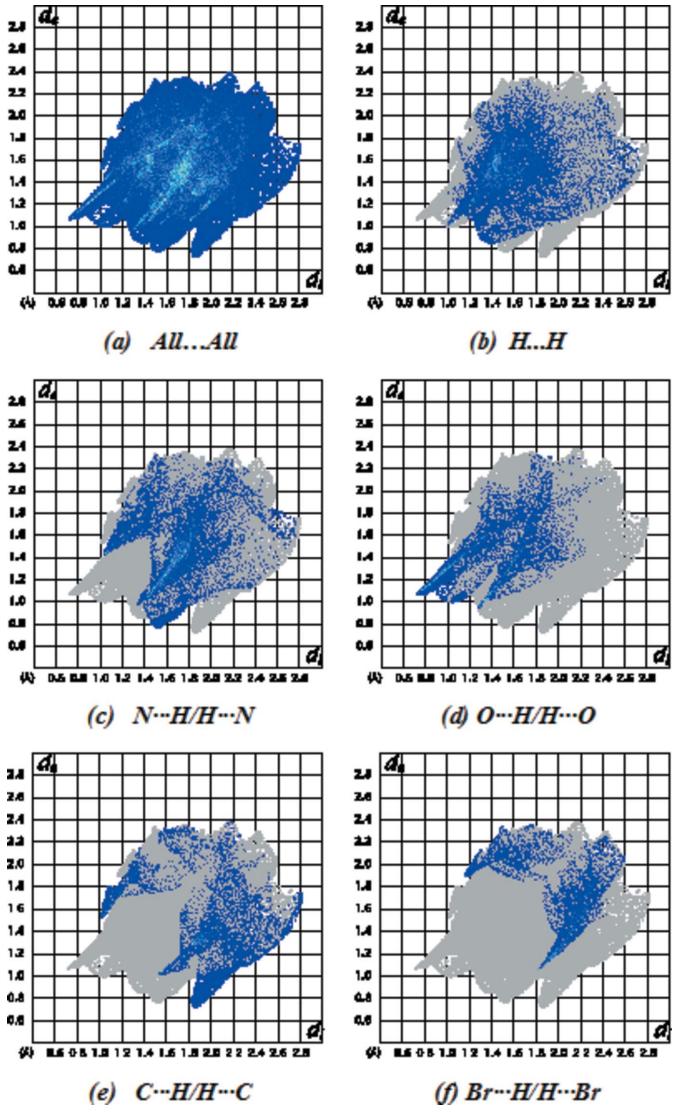


Figure 4
The full 2D fingerprint plots for (1), showing (*a*) all interactions, and delineated into (*b*) H···H, (*c*) N···H/H···N, (*d*) O···H/H···O, (*e*) C···H/H···C and (*f*) Br···H/H···Br interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points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

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.

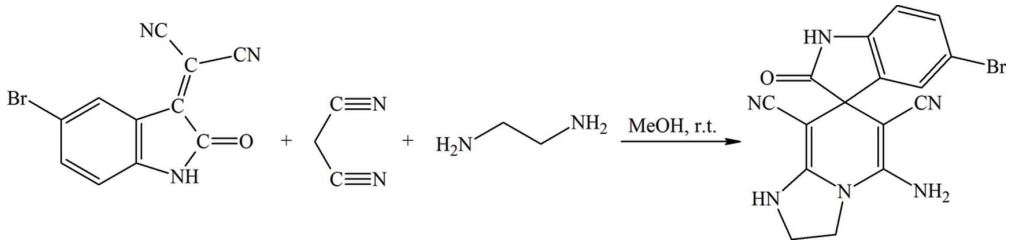


Figure 5
The synthesis of 5-amino-5′-bromo-2′-oxo-2,3-dihydro-1*H*-spiro[imidazo[1,2-*a*]pyridine-7,3′-indoline]-6,8-dicarbonitrile by a reported procedure (Magerramov *et al.*, 2018).

