



Crystal structure of 9-(dibromomethyl)-1,1-difluoro-3,7-dimethyl-1*H*-[1,3,5,2]oxadiazaborinino[3,4-*a*][1,8]naphthyridin-11-ium-1-uide

Bang Zhong Wang, Jun Ping Zhou, Yong Zhou, Jian Song Luo and Shao Ming Chi*

College of Chemistry and Chemical Engineering, Yunnan Normal University, Kunming, 650500, People's Republic of China. *Correspondence e-mail: chishaoming@gmail.com

Received 9 September 2016

Accepted 18 October 2016

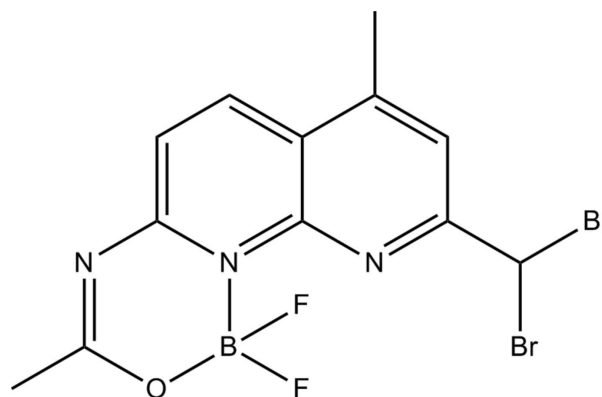
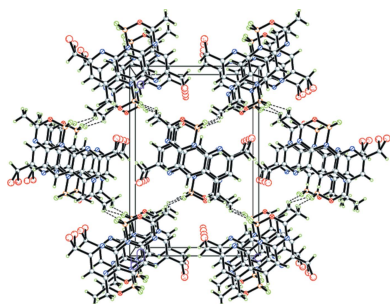
Edited by M. Weil, Vienna University of Technology, Austria

Keywords: crystal structure; 1,8-naphthyridine BF₂ complex; hydrogen bonding.**CCDC reference:** 1510400**Supporting information:** this article has supporting information at journals.iucr.org/e

The molecule of the title 1,8-naphthyridine-BF₂ derivative, C₁₂H₁₀BBr₂F₂N₃O, is located on a mirror plane running parallel to the entire ring system and the attached methyl C atoms. Individual molecules are stacked along the *b*-axis direction. The cohesion in the crystal structure is accomplished by C—H···F hydrogen bonds and additional off-set π – π interactions [centroid-to-centroid distance = 3.6392 (9) Å, slippage 0.472 Å], leading to the formation of a three-dimensional supramolecular network.

1. Chemical context

1,8-Naphthyridines are one of the most widely studied naphthyridine derivatives (Quan *et al.*, 2012). They can exhibit diverse coordination modes and have excellent optical properties or biological activities. They are also widely employed in the synthesis of metal complexes, *e.g.* for the identification of small molecules (Liang *et al.*, 2012; Tanaka *et al.*, 2012) or metal cations (Liu *et al.*, 2014), as luminescent materials and in biomedical fields (Eweas *et al.*, 2014; Di Braccio *et al.*, 2014). BF₂ compounds based on 1,8-naphthyridine ligands are used as fluorescent dyes due to their high fluorescence quantum yields (Zheng *et al.*, 2015) and high photochemical stabilities. Their characteristic absorption and emission spectra (Wu *et al.*, 2013; Li *et al.*, 2010) can be applied in many fields, such as cell imaging, as molecular probes, solar cells and so on (Boens *et al.*, 2012; Loudet & Burgess, 2007). However, only a few BF₂ compounds based on the 1,8-naphthyridine moiety have been described in the literature. In view of their importance, the title compound, 9-(dibromomethyl)-1,1-difluoro-3,7-dimethyl-1*H*-[1,3,5,2]oxadiazaborinino[3,4-*a*][1,8]naphthyridin-11-ium-1-uide, was synthesized and structurally characterized by single crystal X-ray diffraction.



