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Crystal structure of difluorido{2-[(4-hydroxyphenyl)diazenyl]-3,5-dimethylpyrrolido}boron

Huixiao Feng[a,b] and Zhenming Yin[a,b]*

[a]College of Chemistry, Tianjin Key Laboratory of Structure and Performance for Functional Molecules, Tianjin Normal University, Tianjin 300387, People's Republic of China, and [b]Key Laboratory of Inorganic–Organic Hybrid Functional Materials Chemistry, (Tianjin Normal University), Ministry of Education, Tianjin 300387, People's Republic of China. *Correspondence e-mail: tjyinzm@aliyun.com

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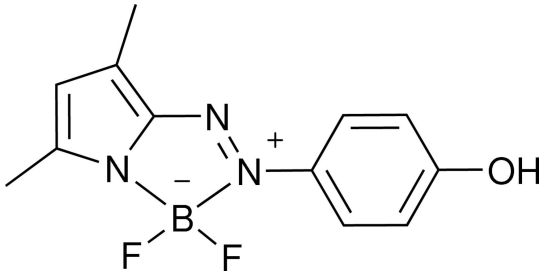
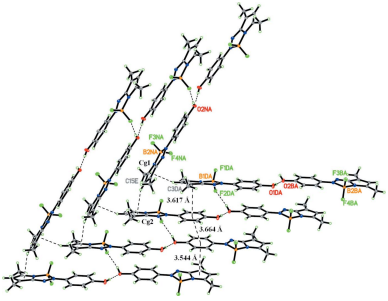
The asymmetric unit of the title azopyrrole-BF_2 complex, $C_{12}H_{12}BF_2N_3O$, contains two independent molecules, which are linked by an O—H···O hydrogen bond. The dimers are further assembled into a one-dimensional ladder-like structure through O—H···F hydrogen bonds and stabilized by π–π interactions. The ladders are further linked by C—H···π contacts.

1. Chemical context

Recently, some unique pyrrole-BF_2-based dyes have emerged as alternatives to 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) dyes because of their easy synthesis, lower symmetry and longer wavelengt absorption. Li *et al.* (2009) have synthesized a series of azopyrroles and their difluoroboron complexes, which possess promising absorption properties. The potentials of a few BF_2–azopyrrole complexes as sensitizers for dye-sensitized solar cells (DSSCs) have been evaluated (Mikroyannidis, Royd *et al.*, 2010). In the meantime, some BF_2–azopyrrole complexes have been used for the fabrication of bulk heterojunction solar cells (Mikroyannidis, Kabanakis *et al.*, 2010). A 2-(dimethylaminophenylazo)-5-ethyl-pyrrole boron difluoride complex has been used as an OFF–ON–OFF-type three-stage binary pH switch (Lee *et al.*, 2012). Previously, we have reported the crystal structures of some azopyrrole compounds (Yin *et al.*, 2008; Li *et al.*, 2011). In an extension of this research, we report herein on the crystal structure of difluorido{2-[(4-hydroxyphenyl)diazenyl]-3,5-dimethylpyrrolido}boron.





2. Structural commentary

The asymmetric unit contains two independent molecules, which show slight differences in some bond lengths [*e.g.* O1—C10 and O2—C22 = 1.358 (3) and 1.382 (3) Å, respectively;

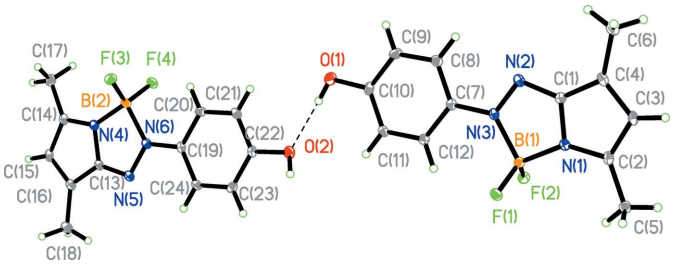


Figure 1
The asymmetric unit of the title compound, with displacement ellipsoids drawn at the 30% probability level. The O—H···O hydrogen bond is shown as a dashed line.

Table 1
Selected bond lengths (Å).

F1—B1	1.369 (3)	F3—B2	1.368 (3)
F2—B1	1.401 (3)	F4—B2	1.380 (3)
O1—C10	1.358 (3)	O2—C22	1.382 (3)
N1—C1	1.377 (3)	N4—C13	1.380 (3)
N1—C2	1.356 (3)	N4—C14	1.353 (3)
N1—B1	1.537 (3)	N4—B2	1.545 (3)
N2—N3	1.318 (3)	N5—N6	1.312 (3)
N2—C1	1.343 (3)	N5—C13	1.338 (3)
N3—C7	1.406 (3)	N6—C19	1.416 (3)
N3—B1	1.613 (3)	N6—B2	1.618 (3)
C1—C4	1.411 (3)	C13—C16	1.415 (3)
C2—C3	1.405 (3)	C14—C15	1.408 (3)
C3—C4	1.389 (3)	C15—C16	1.389 (3)

