Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structure and fluorescence study of (*μ*-*N*-[(3,5-dimethyl-1*H*-pyrrol-2-yl)methylidene]-*N*-{4-[(3,5-dimethyl-1*H*-pyrrol-2-yl)methylideneazaniumyl]phenyl}azanium)bis[difluoridoboron(IV)]

Xiaoxue Liu, Tuo Li and Zhenming Yin*

College of Chemistry, Tianjin Key Laboratory of Structure and Performance for Functional Molecule, Tianjin Normal University, Tianjin 300387, People's Republic of China. *Correspondence e-mail: tjyinzm@aliyun.com

Received 2 December 2020
Accepted 13 January 2021

Edited by J. Ellena, Universidade de São Paulo, Brazil

Keywords: 2-iminopyrrole; BF_2 complex; crystal structure; fluorescence.

CCDC reference: 2055687

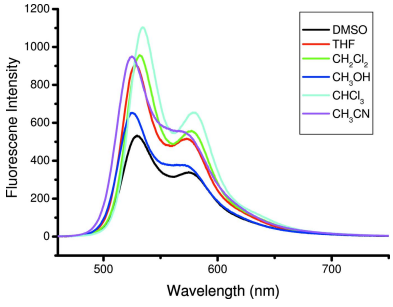
Supporting information: this article has supporting information at journals.iucr.org/e

The title molecule, $C_{20}H_{20}B_2F_4N_4$, assumes a planar conformation with all atoms apart from the F atoms lying on the symmetry plane. Each boron atom is four-coordinated by two fluorine atoms, a pyrrole N atom and an imine N atom. Both imine CH═N groups adopt a *trans* conformation. In the crystal, the molecules self-assemble into a pillar structure through C—H···F hydrogen bonds and *π*–*π* interactions. The UV–vis spectrum and fluorescence spectra of the title compound are also reported.

1. Chemical context

Fluorescent materials are gradually becoming a necessity in modern chemistry and biology because of their unique advantages in the characterization of life activities in living organisms (Zhang *et al.*, 2019). Boron-dipyrromethene (BODIPY) is a frequently reported fluorescent structure (Boens *et al.*, 2015). Its planar structure endows BODIPY compounds with strong fluorescence emission under the action of excitation light. Such compounds also have high molar absorption coefficient, good light stability and excitation wavelengths in the visible to near infrared region. In addition, their structures can easily be modified and they are not easily affected by the environment (Loudet & Burgess, 2007). The success of BODIPY dyes has led to research on similar structures such as aza-BODIPY structures (Bodio & Goze, 2019), boron complexes of iminopyrrolide ligands (BOIMPY; Suresh *et al.*, 2012, 2015; Lee *et al.*, 2016), bis(difluoroboron)-1,2-bis{(pyrrol-2-yl)methylene}hydrazine (BOPHY; Boodts *et al.*, 2018) structures and other novel organoboron fluorescence materials (Frath *et al.*, 2014).

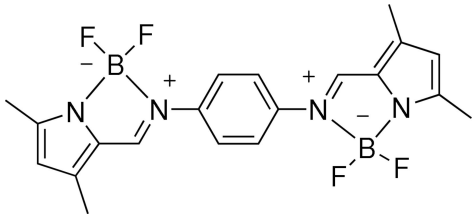
BOIMPY has a similar structure to BODIPY, in which the pyrrole ring is located in the same plane as the aromatic ring, the boron atom and the methylene bridge. More importantly, BOIMPY has the advantage of lower molecular symmetry, which can overcome the shortcoming of the short Stokes shifts of BODIPY (Lee *et al.*, 2016). In contrast to BODIPY, studies on BOIMPY are still rare. Herein, we report the synthesis, crystal structure and spectroscopic properties of a new BOIMPY compound, bis(difluoroboron)bis(pyrrol-2-yl)-methylenediaminophenylene.



2. Structural commentary

The structure of the title compound is shown in Fig. 1. All atoms lie on the symmetry plane except for the F atoms, which

deviate from it by 1.136 (1) Å (F1) and 1.135 (1) Å (F2) on the same side of the molecule. Each boron atom is four-coordinated by two fluorine atoms, a pyrrole N atom and an imine N atom. The N1—B1, N2—B1, N3—B2 and N4—B2 bond lengths [1.544 (4), 1.604 (4), 1.610 (4) and 1.538 (4) Å, respectively] are longer than the accepted mean value for a B—N bond (1.54–1.55Å) in BODIPY compounds reported in the literature (Madhu & Ravikanth, 2014). The two imine CH═N groups adopt a *trans* conformation and at 1.339 (4) and 1.321 (4) Å their bond lengths are longer than that in the free imino-pyrrole ligand (1.263 Å; Xu *et al.*, 2010) while the C8—N2 and C11—N3 bonds [both 1.408 (4) Å] are shorter than in the free imino-pyrrole ligand (1.424 Å; Xu *et al.*, 2010).



