

# Crystal structure and Hirshfeld surface analysis of 10-(3-benzylthiophen-2-yl)-5,5-difluoro-5H-4 $\lambda^4$ ,5 $\lambda^4$ -dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine

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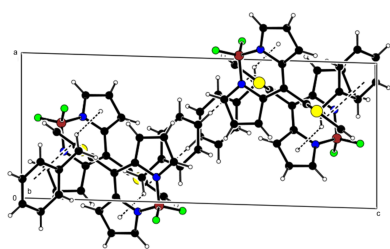
**Supporting information:** this article has supporting information at journals.iucr.org/e

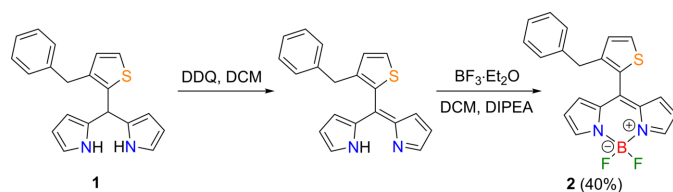
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In the title compound, C<sub>20</sub>H<sub>15</sub>BF<sub>2</sub>N<sub>2</sub>S, the twelve-membered ring system is essentially planar (r.m.s. deviation = 0.001 Å). The dihedral angles between the average plane of this ring and the thiophene and phenyl rings are 58.69 (4) and 61.41 (4)°, respectively. In the crystal, C—H...F interactions generate R<sub>2</sub><sup>2</sup>(10) and three types of R<sub>3</sub><sup>2</sup>(21) ring motifs around a molecule, resulting in layers parallel to the (101) plane. The molecules further form layers parallel to the (10 $\bar{1}$ ) plane through C—H... $\pi$  interactions. According to a Hirshfeld surface analysis, H...H (41.5%), C...H/H...C (23.5%) and F...H/H...F (18.2%) interactions are the most significant contributors to the crystal packing.

## 1. Chemical context

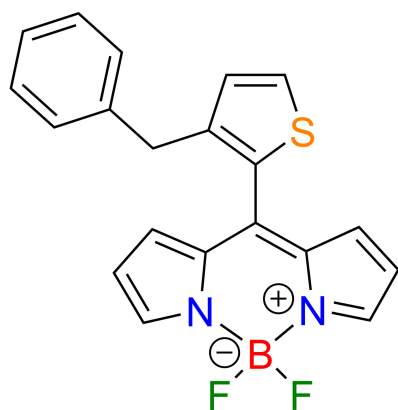
4,4-Difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) complexes represent one of the most versatile classes of small-molecule fluorophores, renowned for their exceptional photophysical properties (Ulrich *et al.*, 2008; Loudet & Burgess, 2007). These properties include high molar absorption coefficients, sharp fluorescence emission peaks with high quantum yields, and remarkable chemical and photochemical stability (Boens *et al.*, 2019; Ni & Wu, 2014). Consequently, BODIPY derivatives have found extensive applications across diverse fields, functioning as fluorescent sensors for bioimaging, agents for photodynamic therapy, laser dyes, and photocatalysts (Poddar & Misra, 2020; Martynov & Pakhomov, 2021; Wang *et al.*, 2023). A key feature that underpins their versatility is the ability to fine-tune their spectroscopic characteristics through rational structural modification of the dipyrromethene core (Waly *et al.*, 2022; Lu *et al.*, 2014). The photophysical behavior of BODIPY is highly sensitive to the nature of the substituent at the *meso*-position (C-8), which plays a critical role in the molecule's electronic distribution (Ozdemir *et al.*, 2014; Lincoln *et al.*, 2014). While the introduction of aryl substituents at this position is well-documented (Spector *et al.*, 2024), replacing the six-membered ring with five-membered aromatic heterocycles, which can lead to the further modulation the electronic properties, are poorly studied. Studies of *meso*-substituted BODIPY with such heterocycles as furan, thiophene, pyrrole and selenophene were firstly carried out and demonstrated that this substitution results in a more planar conformation between