Table 1] and torsion angles [N2—N3—C7—C12 and N5—N6—C19—C20 are −171.1 (2) and 177.9 (2)°, respectively]. The r.m.s. deviation for fitting two molecules = 0.055 Å. The two molecules are linked by the O1—H1···O2 hydrogen bond (Fig. 1, Table 2). The torsion angles between benzene rings and neighboring pyrrole rings in the N1- and N4-containing molecules are 9.43 (12) and 1.34 (12)°, respectively. Each boron atom is four-coordinated by two fluorine atoms, a pyrrole N atom and an azo N atom. The B—N bond distances vary from 1.537 (3) to 1.618 (3) Å (Table 1). The B—$N_{pyrrole}$ bonds are shorter than the B—N_{azo} bonds. The two N—N bonds each adopt a *trans* conformation and at 1.318 (3) and 1.312 (3) Å are much longer than that in the structure of the free azopyrrole ligand (Yin *et al.*, 2008). In addition, the C1—C4, C2—C3, C13—C16 and C14—C15 bonds are lengthened, while the C3—C4 and C15—C16 bonds are shortened compared to the normal bond lengths in pyrrole. This indicates that the azopyrrole moiety of the title compound must be in the hydrazone form (Chen *et al.*, 2014).

3. Supramolecular features and Hirshfeld analysis

The two conformers also show supramolecular differences. One of the conformers only has a hydrogen bond between its hydroxyl group and that of the other conformer molecule (Fig. 1), whereas the hydroxyl group in the other conformer is also involved in intermolecular O—H···F interactions (Fig. 2, Table 2), forming a one-dimensional ladder-like structure

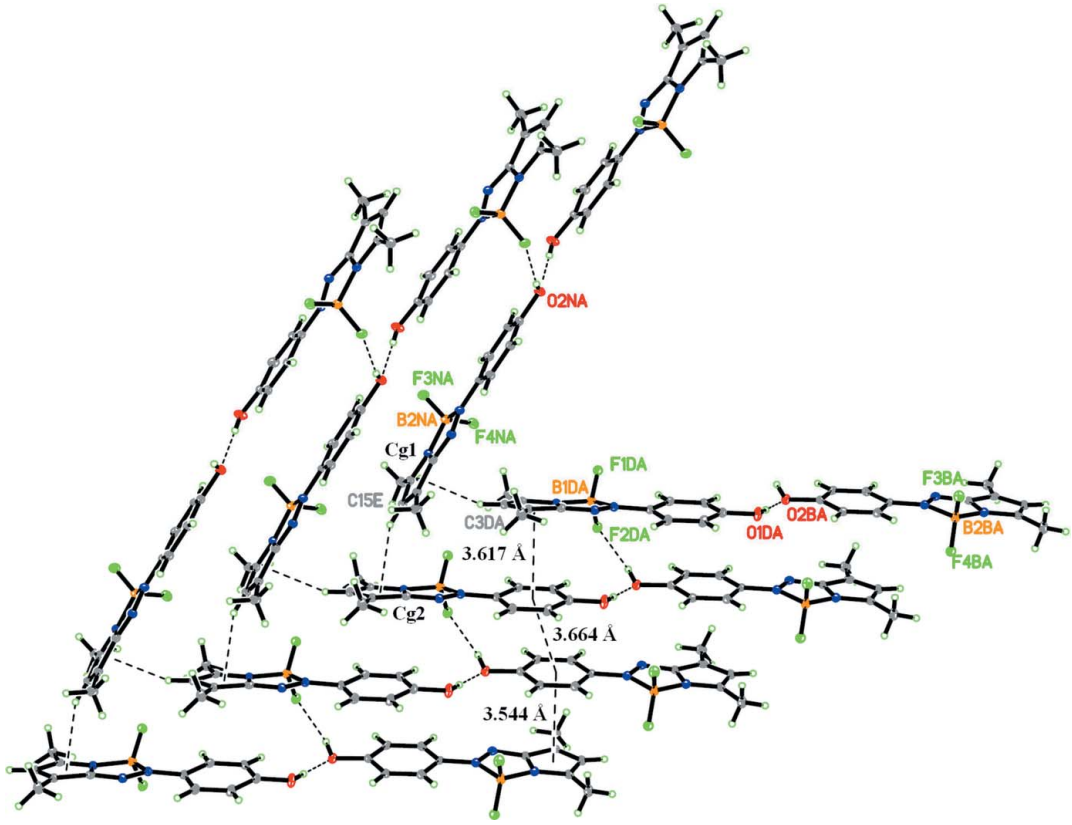


Figure 2
Part of the crystal packing showing molecules linked by O—H···O and O—H···F hydrogen bonds, π–π interactions and C—H···π contacts.

Table 2
Hydrogen-bond geometry (Å, °).