^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ 3.50 (*t*, 4H, 2CH_2N), 6.61 (*s*, 2H, NH_2), 6.78 (*d*, 1H, Ar-H, $^3J_{H\text{-}H}$ = 7.8 Hz), 7.35 (*s*, 1H, Ar-H), 7.37 (*d*, 1H, Ar-H, $^3J_{H\text{-}H}$ = 7.8 Hz), 7.73 (*s*, H, NH), 10.44 (*s*, H, NH). ^{13}C NMR (75 MHz, DMSO-d_6, ppm): δ 42.46 (CH_2N), 45.15 (CH_2N), 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 1.5U_{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 C17*B* and C18*B* atoms of the minor component were refined isotropically. The disordered atoms O2*A*/O2*B*, O3*A*/O3*B*, C19*A*/C19*B* and C20*A*/C20*B* 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.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{11}BrN_6O{\cdot}2C_2H_6OS$
M_r	539.47
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, *b*, *c* (Å)	10.3940 (1), 26.2421 (2), 8.9860 (1)
β (°)	108.056 (1)
V (Å^3)	2330.32 (4)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	4.38
Crystal size (mm)	0.05 × 0.03 × 0.02
Data collection	
Diffractometer	Rigaku XtaLAB Synergy Dualflex HyPix
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2021)
T_{min}, T_{max}	0.793, 0.899
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	31508, 5062, 5047
R_{int}	0.029
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.638
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	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
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.63, −0.41

Computer programs: *CrysAlis PRO* (Rigaku OD, 2021), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

Acknowledgements

The authors would like to thank Baku State University and the Ministry of Education and Science of the Russian Federation for their support of this research. Authors' contributions are as follows. Conceptualization, FNN and IGM; methodology, FNN and IGM; investigation, FNN, MA and APN; writing (original draft), MA and IGM; writing (review and editing of the manuscript), MA and FNN; visualization, MA, FNN and IGM; funding acquisition, VNK, RMR and FNN; resources, AAA, VNK and FNN; supervision, IGM and MA.

Funding information

Funding for this research was provided by: Ministry of Education and Science of the Russian Federation (award No. 075-03-2020-223 (FSSF-2020-0017)).

References

Abdelhamid, A. A., Mohamed, S. K., Khalilov, A. N., Gurbanov, A. V. & Ng, S. W. (2011). *Acta Cryst.* E**67**, o744.

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

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Han, F., Shioda, N., Moriguchi, S., Yamamoto, Y., Raie, A. Y. A., Yamaguchi, Y., Hino, M. & Fukunaga, K. (2008). *J. Pharmacol. Exp. Ther.* **326**, 127–134.

Jun, J., Juan, L., Xinhua, L., Hongxin, L., Haiyan, W. & Hong-Ping, X. (2019). *Synlett*, **30**, 1241–1245.

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

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

Magerramov, A. M., Nagiev, F. N., Mamedova, G. Z. Kh. A., Asadov, Kh. A. & Mamedov, I. G. (2018). *Russ. J. Org. Chem.* **54**, 1713–1715.

Mamedov, I., Naghiyev, F., Maharramov, A., Uwangue, 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. (2014*a*). *Acta Cryst.* E**70**, o604–o605.

Nagalakshmi, R. A., Suresh, J., Sivakumar, S., Kumar, R. R. & Lakshman, P. L. N. (2014*b*). *Acta Cryst.* E**70**, o971–o972.

Nagalakshmi, R. A., Suresh, J., Sivakumar, S., Kumar, R. R. & Lakshman, P. L. N. (2014*c*). *Acta Cryst.* E**70**, 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., Khrustalev, V. N., Khalilov, A. N., Akkurt, M., Akobirshoeva, A. A. & Mamedov, İ. G. (2021*a*). *Acta Cryst.* E**77**, 195–199.

Naghiyev, F. N., Tereshina, T. A., Khrustalev, V. N., Akkurt, M., Khalilov, A. N., Akobirshoeva, A. A. & Mamedov, İ. G. (2021*b*). *Acta Cryst.* E**77**, 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. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Spek, A. L. (2020). *Acta Cryst.* E**76**, 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**, 60–63.

supporting information

Acta Cryst. (2022). E**78**, 554-558 [https://doi.org/10.1107/S2056989022004741]

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

Farid N. Naghiyev, Victor N. Khrustalev, Anton P. Novikov, Mehmet Akkurt, Rovnag M. Rzayev, Anzurat A. Akobirshoeva and Ibrahim G. Mamedov

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-1*H*-spiro[imidazo[1,2-*a*]pyridine-7,3′-indoline]-6,8-dicarbonitrile dimethyl sulfoxide disolvate