3. Supramolecular features

In the crystal, the molecules are linked by C6—H6*B*···F2 hydrogen bonds between methyl group and the fluorine atom (Table 1), and π–π interactions between benzene rings [*Cg*1···*Cg*1($-x+1, y+\frac{1}{2}, -z+1$) = 3.7521 (2) Å; *Cg*1 is the centroid of the C8–C13 ring] into one-dimensional pillars along the *b*-axis direction. Within the pillar, neighbouring molecules are oriented in opposite directions (Fig. 2). The pillars are held together by van der Waals interactions, forming a herringbone structure. A perspective view of the crystal packing within the unit cell is depicted in Fig. 3.

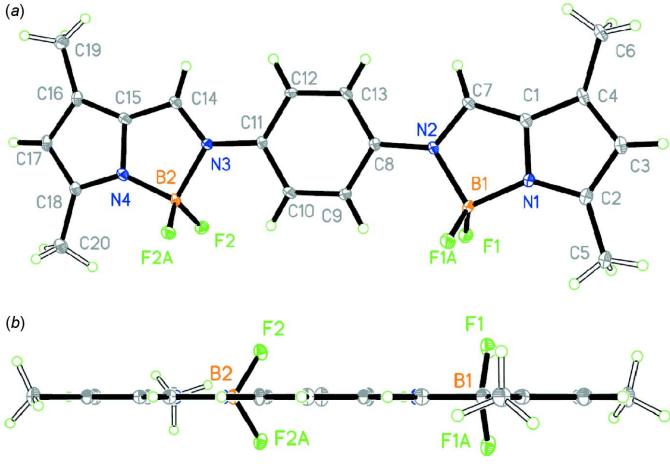


Figure 1
ORTEP diagrams for the title compound, (*a*) top view and (*b*) side view, with displacement ellipsoids drawn at the 30% probability level.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6*B*···F2^{i}	0.96	2.49	3.336 (3)	147

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

4. Database survey

A search in the Cambridge Structural Database (CSD, version 5.41, update of November 2019; Groom *et al.*, 2016) returned 21 entries for iminopyrrolyl boron complexes. Two diphenylboron analogues of the title compound were reported by Gomes and coworkers [KEDHIM (Suresh *et al.*, 2012) and

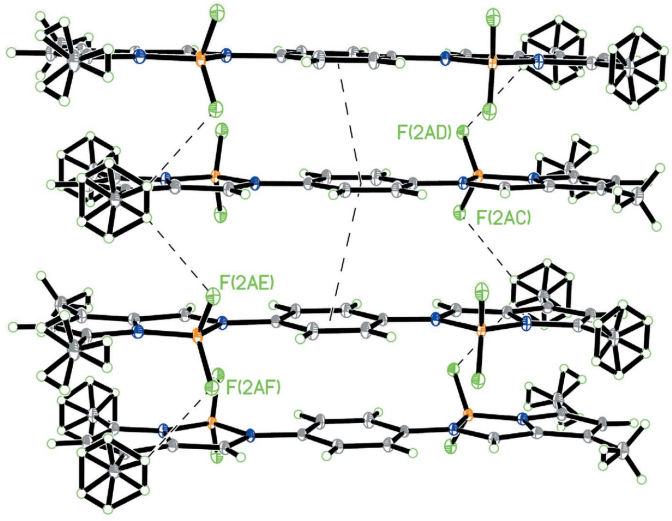


Figure 2
Part of the pillar structure showing molecules linked by C—H···F^{i} hydrogen bonds and π–π interaction [symmetry code: (i) $-x+1, y+\frac{1}{2}, -z+1$].

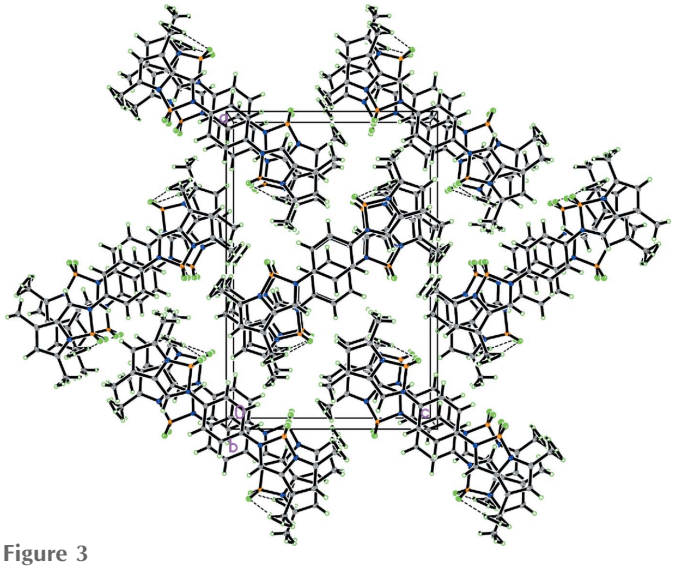


Figure 3
Part of the packing diagram for the title compound.