*Cg*2 and *Cg*6 are the centroids of the N4/C13–C16 and N1/C1–C4 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2	0.82	1.98	2.797 (2)	178
O2—H2···F2^{i}	0.82	2.06	2.812 (2)	152
C3—H3···*Cg*1^{ii}	0.93	2.62	3.501 (2)	158
C15—H15···*Cg*2^{iii}	0.93	2.63	3.506 (2)	157

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$.

along [100]. In the ladder structure, the molecules are arranged in a parallel manner through π–π interactions [*Cg*1···*Cg*4($x-1, y, z$) = 3.544 (1) Å, *Cg*2···*Cg*3($1+x, y, z$) = 3.617 (1) Å and *Cg*3···*Cg*4($1+x, y, z$) = 3.664 (13) Å; *Cg*1, *Cg*2, *Cg*3 and *Cg*4 are the centroids of the N1/C1–C4, C7–C12 and C19–C24 rings, respectively]. The ladders assemble into a layer structure through C—H···π contacts (Table 2).

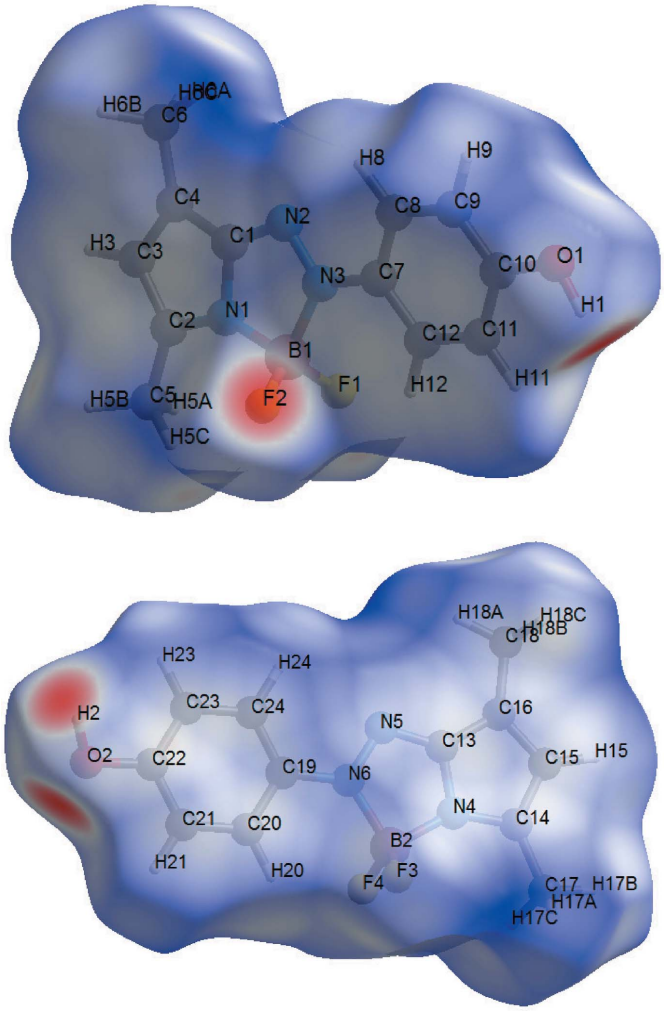


Figure 3
Hirshfeld surfaces of the two conformers mapped over d_{norm} in the range −0.614 to 1.350 a.u. The intermolecular contacts can be seen in red regions.

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_{12}BF_2N_3O$
M_r	263.06
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	6.8080 (4), 24.8217 (18), 14.4744 (9)
β (°)	100.489 (6)
V (Å^3)	2405.1 (3)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.12
Crystal size (mm)	0.25 × 0.22 × 0.2
Data collection	
Diffractometer	Rigaku Oxford Diffraction SuperNova, Dual, Cu at zero, Atlas S2
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.680, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11903, 4228, 3277
R_{int}	0.043
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.116, 1.06
No. of reflections	4228
No. of parameters	349
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.25, −0.26

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009).

The Hirshfeld surfaces of the two conformers were generated using *CrystalExplorer* (Turner *et al.*, 2017). Fig. 3 clearly shows that the two conformers are involved in different supramolecular interactions.

4. Database survey

A search in the Cambridge Structural Database (Version 5.38; Groom *et al.*, 2016) for azopyrrole boron difluoride compounds returned two entries, 2,5-bis(4-dimethylaminophenylazo)pyrrole boron difluoride (Li *et al.*, 2009) and 2-(dimethylaminophenylazo)-5-ethyl-pyrrole boron difluoride (Lee *et al.*, 2012). In both, the boron atoms have same coordination as in the title compound. The N—N bonds also adopt *trans* conformations and their lengths [1.322 (2) and 1.310 (1) Å] are comparable to those in the title compound.