Crystal data

$C_{16}H_{11}BrN_6O\cdot 2C_2H_6OS$
$M_r = 539.47$
Monoclinic, $P2_1/c$
$a = 10.3940$ (1) Å
$b = 26.2421$ (2) Å
$c = 8.9860$ (1) Å
$\beta = 108.056$ (1)°
$V = 2330.32$ (4) Å^3
$Z = 4$
$F(000) = 1104$
$D_x = 1.538$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 27880 reflections
$\theta = 3.4$–79.2°
$\mu = 4.38$ mm^{-1}
$T = 100$ K
Prism, colourless
0.05 × 0.03 × 0.02 mm

Data collection

Rigaku XtaLAB Synergy Dualflex HyPix diffractometer
Radiation source: micro-focus sealed X-ray tube
Detector resolution: 0 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2021)
$T_{min} = 0.793$, $T_{max} = 0.899$
31508 measured reflections
5062 independent reflections
5047 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 79.4°$, $\theta_{min} = 3.4°$
$h = -13\rightarrow13$
$k = -31\rightarrow33$
$l = -11\rightarrow11$

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
$w = 1/[\sigma^2(F_o^2) + (0.0287P)^2 + 4.5523P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.63$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}
Extinction correction: SHELXL (Sheldrick, 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
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 (Å^2)

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

H16	0.798109	0.502105	0.651194	0.029*	
S1A	0.13352 (7)	0.39460 (3)	0.95312 (8)	0.02416 (16)	0.9
O2A	−0.0128 (3)	0.38792 (11)	0.8623 (5)	0.0249 (7)	0.9
C17A	0.2226 (3)	0.38206 (13)	0.8160 (4)	0.0335 (7)	0.9
H17A	0.214127	0.345875	0.787662	0.050*	0.9
H17B	0.318415	0.390664	0.863195	0.050*	0.9
H17C	0.184208	0.402768	0.721890	0.050*	0.9
C18A	0.1618 (4)	0.46142 (14)	0.9724 (5)	0.0453 (9)	0.9
H18A	0.126943	0.477575	0.869331	0.068*	0.9
H18B	0.259115	0.468053	1.015790	0.068*	0.9
H18C	0.115059	0.475458	1.042574	0.068*	0.9
S1B	0.0823 (6)	0.4388 (2)	0.9322 (8)	0.0235 (12)	0.1
O2B	−0.024 (3)	0.3988 (13)	0.874 (6)	0.0249 (7)	0.1
C17B	0.224 (2)	0.4099 (11)	1.073 (3)	0.035 (6)*	0.1
H17D	0.252431	0.379726	1.026836	0.053*	0.1
H17E	0.198648	0.399764	1.165015	0.053*	0.1
H17F	0.299037	0.434301	1.104281	0.053*	0.1
C18B	0.150 (4)	0.4529 (15)	0.778 (3)	0.048 (8)*	0.1
H18D	0.168102	0.421089	0.730947	0.072*	0.1
H18E	0.234154	0.472179	0.819275	0.072*	0.1
H18F	0.084401	0.473284	0.697880	0.072*	0.1
S2A	0.11696 (8)	0.28805 (3)	0.26820 (8)	0.0263 (2)	0.948 (2)
O3A	0.24507 (19)	0.25919 (7)	0.2727 (2)	0.0245 (4)	0.95
C19A	0.1529 (3)	0.32357 (12)	0.4465 (4)	0.0286 (7)	0.95
H19A	0.214320	0.351728	0.444556	0.043*	0.95
H19B	0.195632	0.301184	0.535359	0.043*	0.95
H19C	0.068477	0.337256	0.457128	0.043*	0.95
C20A	0.0076 (3)	0.24245 (15)	0.3136 (6)	0.0422 (11)	0.95
H20A	−0.027573	0.219286	0.224693	0.063*	0.95
H20B	−0.067876	0.260108	0.334906	0.063*	0.95
H20C	0.058216	0.222893	0.406131	0.063*	0.95
S2B	0.0451 (16)	0.2982 (5)	0.2263 (16)	0.0263 (2)	0.052 (2)
O3B	0.165 (3)	0.2865 (13)	0.169 (4)	0.0245 (4)	0.05
C19B	0.149 (6)	0.306 (3)	0.425 (3)	0.0286 (7)	0.05
H19D	0.244796	0.302777	0.430774	0.043*	0.05
H19E	0.127063	0.279408	0.490034	0.043*	0.05
H19F	0.133444	0.339513	0.463042	0.043*	0.05
C20B	0.045 (10)	0.240 (2)	0.326 (11)	0.0422 (11)	0.05
H20D	−0.020108	0.241711	0.385397	0.063*	0.05
H20E	0.135442	0.233028	0.398604	0.063*	0.05
H20F	0.018655	0.211771	0.250113	0.063*	0.05