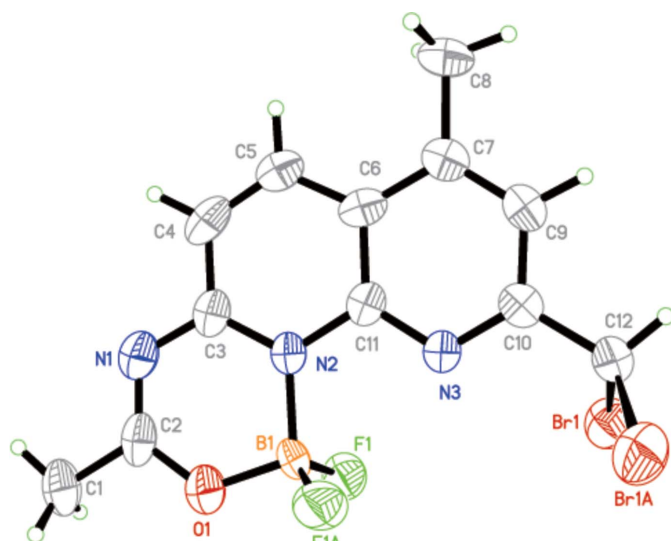


Figure 1
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (A) $x, -y + \frac{1}{2}, z$]

2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. The 1,8-naphthyridine ring system is fused with a mixed difluororoxadiazaborinino unit. The entire oxadiazaborininonaphthyridine ring system is planar due to its location on a mirror plane running parallel to the ring system. In addition, the C atoms of the two methyl groups (C8 and C1) as well as the C atom (C12) of the dibromomethyl group are located on the mirror plane, hence only two pairs of the methyl H atoms, the two Br atoms and the two F atoms are above and below this plane. The $F1-B1-F1^i$ and $Br1^i-C12-Br1$ angles [symmetry code: (i) $x, -y + \frac{1}{2}, z$] are $113.6(7)$ and $110.3(3)^\circ$, and the distances of the Br and F atoms to the plane are $1.5916(6)$ and $1.141(3)$ Å, respectively. The individual F–B bond length is $1.364(5)$ Å and the Br–C bond length $1.940(4)$ Å. Compared with the molecular structure of

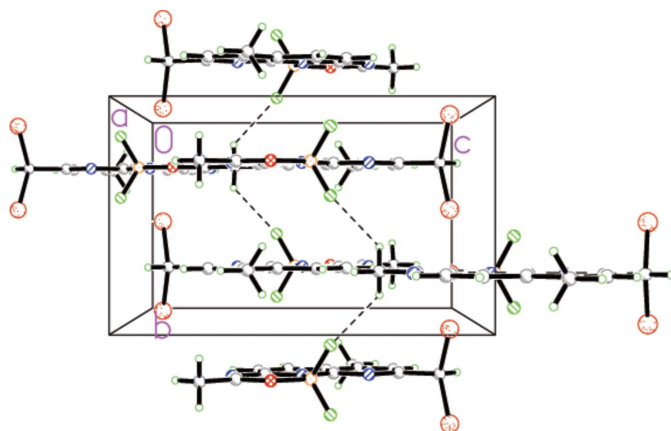


Figure 2
A view along the a axis of the crystal packing of the title compound. Hydrogen bonds are shown as dashed lines.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C1-H1B\cdots F1^i$	0.96	2.41	3.163 (6)	135

Symmetry code: (i) $-x + \frac{1}{2}, -y, z + \frac{1}{2}$.

a related compound (Wu *et al.*, 2012), the difference between the $F1-B1-F1^i$ angles is 2.16° , while the bond lengths and angles in the oxadiazaborine ring moiety of the two structures are almost the same.

3. Supramolecular features

In the crystal structure of the title compound, the molecules are stacked along the b -axis direction and linked into a three-dimensional network through $C-H\cdots F$ hydrogen bonds involving one of the methyl groups as acceptor H atoms (Fig. 2, Table 1). The cohesion in this network is reinforced *via* off-set π - π interactions [$Cg2\cdots Cg2^i = 3.6392(9)$ Å, interplanar distance = $3.6085(1)$ Å, slippage = 0.472 Å; $Cg2$ is the centroid of the $N2/C3-C6/C11$ ring; symmetry code: (i) $-x, -\frac{1}{2} + y, 2 - z$] (Fig. 3).