5. Synthesis and crystallization

To a solution of 2-(4-hydroxylphenylazo)-3,5-dimethyl-1-*H*-pyrrole (2 mmol, 0.43g) and triethylamine (6 mL) in dry dichloromethane (15 mL) was slowly added boron trifluoride ethyl ether (2 mL). The resulting solution was stirred for 40 min, and then saturated potassium carbonate solution was added and stirred for 30 minutes. The resulting solution was extracted with ethyl acetate (10 mL × 3) and evaporated under vacuum to dryness. The residue was purified by column chromatography, eluting with ethyl acetate and petroleum

ether (v/v = 1:14), to give a dark-green product, m.p. = 405 K. Yield 65%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.118 (*s*, 1H, –OH), 7.548–7.526 (*d*, 2H, J = 8.8Hz, Ar–CH), 6.920–6.897(*d*, 2H, J = 9.2Hz, Ar–CH), 6.342 (*s*, 1H, pyrrole–CH), 2.371(*s*, 3H, –CH_3), 2.314 (*s*, 3H, –CH_3). Suitable crystals for X-ray diffraction analysis were obtained by the slow evaporation of an $CHCl_3$/CH_3OH solution of the title compound.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. OH H atoms were located from difference-Fourier maps and refined freely. Other H atoms were placed in calculated positions (C—H = 0.93 or 0.96 Å) and refined using a riding model, with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C-methyl).

Funding information

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Crystal structure of difluorido{2-[(4-hydroxyphenyl)diazenyl]-3,5-dimethylpyrrolido}boron

Huixiao Feng 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: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Difluorido{2-[(4-hydroxyphenyl)diazenyl-κN^2]-3,5-dimethylpyrrolido-\ κN}boron

Crystal data

$C_{12}H_{12}BF_2N_3O$
M_r = 263.06
Monoclinic, $P2_1/n$
a = 6.8080 (4) Å
b = 24.8217 (18) Å
c = 14.4744 (9) Å
β = 100.489 (6)°
V = 2405.1 (3) Å^3
Z = 8
$F(000)$ = 1088
D_x = 1.453 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3432 reflections
θ = 4.1–28.6°
μ = 0.12 mm^{-1}
T = 100 K
Block, dark green
0.25 × 0.22 × 0.2 mm

Data collection

Rigaku Oxford Diffraction SuperNova, Dual, Cu at zero, Atlas S2 diffractometer
Radiation source: micro-focus sealed X-ray tube, SuperNova (Mo) X-ray Source
Mirror monochromator
Detector resolution: 5.2740 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2015)
T_{min} = 0.680, T_{max} = 1.000
11903 measured reflections
4228 independent reflections
3277 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 25.0°, θ_{min} = 3.2°
h = −7→8
k = −29→29
l = −17→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.116
S = 1.06
4228 reflections
349 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0388P)^2 + 1.6938P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
F1	1.31342 (18)	0.53429 (5)	0.89956 (9)	0.0210 (3)
F2	1.46735 (18)	0.45513 (5)	0.87853 (8)	0.0205 (3)
O1	0.5707 (2)	0.40021 (7)	0.61520 (11)	0.0272 (4)
H1	0.5225	0.3893	0.6596	0.041*
N1	1.5952 (3)	0.53806 (7)	0.81633 (12)	0.0156 (4)
N2	1.3878 (3)	0.52607 (8)	0.67448 (13)	0.0178 (4)
N3	1.2967 (3)	0.50217 (7)	0.73622 (13)	0.0162 (4)
C1	1.5603 (3)	0.54666 (9)	0.72074 (15)	0.0162 (5)
C2	1.7710 (3)	0.56211 (9)	0.85288 (16)	0.0166 (5)
C3	1.8484 (3)	0.58566 (9)	0.77884 (16)	0.0182 (5)
H3	1.9686	0.6043	0.7852	0.022*
C4	1.7176 (3)	0.57669 (9)	0.69470 (16)	0.0180 (5)
C5	1.8540 (3)	0.56219 (10)	0.95504 (15)	0.0211 (5)
H5A	1.8228	0.5958	0.9820	0.032*
H5B	1.9964	0.5578	0.9645	0.032*
H5C	1.7965	0.5331	0.9848	0.032*
C6	1.7354 (4)	0.59469 (11)	0.59812 (16)	0.0257 (6)
H6A	1.6381	0.5762	0.5528	0.038*
H6B	1.8669	0.5866	0.5869	0.038*
H6C	1.7125	0.6328	0.5926	0.038*
C7	1.1152 (3)	0.47520 (9)	0.70490 (15)	0.0163 (5)
C8	1.0407 (3)	0.46718 (9)	0.60966 (16)	0.0198 (5)
H8	1.1142	0.4786	0.5650	0.024*
C9	0.8590 (3)	0.44247 (10)	0.58158 (16)	0.0223 (5)
H9	0.8086	0.4380	0.5179	0.027*
C10	0.7495 (3)	0.42404 (9)	0.64779 (16)	0.0190 (5)
C11	0.8254 (3)	0.43105 (9)	0.74289 (16)	0.0179 (5)
H11	0.7541	0.4185	0.7876	0.021*
C12	1.0063 (3)	0.45662 (9)	0.77097 (15)	0.0170 (5)
H12	1.0560	0.4615	0.8346	0.020*
B1	1.4183 (4)	0.50677 (11)	0.84252 (18)	0.0174 (6)
F3	−0.50768 (19)	0.27493 (6)	0.54470 (9)	0.0247 (3)
F4	−0.33107 (18)	0.19699 (6)	0.55925 (9)	0.0237 (3)
O2	0.3980 (2)	0.36293 (7)	0.76431 (11)	0.0226 (4)
H2	0.4090	0.3820	0.8112	0.034*
N4	−0.6118 (3)	0.20404 (8)	0.64279 (13)	0.0172 (4)
N5	−0.4053 (3)	0.23598 (8)	0.77401 (13)	0.0176 (4)