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)

C1	0.0192 (11)	0.0212 (11)	0.0186 (11)	0.0012 (9)	0.0067 (9)	0.0025 (9)
N2	0.0216 (10)	0.0247 (11)	0.0165 (9)	0.0033 (8)	−0.0002 (8)	0.0011 (8)
C2	0.0280 (14)	0.0391 (16)	0.0275 (13)	−0.0081 (12)	0.0106 (11)	−0.0137 (12)
C3	0.0325 (14)	0.0252 (13)	0.0228 (12)	−0.0088 (11)	0.0085 (11)	−0.0084 (10)
N4	0.0179 (9)	0.0202 (10)	0.0161 (9)	−0.0034 (8)	0.0054 (8)	−0.0035 (8)
C5	0.0178 (10)	0.0130 (10)	0.0179 (10)	0.0018 (8)	0.0056 (9)	0.0032 (8)
N5	0.0214 (10)	0.0218 (10)	0.0192 (10)	−0.0040 (8)	0.0074 (8)	−0.0034 (8)
C6	0.0196 (11)	0.0148 (10)	0.0188 (11)	−0.0009 (9)	0.0068 (9)	−0.0007 (8)
C7	0.0185 (11)	0.0136 (10)	0.0164 (10)	0.0000 (8)	0.0044 (9)	−0.0004 (8)
C8	0.0196 (11)	0.0144 (10)	0.0169 (11)	−0.0012 (8)	0.0054 (9)	0.0008 (8)
C8A	0.0176 (11)	0.0136 (10)	0.0192 (11)	0.0012 (8)	0.0052 (9)	0.0021 (8)
C9	0.0247 (12)	0.0192 (11)	0.0240 (12)	−0.0048 (9)	0.0073 (10)	−0.0059 (9)
N9	0.0330 (12)	0.0352 (13)	0.0300 (12)	−0.0105 (10)	0.0162 (10)	−0.0130 (10)
C10	0.0263 (13)	0.0197 (11)	0.0204 (11)	−0.0026 (10)	0.0084 (10)	−0.0031 (9)
N10	0.0312 (12)	0.0331 (13)	0.0339 (13)	−0.0126 (10)	0.0130 (10)	−0.0100 (10)
C11	0.0201 (11)	0.0202 (11)	0.0168 (11)	−0.0012 (9)	0.0025 (9)	0.0007 (9)
C12	0.0187 (11)	0.0159 (11)	0.0171 (11)	−0.0023 (8)	0.0052 (9)	−0.0025 (8)
C13	0.0205 (11)	0.0169 (11)	0.0170 (11)	−0.0019 (9)	0.0037 (9)	−0.0004 (9)
C14	0.0204 (11)	0.0170 (11)	0.0251 (12)	0.0004 (9)	0.0069 (10)	0.0029 (9)
C15	0.0307 (13)	0.0180 (11)	0.0258 (13)	−0.0031 (10)	0.0106 (11)	−0.0058 (10)
C16	0.0273 (13)	0.0243 (12)	0.0195 (11)	−0.0049 (10)	0.0046 (10)	−0.0065 (10)
S1A	0.0207 (3)	0.0278 (4)	0.0216 (3)	−0.0033 (3)	0.0030 (3)	0.0009 (3)
O2A	0.0197 (10)	0.0340 (18)	0.0191 (12)	−0.0052 (12)	0.0032 (8)	0.0003 (13)
C17A	0.0303 (16)	0.0348 (17)	0.0396 (18)	−0.0050 (13)	0.0172 (14)	0.0012 (14)
C18A	0.046 (2)	0.0296 (18)	0.064 (3)	−0.0077 (17)	0.0228 (19)	−0.0129 (17)
S1B	0.023 (3)	0.011 (3)	0.041 (3)	0.004 (2)	0.017 (3)	0.005 (2)
O2B	0.0197 (10)	0.0340 (18)	0.0191 (12)	−0.0052 (12)	0.0032 (8)	0.0003 (13)
S2A	0.0283 (4)	0.0275 (3)	0.0226 (3)	0.0065 (3)	0.0074 (3)	0.0015 (3)
O3A	0.0256 (10)	0.0235 (9)	0.0263 (10)	0.0008 (8)	0.0108 (8)	−0.0013 (7)
C19A	0.0278 (14)	0.0235 (15)	0.0378 (16)	−0.0057 (13)	0.0148 (12)	−0.0156 (12)
C20A	0.028 (2)	0.0434 (18)	0.062 (2)	−0.0157 (15)	0.023 (2)	−0.0283 (17)
S2B	0.0283 (4)	0.0275 (3)	0.0226 (3)	0.0065 (3)	0.0074 (3)	0.0015 (3)
O3B	0.0256 (10)	0.0235 (9)	0.0263 (10)	0.0008 (8)	0.0108 (8)	−0.0013 (7)
C19B	0.0278 (14)	0.0235 (15)	0.0378 (16)	−0.0057 (13)	0.0148 (12)	−0.0156 (12)
C20B	0.028 (2)	0.0434 (18)	0.062 (2)	−0.0157 (15)	0.023 (2)	−0.0283 (17)