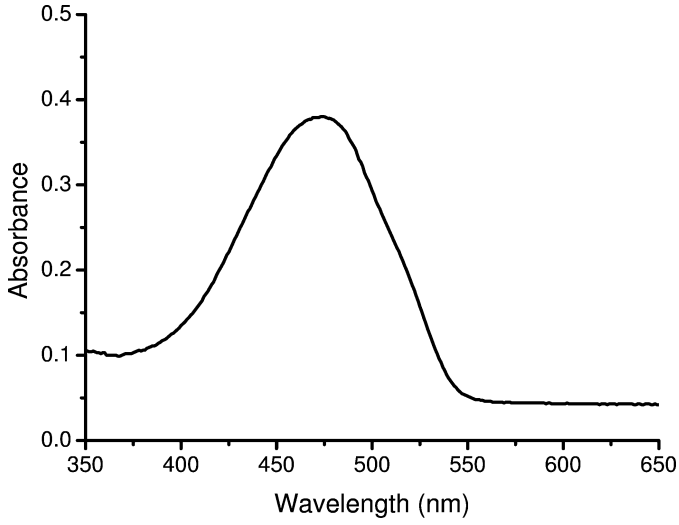


Figure 4
UV–vis spectrum of the title compound in THF solution (1×10^{-5} *M*).

TUJFOV (Suresh *et al.*, 2015)]. In their crystals, the respective dihedral angles between the 2-formiminopyrrolyl unit and the phenyl ring are −47.2 (3) and 46.1 (11)°.

5. UV–vis spectrum and fluorescence spectra

The UV–vis spectrum and fluorescence spectra of the title compound are shown in Figs. 4 and 5, respectively. The UV–vis spectrum is solvent independent. A THF solution of the title compound displays intense broad absorption at 474 nm, which can be assigned to the n–π^* transition of the iminopyrrolyl group. The title compound has two emission peaks at 528 nm and 574 nm. It can be seen that the fluorescence intensity of title compound is greatly affected by the solvents. In the polar solvent DMSO, the fluorescence intensity is much weaker than that in the apolar solvent $CHCl_3$, which is similar to a previous report (Li *et al.*, 2018). The title compound shows substantial

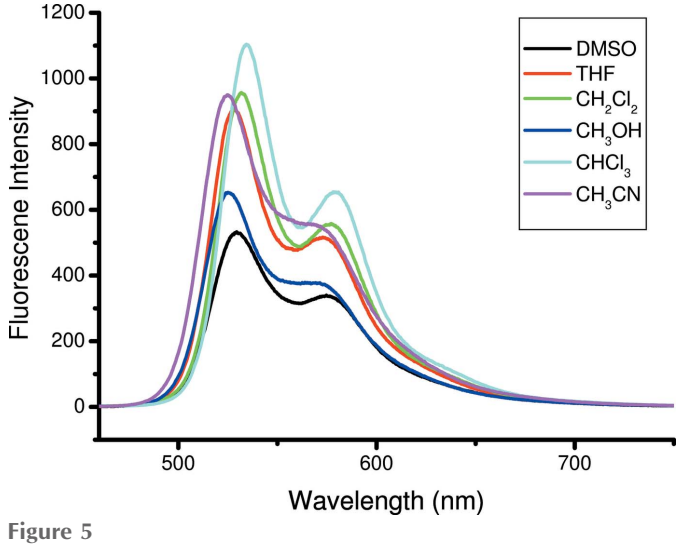


Figure 5
Fluorescence spectra of the title compound in different solutions (1×10^{-5} *M*).