N6	−0.3216 (3)	0.25089 (8)	0.70328 (12)	0.0167 (4)
C13	−0.5729 (3)	0.20907 (9)	0.73934 (15)	0.0168 (5)
C14	−0.7850 (3)	0.17649 (9)	0.61832 (16)	0.0188 (5)
C15	−0.8566 (3)	0.16381 (9)	0.70106 (16)	0.0198 (5)
H15	−0.9737	0.1451	0.7036	0.024*
C16	−0.7251 (3)	0.18365 (9)	0.77825 (16)	0.0193 (5)
C17	−0.8717 (3)	0.16370 (11)	0.51897 (17)	0.0261 (6)
H17A	−0.9208	0.1961	0.4867	0.039*
H17B	−0.9797	0.1386	0.5171	0.039*
H17C	−0.7707	0.1481	0.4889	0.039*
C18	−0.7344 (4)	0.17973 (10)	0.88049 (16)	0.0254 (6)
H18A	−0.6142	0.1943	0.9169	0.038*
H18B	−0.7476	0.1426	0.8971	0.038*
H18C	−0.8474	0.1997	0.8931	0.038*
C19	−0.1401 (3)	0.28017 (9)	0.72225 (15)	0.0155 (5)
C20	−0.0500 (3)	0.29409 (9)	0.64649 (16)	0.0186 (5)
H20	−0.1105	0.2848	0.5857	0.022*
C21	0.1291 (3)	0.32173 (9)	0.66166 (16)	0.0182 (5)
H21	0.1898	0.3308	0.6112	0.022*
C22	0.2179 (3)	0.33579 (9)	0.75205 (16)	0.0170 (5)
C23	0.1294 (3)	0.32146 (9)	0.82758 (16)	0.0183 (5)
H23	0.1907	0.3306	0.8883	0.022*
C24	−0.0496 (3)	0.29372 (9)	0.81286 (15)	0.0180 (5)
H24	−0.1090	0.2842	0.8635	0.022*
B2	−0.4440 (4)	0.23212 (11)	0.60191 (18)	0.0192 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0209 (7)	0.0223 (8)	0.0214 (7)	−0.0015 (6)	0.0079 (5)	−0.0030 (6)
F2	0.0227 (7)	0.0171 (7)	0.0211 (7)	−0.0029 (6)	0.0027 (5)	0.0025 (6)
O1	0.0236 (9)	0.0309 (11)	0.0260 (9)	−0.0135 (8)	0.0014 (7)	0.0018 (8)
N1	0.0156 (9)	0.0132 (10)	0.0185 (10)	0.0009 (8)	0.0048 (7)	−0.0001 (8)
N2	0.0182 (10)	0.0144 (10)	0.0221 (10)	−0.0002 (8)	0.0070 (8)	0.0008 (8)
N3	0.0148 (9)	0.0148 (10)	0.0195 (10)	−0.0007 (8)	0.0047 (8)	0.0007 (8)
C1	0.0174 (11)	0.0136 (12)	0.0176 (12)	0.0017 (10)	0.0031 (9)	0.0001 (10)
C2	0.0141 (11)	0.0117 (12)	0.0243 (12)	0.0026 (9)	0.0040 (9)	−0.0012 (10)
C3	0.0148 (11)	0.0128 (12)	0.0277 (13)	−0.0022 (9)	0.0058 (9)	−0.0003 (10)
C4	0.0182 (12)	0.0129 (12)	0.0248 (12)	0.0002 (10)	0.0087 (9)	0.0005 (10)
C5	0.0204 (12)	0.0209 (13)	0.0218 (12)	−0.0014 (10)	0.0037 (9)	0.0011 (10)
C6	0.0244 (13)	0.0275 (15)	0.0262 (13)	−0.0037 (11)	0.0073 (10)	0.0049 (11)
C7	0.0163 (11)	0.0117 (12)	0.0207 (12)	−0.0006 (9)	0.0033 (9)	0.0013 (10)
C8	0.0220 (12)	0.0185 (13)	0.0198 (12)	−0.0030 (10)	0.0061 (9)	0.0021 (10)
C9	0.0265 (13)	0.0220 (14)	0.0169 (12)	−0.0048 (11)	0.0002 (9)	−0.0001 (10)
C10	0.0146 (11)	0.0152 (13)	0.0263 (13)	−0.0016 (10)	0.0009 (9)	0.0007 (10)
C11	0.0161 (11)	0.0167 (12)	0.0219 (12)	0.0019 (10)	0.0066 (9)	0.0032 (10)
C12	0.0187 (12)	0.0155 (12)	0.0168 (11)	−0.0004 (10)	0.0032 (9)	−0.0006 (10)
B1	0.0169 (13)	0.0168 (14)	0.0185 (13)	−0.0009 (11)	0.0031 (10)	0.0016 (11)