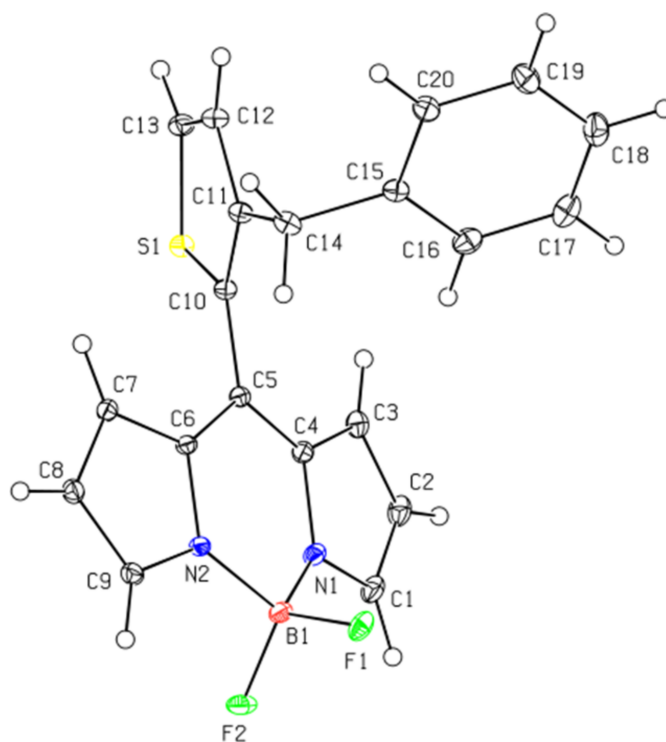
**Figure 1**  
 Synthesis of 10-(3-benzylthiophen-2-yl)-5,5-difluoro-5*H*-4λ<sup>4</sup>,5λ<sup>4</sup>-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine, **2**.

the heterocycle and the dipyrromethene framework, extending  $\pi$ -conjugation and leading to notable bathochromic shifts in absorption and emission spectra, as well as changes in fluorescence quantum yields, compared to their *meso*-aryl counterparts (Kim *et al.*, 2010; Sharma *et al.*, 2016). In this work, we describe the synthesis of a new BODIPY derivative bearing a thiophene moiety at the *meso*-position to explore its impact on the structural, electronic, and photophysical characteristics of the resulting fluorophore. In continuation of our studies on five-membered-heterocycle-substituted dipyrrolmethanes, the recently described 3-benzyl-2-[bis(1*H*-pyrrol-2-yl)methyl]thiophene, **1** (Sadikhova *et al.*, 2024) was utilized as a key precursor. Oxidation with DDQ in CH<sub>2</sub>Cl<sub>2</sub> (30 min), followed by neutralization with DIPEA and subsequent treatment with BF<sub>3</sub>·OEt<sub>2</sub>, provided the corresponding BODIPY complex. The target *meso*-thienyl-substituted BODIPY, **2**, was isolated in 40% yield after silica gel column chromatography (Fig. 1).



## 2. Structural commentary

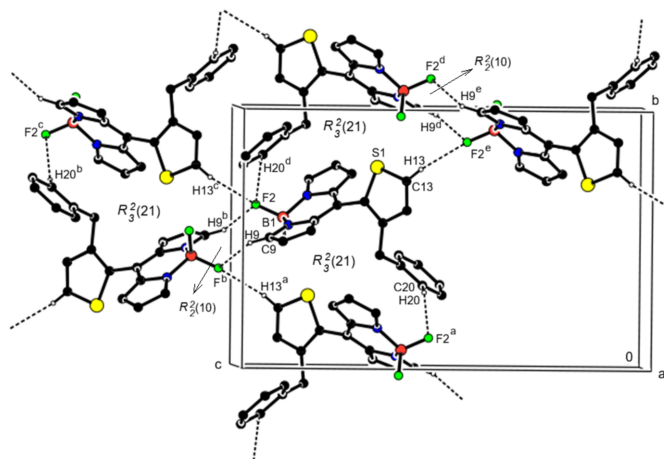
In the title compound (Fig. 2), the twelve-membered ring system (B1/N1/N2/C1–C9) is essentially planar (r.m.s. deviation = 0.001 Å). The dihedral angles between the average plane of this ring and the thiophene (S1/C10–C13) and phenyl (C15–C20) rings are 58.69 (4) and 61.41 (4)°, respectively. The thiophene and phenyl rings subtend an angle of 81.50 (5)°. The F2–B1–F1 angle is 109.39 (8)°. The bond lengths and angles in the title compound are in good agreement with those in the compounds discussed in the *Database survey* section.