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{20}H_{20}B_2F_4N_4$
M_r	414.02
Crystal system, space group	Orthorhombic, *Pnma*
Temperature (K)	110
a, *b*, *c* (Å)	20.2495 (9), 6.8046 (5), 13.4969 (5)
V (Å^3)	1859.74 (17)
Z	4
Radiation type	Cu *Kα*
μ (mm^{-1})	0.99
Crystal size (mm)	0.25 × 0.14 × 0.13
Data collection	
Diffractometer	Rigaku Oxford Diffraction SuperNova, Dual, Cu at zero, AtlasS2
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.478, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4486, 1815, 1375
R_{int}	0.046
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.597
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.126, 1.01
No. of reflections	1815
No. of parameters	179
No. of restraints	6
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.27, −0.32

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

bathochromic shifts in both absorption and emission when compared to the diphenylboron analogues reported by Gomes and coworkers (Suresh *et al.*, 2012), which can be ascribed to the planar structure of the title compound.

6. Synthesis and crystallization

To a solution of bis(pyrrol-2-yl)methylenediaminophenylene (1 mmol, 0.32 g) and triethylamine (4.2 mmol, 6 mL) in dry dichloromethane (15 mL) was slowly added boron trifluoride ethyl ether (7.2 mmol, 2 mL). The resulting solution was stirred overnight, and then saturated potassium carbonate solution was added and stirred for 30 minutes. The resulting solution was extracted and evaporated under vacuum to dryness. The residue was purified by column chromatography eluting with CH_2Cl_2 and petroleum ether (*v*:*v* 1:2) to give an orange product, m.p. 435 K. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.101 (*s*, 2H, ═CH–), 7.519 (*s*, 4H, Ar C—H), 6.007 (*s*, 2H, pyrrole CH), 2.412 (*s*, 6H, –CH_3), 2.270 (*s*, 6H, –CH_3). HRMS (ESI) *m*/*z*: calculated for $C_{20}H_{20}B_2F_4N_4$, $(M + H)^+$ 415.01521; found 415.01533.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were located in a difference-Fourier map, placed in calculated positions (C—H = 0.93 or 0.96 Å) and included in the final cycles of refinement using

a riding model, with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C-methyl). Idealized methyl groups were refined as rotating groups.

Funding information

Funding for this research was provided by: National Natural Science Foundation of China (award No. 21172174).

References

Bodio, E. & Goze, C. (2019). *Dyes Pigments*, **160**, 700–710.
Boens, N., Verbelen, B. & Dehaen, W. (2015). *Eur. J. Org. Chem.* pp. 6577–6595.
Boodts, S., Fron, E., Hofkens, J. & Dehaen, W. (2018). *Coord. Chem. Rev.* **371**, 1–10.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Frath, D., Massue, J., Ulrich, G. & Ziessel, R. (2014). *Angew. Chem. Int. Ed.* **53**, 2290–2310.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Lee, B., Park, B. G., Cho, W., Lee, H. Y., Olasz, A., Chen, C.-H., Park, S. B. & Lee, D. (2016). *Chem. Eur. J.* **22**, 17321–17328.
Li, T., Xu, L. & Yin, Z. (2018). *Chinese J. Struct. Chem*, **37**, 809–904.
Loudet, A. & Burgess, K. (2007). *Chem. Rev.* **107**, 4891–4932.
Madhu, I. & Ravikanth, M. (2014). *Inorg. Chem.* **53**, 1646–1653.
Rigaku, OD (2015). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Suresh, D., Gomes, C. S. B., Gomes, P. T., Di Paolo, R. E., Macanica, A. L., Calhorda, M. J., Charas, A., Morgado, J. & Duarte, M. T. (2012). *Dalton Trans.* **41**, 8902–8905.
Suresh, D., Gomes, C. S. B., Lopes, P. S., Figueira, C. A., Ferreira, B., Gomes, P. T., Di Paolo, R. E., Maçanita, A. L., Duarte, M. T., Charas, A., Morgado, J., Vila-Viçosa, D. & Calhorda, M. J. (2015). *Chem. Eur. J.* **21**, 9133–9149.
Xu, L., Liu, S. Y. & Yin, Z. (2010). *Chin. J. Struct. Chem.* **29**, 613–617.
Zhang, J., Chai, X., He, X.-P., Kim, H.-J., Yoon, J. & Tian, H. (2019). *Chem. Soc. Rev.* **48**, 683–722.

supporting information

Acta Cryst. (2021). E**77**, 126-129 [https://doi.org/10.1107/S2056989021000463]

Crystal structure and fluorescence study of (*μ*-*N*-[(3,5-dimethyl-1*H*-pyrrol-2-yl)methylidene]-*N*-{4-[(3,5-dimethyl-1*H*-pyrrol-2-yl)methylideneazaniumyl]phenyl}azanium)bis[difluoridoboron(IV)]

Xiaoxue Liu, Tuo Li and Zhenming Yin

Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: ShelXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

(*μ*-*N*-[(3,5-Dimethyl-1*H*-pyrrol-2-yl)methylidene]*N*-{{4-[(3,5-dimethyl-1*H*-pyrrol-2-yl)methylideneazaniumyl]phenyl}azanium)bis[difluoridoboron(IV)]