Geometric parameters (Å, º)

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

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
N1—C2—H2B	110.8	S1A—C18A—H18B	109.5
C3—C2—H2B	110.8	H18A—C18A—H18B	109.5
H2A—C2—H2B	108.9	S1A—C18A—H18C	109.5
N4—C3—C2	102.6 (2)	H18A—C18A—H18C	109.5
N4—C3—H3A	111.3	H18B—C18A—H18C	109.5
C2—C3—H3A	111.3	O2B—S1B—C18B	107 (2)
N4—C3—H3B	111.3	O2B—S1B—C17B	108 (2)
C2—C3—H3B	111.3	C18B—S1B—C17B	101.7 (16)

H3A—C3—H3B	109.2	S1B—C17B—H17D	109.5
C5—N4—C8A	121.9 (2)	S1B—C17B—H17E	109.5
C5—N4—C3	125.9 (2)	H17D—C17B—H17E	109.5
C8A—N4—C3	112.2 (2)	S1B—C17B—H17F	109.5
N5—C5—N4	116.1 (2)	H17D—C17B—H17F	109.5
N5—C5—C6	124.8 (2)	H17E—C17B—H17F	109.5
N4—C5—C6	119.1 (2)	S1B—C18B—H18D	109.5
C5—N5—H5A	119.8	S1B—C18B—H18E	109.5
C5—N5—H5B	120.2	H18D—C18B—H18E	109.5
H5A—N5—H5B	120.0	S1B—C18B—H18F	109.5
C5—C6—C9	120.5 (2)	H18D—C18B—H18F	109.5
C5—C6—C7	124.4 (2)	H18E—C18B—H18F	109.5
C9—C6—C7	115.1 (2)	O3A—S2A—C20A	105.94 (15)
C6—C7—C8	110.72 (19)	O3A—S2A—C19A	107.28 (13)
C6—C7—C12	112.51 (19)	C20A—S2A—C19A	96.65 (19)
C8—C7—C12	113.31 (19)	S2A—C19A—H19A	109.5
C6—C7—C1	110.56 (19)	S2A—C19A—H19B	109.5
C8—C7—C1	108.74 (19)	H19A—C19A—H19B	109.5
C12—C7—C1	100.51 (18)	S2A—C19A—H19C	109.5
C8A—C8—C10	120.4 (2)	H19A—C19A—H19C	109.5
C8A—C8—C7	121.5 (2)	H19B—C19A—H19C	109.5
C10—C8—C7	118.2 (2)	S2A—C20A—H20A	109.5
N1—C8A—C8	128.9 (2)	S2A—C20A—H20B	109.5
N1—C8A—N4	108.7 (2)	H20A—C20A—H20B	109.5
C8—C8A—N4	122.3 (2)	S2A—C20A—H20C	109.5
N9—C9—C6	174.4 (3)	H20A—C20A—H20C	109.5
N10—C10—C8	177.5 (3)	H20B—C20A—H20C	109.5
C16—C11—C12	121.8 (2)	O3B—S2B—C20B	97 (4)
C16—C11—N2	128.7 (2)	O3B—S2B—C19B	93 (3)
C12—C11—N2	109.4 (2)	C20B—S2B—C19B	72 (4)
C13—C12—C11	120.7 (2)	S2B—C19B—H19D	109.5
C13—C12—C7	129.7 (2)	S2B—C19B—H19E	109.5
C11—C12—C7	109.5 (2)	H19D—C19B—H19E	109.5
C12—C13—C14	117.1 (2)	S2B—C19B—H19F	109.5
C12—C13—H13	121.4	H19D—C19B—H19F	109.5
C14—C13—H13	121.4	H19E—C19B—H19F	109.5
C15—C14—C13	122.8 (2)	S2B—C20B—H20D	109.5
C15—C14—Br1	119.25 (19)	S2B—C20B—H20E	109.5
C13—C14—Br1	117.94 (18)	H20D—C20B—H20E	109.5
C14—C15—C16	119.6 (2)	S2B—C20B—H20F	109.5
C14—C15—H15	120.2	H20D—C20B—H20F	109.5
C16—C15—H15	120.2	H20E—C20B—H20F	109.5
C11—C16—C15	117.8 (2)		