**Figure 2**  
 Molecular structure of the title compound showing the atom labelling and ellipsoids at the 30% probability level.

## 3. Supramolecular features and Hirshfeld surface analysis

In the crystal, C–H···F interactions form  $R_2^2(10)$  and three types of  $R_3^2(21)$  ring motifs (Bernstein *et al.* 1995; Tables 1 and 2; Figs. 3, 4 and 5) around a molecule, leading to the formation of layers parallel to the (101) plane. The molecules are additionally connected by C–H··· $\pi$  interactions, forming layers parallel to the (10 $\bar{1}$ ) plane (Table 1; Figs. 6 and 7).



**Figure 3**  
 The C–H···F interactions of the title compound showing the ring motifs. Symmetry codes: (a)  $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z$ ; (b)  $1 - x, 1 - y, 2 - z$ ; (c)  $-\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$ ; (d)  $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$ ; (e)  $\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z$ .

**Table 1**

Hydrogen-bond geometry (Å, °).

Cg1 and Cg2 are the centroids of the S1/C10–C13 and N1/C1–C4 rings, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C9–H9 $\cdots$ F2 <sup>i</sup>	0.95	2.36	3.2017 (12)	148
C13–H13 $\cdots$ F2 <sup>ii</sup>	0.95	2.55	3.3113 (12)	137
C20–H20 $\cdots$ F2 <sup>iii</sup>	0.95	2.51	3.3221 (13)	144
C14–H14B $\cdots$ Cg2 <sup>iii</sup>	0.99	2.81	3.5815 (11)	135
C18–H18 $\cdots$ Cg1 <sup>iv</sup>	0.95	2.92	3.7764 (13)	151

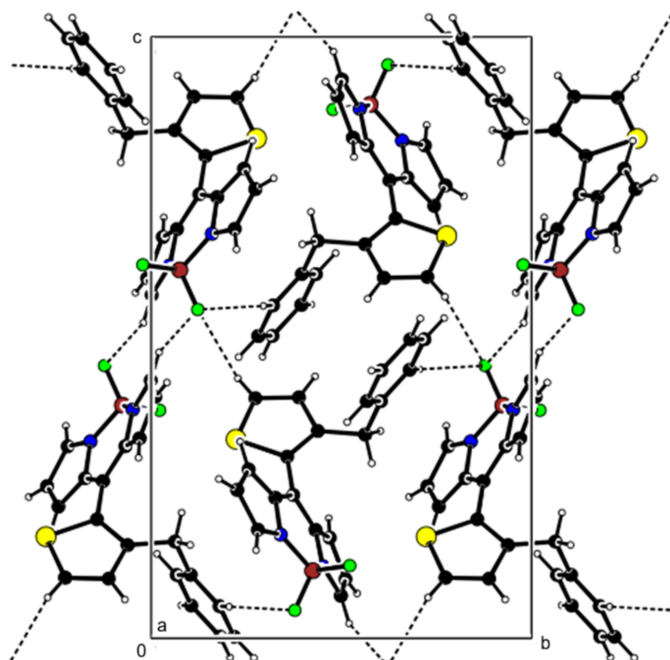
 Symmetry codes: (i)  $-x+1, -y+1, -z+2$ ; (ii)  $x+\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$ ; (iii)  $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$ ; (iv)  $-x+1, -y+1, -z+1$ .