Crystal data

$C_{20}H_{20}B_2F_4N_4$
M_r = 414.02
Orthorhombic, *Pnma*
a = 20.2495 (9) Å
b = 6.8046 (5) Å
c = 13.4969 (5) Å
V = 1859.74 (17) Å^3
Z = 4
F(000) = 856
D_x = 1.479 Mg m^{-3}
Cu *Kα* radiation, *λ* = 1.54184 Å
Cell parameters from 1337 reflections
θ = 3.9–73.0°
μ = 0.99 mm^{-1}
T = 110 K
Block, brown
0.25 × 0.14 × 0.13 mm

Data collection

Rigaku Oxford Diffraction SuperNova, Dual, Cu at zero, AtlasS2 diffractometer
Radiation source: micro-focus sealed X-ray tube, SuperNova (Cu) X-ray Source
Mirror monochromator
Detector resolution: 5.2740 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2015)
T_{min} = 0.478, T_{max} = 1.000
4486 measured reflections
1815 independent reflections
1375 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 67.1°, θ_{min} = 3.9°
h = −17→24
k = −7→8
l = −13→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.126
S = 1.01
1815 reflections
179 parameters
6 restraints
Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0648P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
F1	0.47574 (6)	0.5830 (2)	0.79642 (10)	0.0251 (3)	
F2	0.27560 (6)	0.58327 (19)	0.39551 (9)	0.0214 (3)	
N1	0.57949 (12)	0.750000	0.83332 (18)	0.0181 (6)	
N2	0.54122 (11)	0.750000	0.66808 (19)	0.0152 (5)	
N3	0.37529 (11)	0.750000	0.33323 (18)	0.0146 (5)	
N4	0.27854 (11)	0.750000	0.2358 (2)	0.0167 (6)	
C1	0.63149 (14)	0.750000	0.7670 (2)	0.0175 (6)	
C2	0.60426 (15)	0.750000	0.9262 (2)	0.0196 (7)	
C3	0.67356 (15)	0.750000	0.9190 (2)	0.0215 (7)	
H3	0.702742	0.750000	0.972227	0.026*	
C4	0.69141 (14)	0.750000	0.8194 (2)	0.0183 (6)	
C5	0.56119 (16)	0.750000	1.0158 (2)	0.0256 (7)	
H5A	0.550754	0.617060	1.033709	0.038*	0.5
H5B	0.521163	0.820249	1.001678	0.038*	0.5
H5C	0.583911	0.812692	1.069602	0.038*	0.5
C6	0.76010 (14)	0.750000	0.7777 (3)	0.0223 (7)	
H6A	0.788406	0.827009	0.819538	0.034*	0.5
H6B	0.759521	0.805418	0.712325	0.034*	0.5
H6C	0.776318	0.617573	0.774672	0.034*	0.5
C7	0.60731 (14)	0.750000	0.6711 (2)	0.0174 (6)	
H7	0.633991	0.750000	0.615007	0.021*	
C8	0.50243 (14)	0.750000	0.5815 (2)	0.0153 (6)	
C9	0.43380 (14)	0.750000	0.5922 (2)	0.0190 (7)	
H9	0.415253	0.750000	0.655206	0.023*	
C10	0.39326 (14)	0.750000	0.5099 (2)	0.0212 (7)	
H10	0.347688	0.750000	0.518466	0.025*	
C11	0.41924 (14)	0.750000	0.4141 (2)	0.0150 (6)	
C12	0.48845 (14)	0.750000	0.4035 (2)	0.0169 (6)	
H12	0.507081	0.750000	0.340566	0.020*	
C13	0.52863 (13)	0.750000	0.4856 (2)	0.0183 (7)	
H13	0.574212	0.750000	0.477137	0.022*	
C14	0.39064 (13)	0.750000	0.2381 (2)	0.0172 (6)	
H14	0.433769	0.750000	0.214397	0.021*	
C15	0.33467 (13)	0.750000	0.1766 (2)	0.0169 (6)	