4. Database survey

Owing to the shortage of BF_2 compounds based on 1,8-naphthyridine derivatives, there are only a few examples of similar compounds in the literature. A search of the Cambridge Structural Database (CSD version 5.37; August 19, 2016; Groom *et al.*, 2016) revealed the structure of another very similar compound, *viz.* [N -(5,7-dimethyl-1,8-naphthyridin-2-yl)ethanimidato](difluoroborate) (CSD code MONGED; Du *et al.*, 2014).

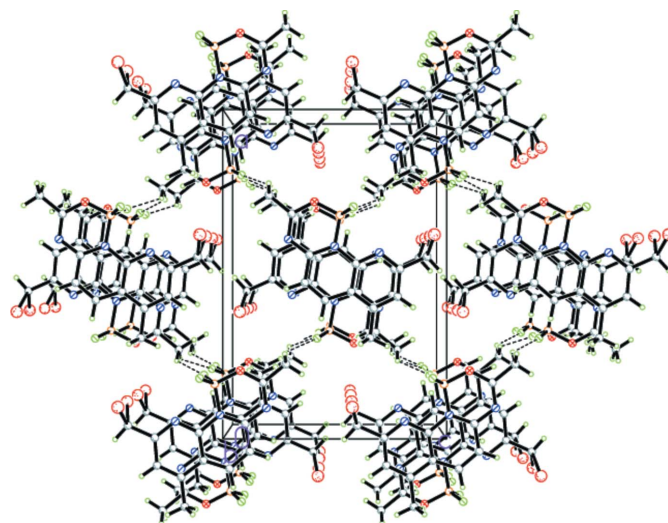


Figure 3
A view along the b axis of the crystal packing of the title compound. Hydrogen bonds are shown as dashed lines.

5. Synthesis and crystallization

BF₃·OEt₂ (2 ml, 16 mmol) was added dropwise to an ice-cooled solution of 2,6-lutidine (1 ml) and *N*-[7-(dibromo-methyl)-5-methyl-1,8-naphthyridin-2-yl]acetamide (0.37 g, 1 mmol) in anhydrous CH₂Cl₂ (80 ml) under a nitrogen atmosphere. After the mixture had been stirred for 24 h under ambient temperature, the reaction was quenched with 20 ml distilled water. The aqueous layer was extracted with CH₂Cl₂ (3 × 50 ml); the organic layer was dried with anhydrous Na₂SO₄ and the solvent removed under reduced pressure. The residue was purified by silica gel chromatography using CH₂Cl₂ as eluent to give the pure product as a bright white powder (yield 0.19 g, 45%). Yellow crystals of the title compound were obtained from its CH₂Cl₂ solution by slow evaporation at room temperature.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were placed in calculated positions and included in the final cycles of refinement using a riding-model approximation with C–H = 0.96 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms.

Acknowledgements

Support from ‘Spring Sunshine’ Plan of the Ministry of Education of China (grant No. Z2011125) and the National Natural Science Foundation of China (grant No. 21262049) is gratefully acknowledged.

References

Boens, N., Leen, V. & Dehaen, W. (2012). *Chem. Soc. Rev.* **41**, 1130–1172.
 Di Braccio, M., Grossi, G., Alfei, S., Ballabeni, V., Tognolini, M., Flammini, L., Giorgio, C., Bertoni, S. & Barocelli, E. (2014). *Eur. J. Med. Chem.* **86**, 394–405.
 Du, M. L., Hu, C. Y., Wang, L. F., Li, C., Han, Y. Y., Gan, X., Chen, Y., Mu, W. H., Huang, M. L. & Fu, W. F. (2014). *Dalton Trans.* **43**, 13924–13931.
 Eweas, A. F., Khalifa, N. M., Ismail, N. S., Al-Omar, M. A. & Soliman, A. M. M. (2014). *Med. Chem. Res.* **23**, 76–86.
 Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
 Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
 Li, H. J., Fu, W. F., Li, L., Gan, X., Mu, W. H., Chen, W. Q., Duan, X. M. & Song, H. B. (2010). *Org. Lett.* **12**, 2924–2927.

Table 2

Experimental details.