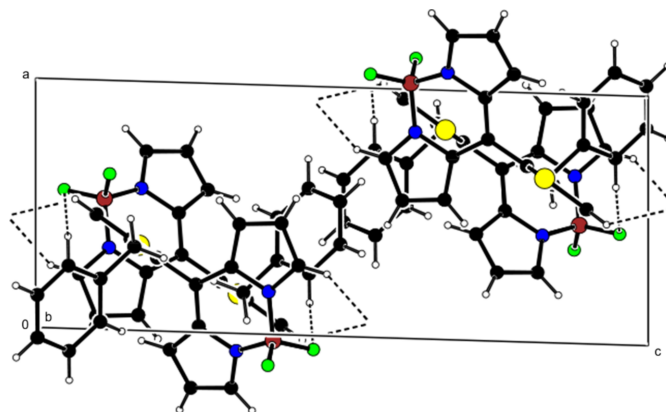
**Table 2**

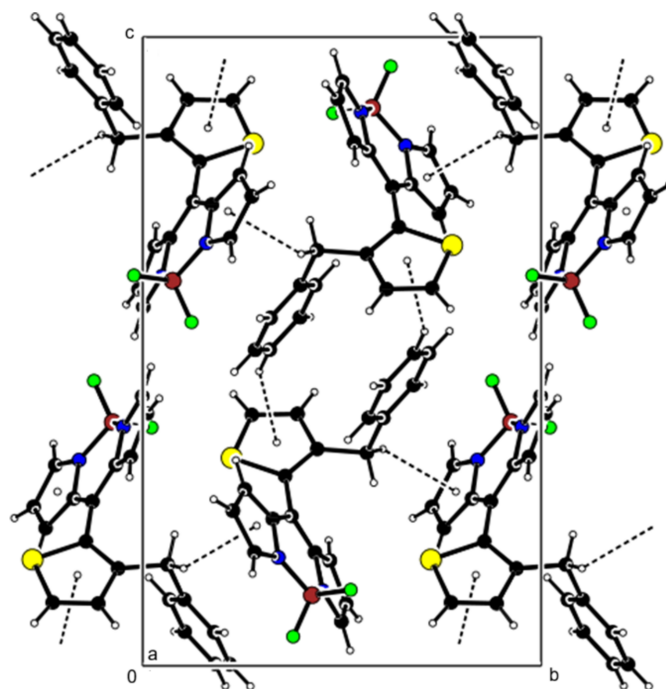
Summary of short interatomic contacts (Å).

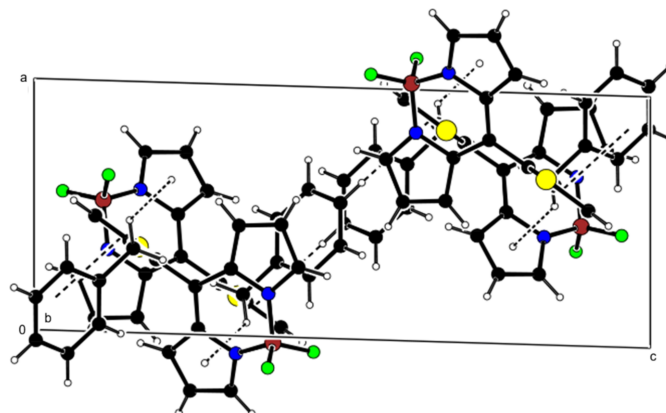
Contact	Distance	Symmetry operation
H8 $\cdots$ F1	2.70	$1+x, y, z$
F2 $\cdots$ H20	2.51	$\frac{3}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$
H18 $\cdots$ C13	2.87	$1-x, 1-y, 1-z$
H9 $\cdots$ F2	2.36	$1-x, 1-y, 2-z$
F2 $\cdots$ H13	2.55	$-\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$
H1 $\cdots$ C17	2.80	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$
H9 $\cdots$ H8	2.52	$2-x, 1-y, 2-z$
H19 $\cdots$ H13	2.53	$2-x, 1-y, 1-z$
H8 $\cdots$ H19	2.54	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$

A Hirshfeld surface analysis was conducted using *Crystal Explorer 17.5* (Spackman *et al.*, 2021) to view and quantify intermolecular interactions, and to create the corresponding two-dimensional fingerprint plots. The Hirshfeld surfaces were mapped over  $d_{\text{norm}}$  in the range  $-0.2379$  (red) to  $+1.5528$  (blue) a.u. (Fig. 8). The most important intermolecular interactions are the H $\cdots$ H interaction (41.5%), which appear at the central region of the fingerprint plot with  $d_e = d_i \approx 1.15$  Å

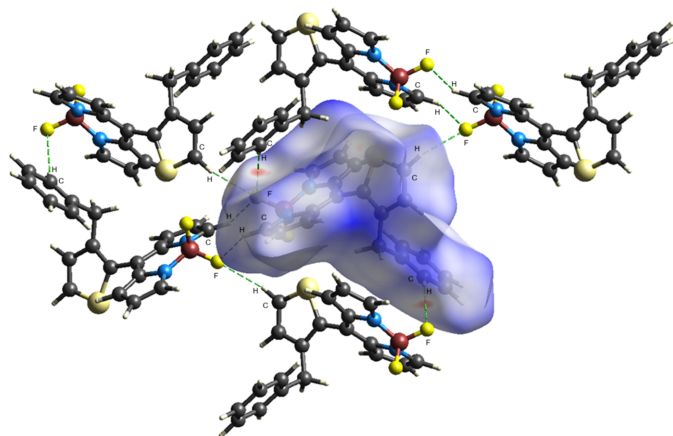

**Figure 4**

 Crystal packing along the  $a$  axis showing C–H $\cdots$ F interactions (dashed lines).