F3	0.0265 (7)	0.0242 (8)	0.0230 (7)	−0.0026 (6)	0.0035 (6)	0.0065 (6)
F4	0.0227 (7)	0.0267 (8)	0.0234 (7)	−0.0033 (6)	0.0089 (6)	−0.0067 (6)
O2	0.0197 (8)	0.0208 (10)	0.0278 (9)	−0.0056 (7)	0.0056 (7)	−0.0043 (8)
N4	0.0170 (10)	0.0160 (11)	0.0190 (10)	−0.0010 (8)	0.0049 (8)	0.0002 (8)
N5	0.0191 (10)	0.0141 (10)	0.0211 (10)	0.0006 (8)	0.0073 (8)	−0.0002 (8)
N6	0.0181 (10)	0.0139 (10)	0.0193 (10)	−0.0016 (8)	0.0064 (8)	0.0009 (8)
C13	0.0171 (12)	0.0132 (12)	0.0210 (12)	0.0021 (10)	0.0063 (9)	0.0006 (10)
C14	0.0159 (11)	0.0142 (12)	0.0266 (13)	0.0009 (10)	0.0047 (9)	0.0010 (10)
C15	0.0143 (11)	0.0153 (12)	0.0309 (13)	−0.0009 (10)	0.0065 (10)	0.0020 (11)
C16	0.0208 (12)	0.0137 (12)	0.0250 (12)	0.0029 (10)	0.0084 (10)	0.0030 (10)
C17	0.0200 (12)	0.0292 (15)	0.0280 (14)	−0.0039 (11)	0.0018 (10)	0.0011 (12)
C18	0.0283 (13)	0.0231 (14)	0.0275 (13)	0.0005 (11)	0.0123 (10)	0.0035 (11)
C19	0.0148 (11)	0.0101 (12)	0.0220 (12)	−0.0003 (9)	0.0046 (9)	0.0000 (10)
C20	0.0225 (12)	0.0171 (13)	0.0162 (11)	−0.0015 (10)	0.0039 (9)	−0.0007 (10)
C21	0.0197 (12)	0.0147 (12)	0.0223 (12)	0.0007 (10)	0.0094 (9)	0.0025 (10)
C22	0.0145 (11)	0.0130 (12)	0.0237 (12)	0.0001 (9)	0.0039 (9)	−0.0003 (10)
C23	0.0196 (12)	0.0146 (12)	0.0191 (12)	0.0001 (10)	−0.0004 (9)	−0.0028 (10)
C24	0.0194 (12)	0.0169 (13)	0.0193 (12)	0.0005 (10)	0.0079 (9)	0.0018 (10)
B2	0.0203 (13)	0.0203 (15)	0.0178 (13)	−0.0031 (12)	0.0059 (10)	0.0004 (12)

Geometric parameters (Å, º)

F1—B1	1.369 (3)	F3—B2	1.368 (3)
F2—B1	1.401 (3)	F4—B2	1.380 (3)
O1—H1	0.8200	O2—H2	0.8200
O1—C10	1.358 (3)	O2—C22	1.382 (3)
N1—C1	1.377 (3)	N4—C13	1.380 (3)
N1—C2	1.356 (3)	N4—C14	1.353 (3)
N1—B1	1.537 (3)	N4—B2	1.545 (3)
N2—N3	1.318 (3)	N5—N6	1.312 (3)
N2—C1	1.343 (3)	N5—C13	1.338 (3)
N3—C7	1.406 (3)	N6—C19	1.416 (3)
N3—B1	1.613 (3)	N6—B2	1.618 (3)
C1—C4	1.411 (3)	C13—C16	1.415 (3)
C2—C3	1.405 (3)	C14—C15	1.408 (3)
C2—C5	1.484 (3)	C14—C17	1.486 (3)
C3—H3	0.9300	C15—H15	0.9300
C3—C4	1.389 (3)	C15—C16	1.389 (3)
C4—C6	1.493 (3)	C16—C18	1.496 (3)
C5—H5A	0.9600	C17—H17A	0.9600
C5—H5B	0.9600	C17—H17B	0.9600
C5—H5C	0.9600	C17—H17C	0.9600
C6—H6A	0.9600	C18—H18A	0.9600
C6—H6B	0.9600	C18—H18B	0.9600
C6—H6C	0.9600	C18—H18C	0.9600
C7—C8	1.394 (3)	C19—C20	1.394 (3)
C7—C12	1.391 (3)	C19—C24	1.385 (3)
C8—H8	0.9300	C20—H20	0.9300