Crystal data	
Chemical formula	C ₁₂ H ₁₀ BBr ₂ F ₂ N ₃ O
<i>M_r</i>	420.86
Crystal system, space group	Orthorhombic, <i>Pnma</i>
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	17.161 (3), 7.2169 (14), 11.678 (2)
<i>V</i> (Å ³)	1446.3 (5)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	5.63
Crystal size (mm)	0.32 × 0.30 × 0.28
Data collection	
Diffractionmeter	Rigaku R-AXIS RAPID
Absorption correction	Multi-scan (<i>ABSCOR</i> ; Higashi, 1995)
<i>T_{min}</i> , <i>T_{max}</i>	0.266, 0.302
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	13517, 1765, 937
<i>R_{int}</i>	0.139
(sin θ/λ) _{max} (Å ⁻¹)	0.647
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.054, 0.120, 0.95
No. of reflections	1765
No. of parameters	122
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.50, -0.37

Computer programs: *PROCESS-AUTO* (Rigaku, 1998), *CrystalStructure* (Rigaku/MS, 2006), *SHELXS97*, *SHELXL97* and *XP* in *SHELXTL* (Sheldrick, 2008).

Liang, F., Lindsay, S. & Zhang, P. (2012). *Org. Biomol. Chem.* **10**, 8654–8659.
 Liu, X. J., Chen, M. X., Liu, Z. P., Yu, M. M., Wei, L. H. & Li, Z. X. (2014). *Tetrahedron*, **70**, 658–663.
 Loudet, A. & Burgess, K. (2007). *Chem. Rev.* **107**, 4891–4932.
 Quan, L., Chen, Y., Lv, X. J. & Fu, W. F. (2012). *Chem. Eur. J.* **18**, 14599–14604.
 Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
 Rigaku/MS (2006). *CrystalStructure*. Rigaku/MS, The Woodlands, Texas, USA.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Tanaka, K., Murakami, M., Jeon, J.-H. & Chujo, Y. (2012). *Org. Biomol. Chem.* **10**, 90–95.
 Wu, Y. Y., Chen, Y., Gou, G. Z., Mu, W. H., Lv, X. J., Du, M. L. & Fu, W. F. (2012). *Org. Lett.* **14**, 5226–5229.
 Wu, Y. Y., Chen, Y., Mu, W. H., Lv, X. J. & Fu, W. F. (2013). *J. Photochem. Photobiol. Chem.* **272**, 73–79.
 Zheng, J., Huang, F., Li, Y. J., Xu, T. W., Xu, H., Jia, J. H., Ye, Q. & Gao, J. R. (2015). *Dyes Pigments*, **113**, 502–509.

supporting information

Acta Cryst. (2016). E72, 1642-1644 [https://doi.org/10.1107/S2056989016016704]

Crystal structure of 9-(dibromomethyl)-1,1-difluoro-3,7-dimethyl-1*H*-[1,3,5,2]oxadiazaborinino[3,4-*a*][1,8]naphthyridin-11-ium-1-uide

Bang Zhong Wang, Jun Ping Zhou, Yong Zhou, Jian Song Luo and Shao Ming Chi

Computing details

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO* (Rigaku, 1998); data reduction: *CrystalStructure* (Rigaku/MSO, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

9-(Dibromomethyl)-1,1-difluoro-3,7-dimethyl-1*H*-[1,3,5,2]oxadiazaborinino[3,4-*a*][1,8]naphthyridin-11-ium-1-uide

Crystal data

C₁₂H₁₀BBr₂F₂N₃O

M_r = 420.86

Orthorhombic, *Pnma*

Hall symbol: -P 2ac 2n

a = 17.161 (3) Å

b = 7.2169 (14) Å

c = 11.678 (2) Å

V = 1446.3 (5) Å³

Z = 4

F(000) = 816

D_x = 1.933 Mg m⁻³

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 1765 reflections

θ = 3.1–26.0°

μ = 5.63 mm⁻¹

T = 293 K

Block, yellow

0.32 × 0.30 × 0.28 mm

Data collection

Rigaku R-AXIS RAPID
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan
(*ABSCOR*; Higashi, 1995)