**Figure 5**

 View of the C–H $\cdots$ F interactions in Fig. 4 along the  $b$  axis.

**Figure 6**

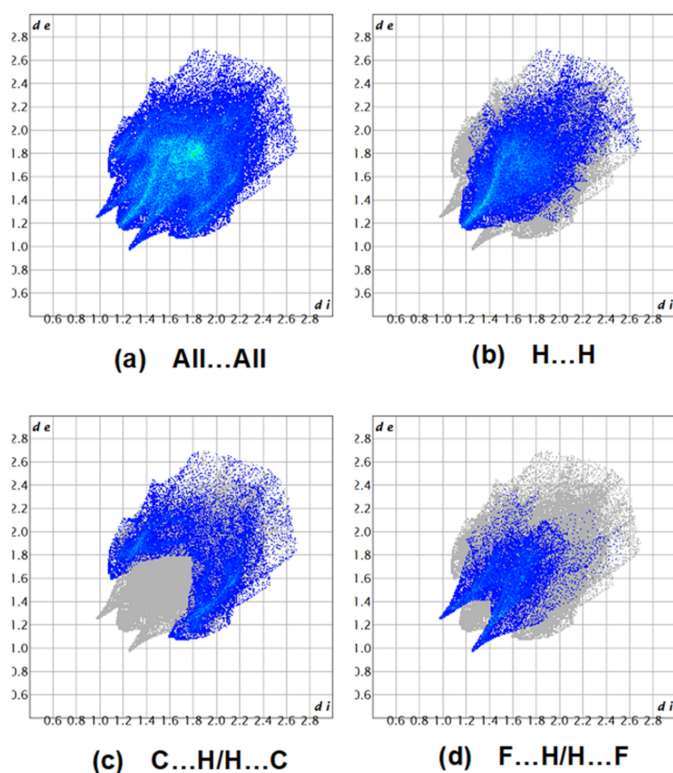
 Crystal packing along the  $a$  axis showing C–H $\cdots$  $\pi$  interactions (dashed lines).

**Figure 7**

 View of the C–H $\cdots$  $\pi$  interactions in Fig. 6 along the  $b$  axis.



**Figure 8**  
The three-dimensional Hirshfeld surface for the title compound, plotted over  $d_{\text{norm}}$ , showing C—H...F interactions (dashed lines).

(Fig. 9*b*). The reciprocal C...H/H...C interactions appear as two symmetrical broad wings with  $d_e + d_i \simeq 2.75$  Å and contribute 23.5% to the Hirshfeld surface (Fig. 9*c*). The reciprocal F...H/H...F interaction with an 18.2% contribution is present as sharp symmetrical wings at diagonal axes  $d_e + d_i \simeq 2.2$  (Fig. 9*d*). Other smaller contributions are made by S...H/H...S (6.2%), C...C (4.2%), N...H/H...N (2.3%), S...C/C...S (1.8%), S...N/N...S (0.9%), S...F/F...S (0.6%), N...C/C...N (0.5%) and F...F (0.2%) interactions.



**Figure 9**  
The two-dimensional fingerprint plots for the title molecule showing (a) all interactions, and delineated into (b) H...H, (c) C...H/H...C and (d) F...H/H...F interactions. The  $d_i$  and  $d_e$  values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