C8—C9	1.375 (3)	C20—C21	1.382 (3)
C9—H9	0.9300	C21—H21	0.9300
C9—C10	1.394 (3)	C21—C22	1.382 (3)
C10—C11	1.390 (3)	C22—C23	1.387 (3)
C11—H11	0.9300	C23—H23	0.9300
C11—C12	1.380 (3)	C23—C24	1.382 (3)
C12—H12	0.9300	C24—H24	0.9300
C10—O1—H1	109.5	C22—O2—H2	109.5
C1—N1—B1	109.05 (17)	C13—N4—B2	109.16 (18)
C2—N1—C1	107.60 (18)	C14—N4—C13	107.95 (18)
C2—N1—B1	143.30 (19)	C14—N4—B2	142.88 (19)
N3—N2—C1	108.06 (18)	N6—N5—C13	108.05 (18)
N2—N3—C7	119.34 (18)	N5—N6—C19	118.74 (18)
N2—N3—B1	113.07 (17)	N5—N6—B2	113.64 (17)
C7—N3—B1	127.56 (18)	C19—N6—B2	127.62 (18)
N1—C1—C4	110.47 (18)	N4—C13—C16	110.09 (19)
N2—C1—N1	114.66 (19)	N5—C13—N4	114.72 (19)
N2—C1—C4	134.9 (2)	N5—C13—C16	135.2 (2)
N1—C2—C3	108.23 (19)	N4—C14—C15	108.08 (19)
N1—C2—C5	122.6 (2)	N4—C14—C17	122.4 (2)
C3—C2—C5	129.2 (2)	C15—C14—C17	129.6 (2)
C2—C3—H3	125.3	C14—C15—H15	125.3
C4—C3—C2	109.40 (19)	C16—C15—C14	109.4 (2)
C4—C3—H3	125.3	C16—C15—H15	125.3
C1—C4—C6	127.1 (2)	C13—C16—C18	126.1 (2)
C3—C4—C1	104.30 (19)	C15—C16—C13	104.4 (2)
C3—C4—C6	128.6 (2)	C15—C16—C18	129.5 (2)
C2—C5—H5A	109.5	C14—C17—H17A	109.5
C2—C5—H5B	109.5	C14—C17—H17B	109.5
C2—C5—H5C	109.5	C14—C17—H17C	109.5
H5A—C5—H5B	109.5	H17A—C17—H17B	109.5
H5A—C5—H5C	109.5	H17A—C17—H17C	109.5
H5B—C5—H5C	109.5	H17B—C17—H17C	109.5
C4—C6—H6A	109.5	C16—C18—H18A	109.5
C4—C6—H6B	109.5	C16—C18—H18B	109.5
C4—C6—H6C	109.5	C16—C18—H18C	109.5
H6A—C6—H6B	109.5	H18A—C18—H18B	109.5
H6A—C6—H6C	109.5	H18A—C18—H18C	109.5
H6B—C6—H6C	109.5	H18B—C18—H18C	109.5
C8—C7—N3	121.8 (2)	C20—C19—N6	117.90 (19)
C12—C7—N3	118.89 (19)	C24—C19—N6	122.0 (2)
C12—C7—C8	119.3 (2)	C24—C19—C20	120.1 (2)
C7—C8—H8	119.9	C19—C20—H20	120.0
C9—C8—C7	120.1 (2)	C21—C20—C19	120.0 (2)
C9—C8—H8	119.9	C21—C20—H20	120.0
C8—C9—H9	119.7	C20—C21—H21	120.1
C8—C9—C10	120.6 (2)	C20—C21—C22	119.8 (2)

C10—C9—H9	119.7	C22—C21—H21	120.1
O1—C10—C9	117.5 (2)	O2—C22—C21	118.0 (2)
O1—C10—C11	123.1 (2)	O2—C22—C23	121.8 (2)
C11—C10—C9	119.4 (2)	C21—C22—C23	120.2 (2)
C10—C11—H11	120.0	C22—C23—H23	119.9
C12—C11—C10	120.0 (2)	C24—C23—C22	120.2 (2)
C12—C11—H11	120.0	C24—C23—H23	119.9
C7—C12—H12	119.7	C19—C24—H24	120.2
C11—C12—C7	120.6 (2)	C23—C24—C19	119.7 (2)
C11—C12—H12	119.7	C23—C24—H24	120.2
F1—B1—F2	110.33 (19)	F3—B2—F4	111.15 (19)
F1—B1—N1	114.5 (2)	F3—B2—N4	114.04 (19)
F1—B1—N3	112.16 (18)	F3—B2—N6	112.3 (2)
F2—B1—N1	114.19 (18)	F4—B2—N4	113.4 (2)
F2—B1—N3	109.65 (19)	F4—B2—N6	110.52 (18)
N1—B1—N3	95.14 (17)	N4—B2—N6	94.42 (16)