T_{min} = 0.266, *T_{max}* = 0.302

13517 measured reflections

1765 independent reflections

937 reflections with *I* > 2σ(*I*)

R_{int} = 0.139

θ_{max} = 27.4°, θ_{min} = 3.3°

h = -22→22

k = -8→9

l = -15→15

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.054

wR(*F*²) = 0.120

S = 0.95

1765 reflections

122 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(*F_o*²) + (0.0519*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.50 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.37 \text{ e } \text{\AA}^{-3}$

Extinction correction: SHELXL,
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0042 (6)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.11449 (3)	0.02946 (8)	0.57510 (5)	0.0624 (3)
B1	0.1752 (5)	0.2500	0.9765 (7)	0.041 (2)
F1	0.19639 (16)	0.0919 (4)	0.9205 (3)	0.0585 (8)
N1	0.1041 (4)	0.2500	1.2022 (6)	0.0524 (16)
N2	0.0835 (3)	0.2500	1.0005 (5)	0.0349 (13)
N3	0.0640 (3)	0.2500	0.8049 (5)	0.0385 (14)
O1	0.2143 (3)	0.2500	1.0882 (5)	0.0558 (14)
C1	0.2326 (5)	0.2500	1.2869 (8)	0.063 (2)
H1A	0.2025	0.2500	1.3562	0.095*
H1B	0.2649	0.1414	1.2847	0.095*
C2	0.1794 (5)	0.2500	1.1872 (7)	0.0450 (19)
C3	0.0572 (4)	0.2500	1.1095 (7)	0.0408 (18)
C4	-0.0249 (5)	0.2500	1.1303 (8)	0.055 (2)
H4A	-0.0433	0.2500	1.2079	0.065*
C5	-0.0760 (4)	0.2500	1.0421 (8)	0.049 (2)
H5A	-0.1309	0.2500	1.0579	0.059*
C6	-0.0513 (4)	0.2500	0.9274 (8)	0.0417 (18)
C7	-0.1003 (4)	0.2500	0.8304 (7)	0.0435 (19)
C8	-0.1880 (4)	0.2500	0.8438 (8)	0.060 (2)
H8A	-0.2125	0.2500	0.7698	0.089*
H8B	-0.2036	0.1414	0.8854	0.089*
C9	-0.0662 (4)	0.2500	0.7256 (7)	0.0463 (19)
H9A	-0.0981	0.2500	0.6580	0.056*
C10	0.0160 (4)	0.2500	0.7152 (7)	0.0424 (18)
C11	0.0314 (4)	0.2500	0.9079 (6)	0.0349 (17)
C12	0.0518 (4)	0.2500	0.5979 (7)	0.050 (2)
H12A	0.0104	0.2500	0.5425	0.059*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0685 (4)	0.0646 (4)	0.0542 (5)	0.0055 (3)	0.0040 (3)	-0.0122 (3)

B1	0.037 (5)	0.055 (5)	0.029 (5)	0.000	-0.010 (4)	0.000
F1	0.0538 (17)	0.0646 (18)	0.057 (2)	0.0161 (15)	-0.0013 (15)	-0.0145 (17)
N1	0.062 (4)	0.059 (4)	0.037 (4)	0.000	0.004 (4)	0.000
N2	0.042 (3)	0.033 (3)	0.030 (4)	0.000	-0.002 (3)	0.000
N3	0.040 (3)	0.044 (3)	0.032 (4)	0.000	0.000 (3)	0.000
O1	0.055 (3)	0.076 (4)	0.036 (4)	0.000	-0.006 (3)	0.000
C1	0.079 (6)	0.068 (5)	0.042 (6)	0.000	-0.016 (5)	0.000
C2	0.073 (6)	0.031 (4)	0.031 (5)	0.000	-0.003 (4)	0.000
C3	0.056 (5)	0.033 (3)	0.034 (5)	0.000	0.004 (4)	0.000
C4	0.065 (5)	0.053 (4)	0.046 (6)	0.000	0.023 (5)	0.000
C5	0.044 (4)	0.051 (4)	0.053 (6)	0.000	0.011 (4)	0.000
C6	0.037 (4)	0.035 (3)	0.053 (5)	0.000	0.008 (4)	0.000
C7	0.040 (4)	0.036 (4)	0.055 (6)	0.000	-0.002 (4)	0.000
C8	0.036 (4)	0.063 (5)	0.080 (7)	0.000	0.004 (4)	0.000
C9	0.047 (4)	0.047 (4)	0.045 (6)	0.000	-0.009 (4)	0.000
C10	0.043 (4)	0.040 (4)	0.044 (5)	0.000	-0.004 (4)	0.000
C11	0.046 (4)	0.024 (3)	0.035 (5)	0.000	0.004 (3)	0.000
C12	0.046 (4)	0.063 (5)	0.039 (6)	0.000	-0.006 (4)	0.000