C16	0.31589 (16)	0.750000	0.0770 (2)	0.0199 (7)	
C17	0.24674 (15)	0.750000	0.0784 (2)	0.0208 (7)	
H17	0.219502	0.750000	0.022896	0.025*	
C18	0.22542 (14)	0.750000	0.1769 (2)	0.0192 (7)	
C19	0.35899 (15)	0.750000	−0.0125 (2)	0.0260 (7)	
H19A	0.358113	0.622295	−0.042734	0.039*	0.5
H19B	0.403441	0.781639	0.006382	0.039*	0.5
H19C	0.343184	0.846066	−0.058910	0.039*	0.5
C20	0.15647 (15)	0.750000	0.2183 (3)	0.0276 (8)	
H20A	0.138964	0.881066	0.216494	0.041*	0.5
H20B	0.157389	0.704099	0.285535	0.041*	0.5
H20C	0.129033	0.664835	0.179283	0.041*	0.5
B1	0.51243 (16)	0.750000	0.7788 (2)	0.0164 (7)	
B2	0.29629 (15)	0.750000	0.3467 (3)	0.0163 (7)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0203 (6)	0.0351 (8)	0.0197 (6)	−0.0089 (6)	−0.0011 (5)	0.0052 (6)
F2	0.0177 (6)	0.0275 (7)	0.0190 (6)	−0.0052 (5)	0.0007 (5)	0.0037 (6)
N1	0.0159 (12)	0.0255 (14)	0.0128 (12)	0.000	−0.0019 (10)	0.000
N2	0.0108 (10)	0.0211 (13)	0.0137 (12)	0.000	−0.0022 (10)	0.000
N3	0.0109 (11)	0.0196 (12)	0.0133 (12)	0.000	0.0000 (10)	0.000
N4	0.0114 (11)	0.0199 (13)	0.0187 (13)	0.000	−0.0012 (10)	0.000
C1	0.0144 (13)	0.0195 (15)	0.0186 (15)	0.000	−0.0019 (12)	0.000
C2	0.0233 (15)	0.0194 (15)	0.0163 (15)	0.000	−0.0034 (13)	0.000
C3	0.0203 (15)	0.0230 (16)	0.0213 (15)	0.000	−0.0064 (13)	0.000
C4	0.0147 (13)	0.0166 (14)	0.0235 (15)	0.000	−0.0078 (12)	0.000
C5	0.0239 (14)	0.0358 (19)	0.0169 (15)	0.000	−0.0045 (13)	0.000
C6	0.0140 (13)	0.0262 (17)	0.0267 (17)	0.000	−0.0062 (13)	0.000
C7	0.0115 (13)	0.0221 (15)	0.0185 (15)	0.000	−0.0007 (12)	0.000
C8	0.0136 (13)	0.0182 (14)	0.0142 (15)	0.000	−0.0024 (11)	0.000
C9	0.0136 (13)	0.0309 (17)	0.0126 (14)	0.000	0.0015 (12)	0.000
C10	0.0099 (12)	0.0345 (17)	0.0193 (16)	0.000	0.0000 (12)	0.000
C11	0.0128 (13)	0.0179 (14)	0.0144 (14)	0.000	−0.0024 (11)	0.000
C12	0.0123 (13)	0.0259 (15)	0.0124 (14)	0.000	0.0029 (11)	0.000
C13	0.0085 (12)	0.0255 (16)	0.0209 (16)	0.000	−0.0008 (12)	0.000
C14	0.0118 (13)	0.0200 (15)	0.0198 (15)	0.000	−0.0010 (12)	0.000
C15	0.0119 (12)	0.0179 (14)	0.0209 (16)	0.000	0.0006 (12)	0.000
C16	0.0213 (14)	0.0212 (15)	0.0173 (14)	0.000	−0.0064 (13)	0.000
C17	0.0196 (14)	0.0264 (17)	0.0166 (15)	0.000	−0.0093 (13)	0.000
C18	0.0158 (14)	0.0235 (16)	0.0183 (15)	0.000	−0.0044 (12)	0.000
C19	0.0229 (15)	0.0370 (18)	0.0182 (16)	0.000	−0.0004 (13)	0.000
C20	0.0148 (14)	0.045 (2)	0.0234 (17)	0.000	−0.0037 (13)	0.000
B1	0.0160 (15)	0.0232 (18)	0.0100 (16)	0.000	−0.0018 (13)	0.000
B2	0.0092 (14)	0.0238 (18)	0.0158 (15)	0.000	−0.0036 (13)	0.000

Geometric parameters (Å, º)