O1—C10—C11—C12	−178.6 (2)	O2—C22—C23—C24	−179.2 (2)
N1—C1—C4—C3	0.1 (3)	N4—C13—C16—C15	−0.5 (3)
N1—C1—C4—C6	−179.5 (2)	N4—C13—C16—C18	179.0 (2)
N1—C2—C3—C4	0.7 (3)	N4—C14—C15—C16	−0.2 (3)
N2—N3—C7—C8	8.1 (3)	N5—N6—C19—C20	177.9 (2)
N2—N3—C7—C12	−171.1 (2)	N5—N6—C19—C24	−0.4 (3)
N2—N3—B1—F1	117.8 (2)	N5—N6—B2—F3	118.5 (2)
N2—N3—B1—F2	−119.2 (2)	N5—N6—B2—F4	−116.8 (2)
N2—N3—B1—N1	−1.2 (2)	N5—N6—B2—N4	0.2 (2)
N2—C1—C4—C3	178.7 (3)	N5—C13—C16—C15	179.5 (2)
N2—C1—C4—C6	−0.8 (4)	N5—C13—C16—C18	−1.0 (4)
N3—N2—C1—N1	−0.3 (3)	N6—N5—C13—N4	0.2 (3)
N3—N2—C1—C4	−178.9 (2)	N6—N5—C13—C16	−179.8 (3)
N3—C7—C8—C9	−177.5 (2)	N6—C19—C20—C21	−178.7 (2)
N3—C7—C12—C11	178.5 (2)	N6—C19—C24—C23	178.8 (2)
C1—N1—C2—C3	−0.6 (2)	C13—N4—C14—C15	−0.1 (3)
C1—N1—C2—C5	178.5 (2)	C13—N4—C14—C17	−179.9 (2)
C1—N1—B1—F1	−116.2 (2)	C13—N4—B2—F3	−116.9 (2)
C1—N1—B1—F2	115.2 (2)	C13—N4—B2—F4	114.5 (2)
C1—N1—B1—N3	1.0 (2)	C13—N4—B2—N6	−0.1 (2)
C1—N2—N3—C7	−177.34 (19)	C13—N5—N6—C19	−179.84 (19)
C1—N2—N3—B1	1.0 (2)	C13—N5—N6—B2	−0.3 (2)
C2—N1—C1—N2	−178.58 (19)	C14—N4—C13—N5	−179.60 (19)
C2—N1—C1—C4	0.4 (3)	C14—N4—C13—C16	0.4 (3)
C2—N1—B1—F1	60.6 (4)	C14—N4—B2—F3	62.3 (4)
C2—N1—B1—F2	−68.0 (4)	C14—N4—B2—F4	−66.2 (4)
C2—N1—B1—N3	177.8 (3)	C14—N4—B2—N6	179.2 (3)
C2—C3—C4—C1	−0.4 (3)	C14—C15—C16—C13	0.5 (3)
C2—C3—C4—C6	179.1 (2)	C14—C15—C16—C18	−179.0 (2)
C5—C2—C3—C4	−178.4 (2)	C17—C14—C15—C16	179.6 (2)
C7—N3—B1—F1	−64.0 (3)	C19—N6—B2—F3	−62.0 (3)

C7—N3—B1—F2	59.0 (3)	C19—N6—B2—F4	62.7 (3)
C7—N3—B1—N1	176.9 (2)	C19—N6—B2—N4	179.7 (2)
C7—C8—C9—C10	−1.6 (4)	C19—C20—C21—C22	−0.4 (3)
C8—C7—C12—C11	−0.7 (3)	C20—C19—C24—C23	0.5 (3)
C8—C9—C10—O1	179.7 (2)	C20—C21—C22—O2	179.4 (2)
C8—C9—C10—C11	0.3 (4)	C20—C21—C22—C23	1.1 (3)
C9—C10—C11—C12	0.8 (3)	C21—C22—C23—C24	−1.0 (3)
C10—C11—C12—C7	−0.5 (3)	C22—C23—C24—C19	0.1 (3)
C12—C7—C8—C9	1.8 (4)	C24—C19—C20—C21	−0.4 (3)
B1—N1—C1—N2	−0.6 (3)	B2—N4—C13—N5	−0.1 (3)
B1—N1—C1—C4	178.34 (19)	B2—N4—C13—C16	179.92 (19)
B1—N1—C2—C3	−177.4 (3)	B2—N4—C14—C15	−179.3 (3)
B1—N1—C2—C5	1.7 (4)	B2—N4—C14—C17	0.9 (5)
B1—N3—C7—C8	−170.0 (2)	B2—N6—C19—C20	−1.6 (3)
B1—N3—C7—C12	10.8 (3)	B2—N6—C19—C24	−179.8 (2)

Hydrogen-bond geometry (Å, º)

Cg2 and Cg6 are the centroids of the N4/C13–C16 and N1/C1–C4 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2	0.82	1.98	2.797 (2)	178
O2—H2···F2^{i}	0.82	2.06	2.812 (2)	152
C3—H3···*Cg*1^{ii}	0.93	2.62	3.501 (2)	158
C15—H15···*Cg*2^{iii}	0.93	2.63	3.506 (2)	157

Symmetry codes: (i) *x*−1, *y*, *z*; (ii) −*x*+3/2, *y*+1/2, −*z*+3/2; (iii) −*x*+1/2, *y*−1/2, −*z*+3/2.