Geometric parameters (Å, °)

Br1—C12	1.940 (4)	C4—C5	1.353 (11)
B1—F1	1.364 (5)	C4—H4A	0.9600
B1—F1 ⁱ	1.364 (5)	C5—C6	1.406 (11)
B1—O1	1.467 (9)	C5—H5A	0.9600
B1—N2	1.599 (10)	C6—C7	1.410 (11)
N1—C2	1.303 (9)	C6—C11	1.437 (9)
N1—C3	1.349 (9)	C7—C9	1.357 (10)
N2—C3	1.351 (9)	C7—C8	1.514 (9)
N2—C11	1.403 (9)	C8—H8A	0.9600
N3—C11	1.327 (8)	C8—H8B	0.9600
N3—C10	1.332 (9)	C9—C10	1.416 (9)
O1—C2	1.302 (9)	C9—H9A	0.9600
C1—C2	1.481 (11)	C10—C12	1.501 (10)
C1—H1A	0.9600	C12—Br1 ⁱ	1.940 (4)
C1—H1B	0.9600	C12—H12A	0.9600
C3—C4	1.431 (10)		
F1—B1—F1 ⁱ	113.6 (7)	C6—C5—H5A	118.7
F1—B1—O1	107.7 (4)	C5—C6—C7	125.8 (6)
F1 ⁱ —B1—O1	107.7 (4)	C5—C6—C11	116.7 (7)
F1—B1—N2	110.2 (4)	C7—C6—C11	117.5 (7)
F1 ⁱ —B1—N2	110.2 (4)	C9—C7—C6	117.8 (7)
O1—B1—N2	107.1 (6)	C9—C7—C8	121.5 (7)
C2—N1—C3	118.9 (7)	C6—C7—C8	120.7 (7)
C3—N2—C11	120.9 (6)	C7—C8—H8A	110.0
C3—N2—B1	119.6 (6)	C7—C8—H8B	109.2
C11—N2—B1	119.5 (6)	H8A—C8—H8B	109.5

C11—N3—C10	116.9 (6)	C7—C9—C10	120.5 (7)
C2—O1—B1	125.4 (6)	C7—C9—H9A	119.7
C2—C1—H1A	109.3	C10—C9—H9A	119.8
C2—C1—H1B	109.5	N3—C10—C9	123.2 (7)
H1A—C1—H1B	109.5	N3—C10—C12	117.7 (6)
N1—C2—O1	125.2 (7)	C9—C10—C12	119.1 (7)
N1—C2—C1	120.4 (8)	N3—C11—N2	115.5 (6)
O1—C2—C1	114.4 (7)	N3—C11—C6	124.0 (7)
N2—C3—N1	123.9 (7)	N2—C11—C6	120.5 (7)
N2—C3—C4	119.2 (7)	C10—C12—Br1 ⁱ	110.6 (3)
N1—C3—C4	116.9 (7)	C10—C12—Br1	110.6 (3)
C5—C4—C3	120.7 (8)	Br1 ⁱ —C12—Br1	110.3 (3)
C5—C4—H4A	120.4	C10—C12—H12A	108.2
C3—C4—H4A	119.0	Br1 ⁱ —C12—H12A	108.5
C4—C5—C6	122.0 (7)	Br1—C12—H12A	108.5
C4—C5—H5A	119.3		

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1B ⁱⁱ ⋯F1 ⁱⁱ	0.96	2.41	3.163 (6)	135

Symmetry code: (ii) $-x+1/2, -y, z+1/2$.