#### 4. Database survey

A search in the Cambridge Structural Database (CSD, version 6.00, update April 2025; Groom *et al.*, 2016) for 2,2-difluoro-3-aza-1-azonia-2-boranuidatricyclo[7.3.0.03,7]dodeca-1(12)\4,6,8,10-pentaene (twelve-membered ring moiety) gives thirteen hits, *viz.* **I** (DUTLOX: Shchevnikov *et al.*, 2025), **II** (GATDIQ: Khan & Ravikanth, 2012), **III** (GATDOW: Khan & Ravikanth, 2012), **IV** (KETDAQ: Jun *et al.*, 2012*a*), **V** (NARSAC: Khan *et al.*, 2012), **VI** (NARSEG: Khan *et al.*, 2012), **VII** (ROZGEU: Zhao *et al.*, 2015), **VIII** (ROZHAR: Zhao *et al.*, 2015), **IX** (ROZHEV: Zhao *et al.*, 2015), **X** (UKANUQ: Kim *et al.*, 2010), **XI** (UKANUQ01: Khan *et al.*, 2012), **XII** (ULAQOP: Sharma *et al.*, 2016) and **XIII** (XELDAV: Jun *et al.*, 2012*b*).

**II**, **III**, **VII** and **VIII** crystallize in the triclinic space group  $P\bar{1}$ . **IV** and **XII** crystallize in the orthorhombic space groups  $Pbca$  and  $Pna_21$ , respectively. **V**, **IX**, **X** and **XI** crystallize in the monoclinic space group  $P2_1/c$ , while **VI**, **XIII** and **I** crystallize in the monoclinic space groups  $P2_1/n$ ,  $C2/c$  and  $C2/c$ , respectively.

The dihedral angle between the two ring systems (furan/thiophene substituent and twelve-membered ring moiety) varies between 25.93 (10) and 88.13 (14)°, and is influenced by the substitution pattern and molecular environment. In **I**, a thiophene ring is affixed to the twelve-membered ring system, whilst the others are connected to a furan ring. In **I** 33.34 (6)°, in **II**, with two independent molecules in the asymmetric unit, the dihedral angles are 33.31 (10) and 33.85 (9)°, in **III** 44.4 (5)°, in **IV** 88.13 (14)°, in **VIII** 84.82 (8)°, in **IX** 78.02 (9)°, in **XII** 31.24 (16)°, in **XIII** 75.60 (13)°, and in **V**, with two independent molecules in the asymmetric unit, 29.4 (2) and 32.2 (2)°, respectively. In **VI**, the furan ring is disordered over two positions, the dihedral angles are 83.0 (3) and 36.9 (2)°, respectively. In **X**, with two independent molecules in the asymmetric unit, the dihedral angles are 26.59 (16) and 26.92 (17)°, with similar values for **XI** [26.65 (10) and 25.93 (10)°].

In **IV**, **VII** and **IX**, C—H...F intramolecular interactions are observed, while in **VIII** there are C—H...S and C—H...F interactions. In the remaining compounds, there are intramolecular C—H...O hydrogen bonds involving the O atom of the furan ring. Additionally, in **VI** and **XII**, besides C—H...O, there are also C—H...F interactions, and in **XIII**, intramolecular C—H...S interactions are present as well.

In compounds **I**, **II**, **III**, **V**, **VI**, **VII**, **X**, **XI**, **XII**, and **XIII**, the intramolecular C—H...O interactions have H...O distances ranging from 2.29 to 2.05 Å, and C—H...O angles ranging from 109 to 169°. In compounds **II**, **III**, **IV**, **V**, **VI**, **VII**, **VIII**, **IX**, **X**, **XI**, **XII**, and **XIII**, the intramolecular C—H...F interactions have H...F distances ranging from 2.29 to 2.55 Å, and C—H...F angles ranging from 110 to 179°. In compounds **VIII** and **XIII**, the intramolecular C—H...S interactions have H...S distances ranging from 2.77 to 2.85 Å, and C—H...S angles ranging from 105 to 111°. Intramolecular interactions can arise from the presence of different components attached to the main group of the molecules.