F1—B1	1.378 (2)	C6—H6C	0.9600
F2—B2	1.377 (2)	C7—H7	0.9300
N1—C1	1.382 (4)	C8—C9	1.397 (4)
N1—C2	1.350 (4)	C8—C13	1.399 (4)
N1—B1	1.544 (4)	C9—H9	0.9300
N2—C7	1.339 (4)	C9—C10	1.381 (4)
N2—C8	1.408 (4)	C10—H10	0.9300
N2—B1	1.604 (4)	C10—C11	1.396 (4)
N3—C11	1.408 (4)	C11—C12	1.409 (4)
N3—C14	1.321 (4)	C12—H12	0.9300
N3—B2	1.610 (4)	C12—C13	1.374 (4)
N4—C15	1.389 (4)	C13—H13	0.9300
N4—C18	1.338 (4)	C14—H14	0.9300
N4—B2	1.538 (4)	C14—C15	1.404 (4)
C1—C4	1.404 (4)	C15—C16	1.398 (4)
C1—C7	1.384 (4)	C16—C17	1.400 (4)
C2—C3	1.407 (4)	C16—C19	1.491 (5)
C2—C5	1.491 (5)	C17—H17	0.9300
C3—H3	0.9300	C17—C18	1.398 (5)
C3—C4	1.393 (5)	C18—C20	1.504 (4)
C4—C6	1.500 (4)	C19—H19A	0.9600
C5—H5A	0.9600	C19—H19B	0.9600
C5—H5B	0.9600	C19—H19C	0.9600
C5—H5C	0.9600	C20—H20A	0.9600
C6—H6A	0.9600	C20—H20B	0.9600
C6—H6B	0.9600	C20—H20C	0.9600

C1—N1—B1	111.2 (2)	N3—C11—C12	123.4 (3)
C2—N1—C1	108.6 (2)	C10—C11—N3	118.7 (2)
C2—N1—B1	140.2 (3)	C10—C11—C12	117.9 (3)
C7—N2—C8	125.6 (3)	C11—C12—H12	119.7
C7—N2—B1	109.6 (2)	C13—C12—C11	120.5 (3)
C8—N2—B1	124.8 (2)	C13—C12—H12	119.7
C11—N3—B2	122.7 (2)	C8—C13—H13	119.3
C14—N3—C11	127.2 (2)	C12—C13—C8	121.4 (3)
C14—N3—B2	110.1 (2)	C12—C13—H13	119.3
C15—N4—B2	111.6 (2)	N3—C14—H14	123.7
C18—N4—C15	108.4 (3)	N3—C14—C15	112.6 (3)
C18—N4—B2	140.0 (3)	C15—C14—H14	123.7
N1—C1—C4	109.4 (3)	N4—C15—C14	108.7 (3)
N1—C1—C7	109.6 (2)	N4—C15—C16	109.3 (2)
C7—C1—C4	140.9 (3)	C16—C15—C14	142.0 (3)
N1—C2—C3	107.9 (3)	C15—C16—C17	105.0 (3)
N1—C2—C5	122.4 (3)	C15—C16—C19	128.4 (3)
C3—C2—C5	129.8 (3)	C17—C16—C19	126.6 (3)
C2—C3—H3	125.5	C16—C17—H17	125.6

C4—C3—C2	109.0 (3)	C18—C17—C16	108.7 (3)
C4—C3—H3	125.5	C18—C17—H17	125.6
C1—C4—C6	127.8 (3)	N4—C18—C17	108.5 (3)
C3—C4—C1	105.2 (3)	N4—C18—C20	121.7 (3)
C3—C4—C6	127.1 (3)	C17—C18—C20	129.8 (3)
C2—C5—H5A	109.5	C16—C19—H19A	109.5
C2—C5—H5B	109.5	C16—C19—H19B	109.5
C2—C5—H5C	109.5	C16—C19—H19C	109.5
H5A—C5—H5B	109.5	H19A—C19—H19B	109.5
H5A—C5—H5C	109.5	H19A—C19—H19C	109.5
H5B—C5—H5C	109.5	H19B—C19—H19C	109.5
C4—C6—H6A	109.5	C18—C20—H20A	109.5
C4—C6—H6B	109.5	C18—C20—H20B	109.5
C4—C6—H6C	109.5	C18—C20—H20C	109.5
H6A—C6—H6B	109.5	H20A—C20—H20B	109.5
H6A—C6—H6C	109.5	H20A—C20—H20C	109.5
H6B—C6—H6C	109.5	H20B—C20—H20C	109.5
N2—C7—C1	112.5 (3)	F1—B1—F1^{i}	111.1 (3)
N2—C7—H7	123.8	F1—B1—N1	113.08 (16)
C1—C7—H7	123.8	F1^{i}—B1—N1	113.08 (16)
C9—C8—N2	118.0 (3)	F1—B1—N2	110.87 (17)
C9—C8—C13	118.2 (3)	F1^{i}—B1—N2	110.87 (17)
C13—C8—N2	123.8 (3)	N1—B1—N2	97.1 (2)
C8—C9—H9	119.7	F2—B2—F2^{i}	110.9 (2)
C10—C9—C8	120.6 (3)	F2—B2—N3	110.86 (15)
C10—C9—H9	119.7	F2^{i}—B2—N3	110.86 (15)
C9—C10—H10	119.3	F2—B2—N4	113.23 (15)
C9—C10—C11	121.4 (3)	F2^{i}—B2—N4	113.23 (15)
C11—C10—H10	119.3	N4—B2—N3	97.0 (2)