O1—C1—N2—C11	−175.7 (2)	C2—N1—C8A—C8	−178.1 (3)
C7—C1—N2—C11	5.0 (3)	C2—N1—C8A—N4	0.9 (3)
C8A—N1—C2—C3	1.0 (3)	C10—C8—C8A—N1	0.9 (4)
N1—C2—C3—N4	−2.3 (3)	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—N5	−179.2 (2)	C5—N4—C8A—N1	178.8 (2)
C3—N4—C5—N5	2.4 (3)	C3—N4—C8A—N1	−2.6 (3)
C8A—N4—C5—C6	0.3 (3)	C5—N4—C8A—C8	−2.1 (3)
C3—N4—C5—C6	−178.2 (2)	C3—N4—C8A—C8	176.5 (2)
N5—C5—C6—C9	2.8 (4)	C1—N2—C11—C16	175.8 (3)
N4—C5—C6—C9	−176.6 (2)	C1—N2—C11—C12	−2.6 (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)
C5—C6—C7—C8	−1.8 (3)	C16—C11—C12—C7	−179.5 (2)
C9—C6—C7—C8	176.6 (2)	N2—C11—C12—C7	−1.0 (3)
C5—C6—C7—C12	126.2 (2)	C6—C7—C12—C13	−55.6 (3)
C9—C6—C7—C12	−55.4 (3)	C8—C7—C12—C13	70.9 (3)
C5—C6—C7—C1	−122.3 (2)	C1—C7—C12—C13	−173.2 (2)
C9—C6—C7—C1	56.1 (3)	C6—C7—C12—C11	121.2 (2)
O1—C1—C7—C6	56.6 (3)	C8—C7—C12—C11	−112.3 (2)
N2—C1—C7—C6	−124.1 (2)	C1—C7—C12—C11	3.6 (2)
O1—C1—C7—C8	−65.2 (3)	C11—C12—C13—C14	0.0 (4)
N2—C1—C7—C8	114.1 (2)	C7—C12—C13—C14	176.5 (2)
O1—C1—C7—C12	175.6 (2)	C12—C13—C14—C15	2.3 (4)
N2—C1—C7—C12	−5.1 (2)	C12—C13—C14—Br1	−176.74 (18)
C6—C7—C8—C8A	0.0 (3)	C13—C14—C15—C16	−2.1 (4)
C12—C7—C8—C8A	−127.5 (2)	Br1—C14—C15—C16	176.9 (2)
C1—C7—C8—C8A	121.6 (2)	C12—C11—C16—C15	2.5 (4)
C6—C7—C8—C10	179.8 (2)	N2—C11—C16—C15	−175.7 (2)
C12—C7—C8—C10	52.4 (3)	C14—C15—C16—C11	−0.3 (4)
C1—C7—C8—C10	−58.5 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2*A*^{i}	0.90	1.98	2.855 (4)	165
N1—H1···O2*B*^{i}	0.90	2.00	2.87 (4)	160
N2—H2···O2*A*^{ii}	0.90	1.91	2.793 (5)	166
N2—H2···O2*B*^{ii}	0.90	1.94	2.82 (5)	166
N5—H5*A*···O3*A*^{iii}	0.90	2.20	3.034 (3)	155
N5—H5*B*···O3*A*	0.90	2.06	2.918 (3)	160
C2—H2*B*···N9^{iv}	0.99	2.59	3.469 (4)	148
C19*A*—H19*A*···N9	0.98	2.41	3.114 (5)	128
C19*A*—H19*C*···O1^{v}	0.98	2.52	3.392 (4)	148
C20*A*—H20*B*···O1^{v}	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*.