N1—C1—C4—C3	0.000 (1)	C11—N3—C14—C15	180.000 (1)
N1—C1—C4—C6	180.000 (1)	C11—N3—B2—F2^{i}	61.82 (18)
N1—C1—C7—N2	0.000 (1)	C11—N3—B2—F2	−61.81 (18)
N1—C2—C3—C4	0.000 (1)	C11—N3—B2—N4	180.000 (1)
N2—C8—C9—C10	180.000 (1)	C11—C12—C13—C8	0.000 (1)
N2—C8—C13—C12	180.000 (1)	C13—C8—C9—C10	0.000 (1)
N3—C11—C12—C13	180.000 (1)	C14—N3—C11—C10	180.000 (1)
N3—C14—C15—N4	0.000 (1)	C14—N3—C11—C12	0.000 (1)
N3—C14—C15—C16	180.000 (1)	C14—N3—B2—F2	118.19 (18)
N4—C15—C16—C17	0.000 (1)	C14—N3—B2—F2^{i}	−118.18 (18)
N4—C15—C16—C19	180.000 (1)	C14—N3—B2—N4	0.000 (1)
C1—N1—C2—C3	0.000 (1)	C14—C15—C16—C17	180.000 (1)
C1—N1—C2—C5	180.000 (1)	C14—C15—C16—C19	0.000 (1)
C1—N1—B1—F1^{i}	−116.3 (2)	C15—N4—C18—C17	0.000 (1)
C1—N1—B1—F1	116.3 (2)	C15—N4—C18—C20	180.000 (1)
C1—N1—B1—N2	0.000 (1)	C15—N4—B2—F2^{i}	116.33 (18)
C2—N1—C1—C4	0.000 (1)	C15—N4—B2—F2	−116.32 (18)
C2—N1—C1—C7	180.000 (1)	C15—N4—B2—N3	0.000 (1)

C2—N1—B1—F1	−63.7 (2)	C15—C16—C17—C18	0.000 (1)
C2—N1—B1—F1^{i}	63.7 (2)	C16—C17—C18—N4	0.000 (1)
C2—N1—B1—N2	180.000 (1)	C16—C17—C18—C20	180.000 (1)
C2—C3—C4—C1	0.000 (1)	C18—N4—C15—C14	180.000 (1)
C2—C3—C4—C6	180.000 (1)	C18—N4—C15—C16	0.000 (1)
C4—C1—C7—N2	180.000 (1)	C18—N4—B2—F2^{i}	−63.67 (18)
C5—C2—C3—C4	180.000 (1)	C18—N4—B2—F2	63.68 (18)
C7—N2—C8—C9	180.000 (1)	C18—N4—B2—N3	180.000 (1)
C7—N2—C8—C13	0.000 (1)	C19—C16—C17—C18	180.0
C7—N2—B1—F1^{i}	118.07 (18)	B1—N1—C1—C4	180.000 (1)
C7—N2—B1—F1	−118.07 (18)	B1—N1—C1—C7	0.000 (1)
C7—N2—B1—N1	0.000 (1)	B1—N1—C2—C3	180.000 (1)
C7—C1—C4—C3	180.000 (1)	B1—N1—C2—C5	0.000 (1)
C7—C1—C4—C6	0.000 (1)	B1—N2—C7—C1	0.000 (1)
C8—N2—C7—C1	180.000 (1)	B1—N2—C8—C9	0.000 (1)
C8—N2—B1—F1^{i}	−61.93 (18)	B1—N2—C8—C13	180.000 (1)
C8—N2—B1—F1	61.93 (18)	B2—N3—C11—C10	0.000 (1)
C8—N2—B1—N1	180.000 (1)	B2—N3—C11—C12	180.000 (1)
C8—C9—C10—C11	0.000 (1)	B2—N3—C14—C15	0.000 (1)
C9—C8—C13—C12	0.000 (1)	B2—N4—C15—C14	0.000 (1)
C9—C10—C11—N3	180.000 (1)	B2—N4—C15—C16	180.000 (1)
C9—C10—C11—C12	0.000 (1)	B2—N4—C18—C17	180.000 (1)
C10—C11—C12—C13	0.000 (1)	B2—N4—C18—C20	0.000 (1)

Symmetry code: (i) x, $-y+3/2$, z.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6*B*···F2^{ii}	0.96	2.49	3.336 (3)	147

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