## 5. Synthesis and crystallization

The BODIPY synthesis procedure was reported previously (Shchevnikov *et al.*, 2025). Dipyrrolmethane **1** (Sadikhova *et al.*, 2024) (418 mg, 1.3 mmol) was dissolved in dry DCM (20 mL), after that 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ, 890 mg, 3.9 mmol) was added; the reaction mixture was stirred for 30 min at r.t (TLC control), poured into water (50 mL) and extracted with DCM (3 × 30 mL). The organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated *in vacuo* and the residue was dissolved in dry DCM (20 mL). Boron trifluoride etherate (3.3 ml, 26.3 mmol) and an equal volume of diisopropylethylamine (DIPEA, 3.3 ml) were added to the solution. The reaction mixture was stirred at r.t. for 1 h (TLC control) and then poured into water (50 mL), extracted with DCM (3 × 30 mL) and washed with saturated Na<sub>2</sub>CO<sub>3</sub> (3 × 30 mL). The organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, the target product **2** was purified by column chromatography (eluent: ethyl acetate/hexane 1:10) to give red crystals, yield 40%, 188 mg (0.52 mmol), m.p. 407–409 K. Single crystals of the title compound were grown from a mixture of ethyl acetate/hexane. IR (KBr),  $\nu$  (cm<sup>-1</sup>): 1551, 1410, 1386, 1110, 1074, 828. <sup>1</sup>H NMR (700.2 MHz, CDCl<sub>3</sub>) (*J*, Hz):  $\delta$  7.93 (*br.s*, 2H, H Pyr), 7.49 (*d*, *J* = 5.25 Hz, 1H, H-5 Thien), 7.21 (*t*, *J* = 7.39 Hz, 2H, H-3,5 Ph), 7.15 (*t*, *J* = 7.39 Hz, 1H, H-4 Ph), 7.01–6.98 (*m*, 5H, H Aryl + H Pyr + H-4 Thien), 6.54 (*m*, 2H, H Pyr), 3.96 (*s*, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (176.1 MHz, CDCl<sub>3</sub>):  $\delta$  167.8, 144.6 (2C), 142.9, 139.6, 139.3, 135.8, 132.5, 131.5, 130.9, 130.1, 128.8, 128.6 (2C), 128.5 (2C), 128.1, 126.4, 118.7, 35.6. <sup>19</sup>F NMR (658.8 MHz, CDCl<sub>3</sub>):  $\delta$  -144.8 – -145.5 (*m*, 2F). GC-MS (EI, 70 eV): *m/z* (%) = 364 (62) [*M*<sup>+</sup>], 363 (87), 343 (17), 342 (17), 288 (15), 287 (84), 286 (88), 268 (10), 267 (58), 266 (100), 172 (10).

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All C-bound H atoms were positioned geometrically (C–H = 0.95 and 0.99 Å) and refined using a riding model with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . Owing to poor agreement between observed and calculated intensities, one outlier (0 0 2) was omitted in the final cycles of refinement.

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The authors' contributions are as follows; conceptualization MA and GMM; synthesis, ZAP and ASL; X-ray analysis VNK; founding ZAP, NAG and KIH; writing (review and editing of the manuscript) NAG, KIH and MA; supervision MA and GMM.

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**Table 3**

Experimental details.

Crystal data	
Chemical formula	C <sub>20</sub> H <sub>15</sub> BF <sub>2</sub> N <sub>2</sub> S
<i>M<sub>r</sub></i>	364.21
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.6652 (2), 11.9170 (2), 18.8416 (4)
$\beta$ (°)	91.7200 (8)
<i>V</i> (Å <sup>3</sup> )	1720.33 (6)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.21
Crystal size (mm)	0.27 × 0.15 × 0.04
Data collection	
Diffractometer	Bruker D8 QUEST PHOTON-III area detector
Absorption correction	Analytical ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.702, 0.746
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	64200, 6292, 5312
<i>R<sub>int</sub></i>	0.041
( $\sin \theta/\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.759
Refinement	
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , <i>S</i>	0.034, 0.090, 1.03
No. of reflections	6292
No. of parameters	235
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.45, -0.31

Computer programs: *APEX3* and *SAINT* (Bruker, 2018), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

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## supporting information

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## Crystal structure and Hirshfeld surface analysis of 10-(3-benzylthiophen-2-yl)-5,5-difluoro-5*H*-4 $\lambda^4$ ,5 $\lambda^4$ -dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine

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### Computing details

#### 10-(3-Benzylthiophen-2-yl)-5,5-difluoro-5*H*-4 $\lambda^4$ ,5 $\lambda^4$ -dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine

##### Crystal data

C<sub>20</sub>H<sub>15</sub>BF<sub>2</sub>N<sub>2</sub>S

*M<sub>r</sub>* = 364.21

Monoclinic, *P*2<sub>1</sub>/*n*

*a* = 7.6652 (2) Å

*b* = 11.9170 (2) Å

*c* = 18.8416 (4) Å

$\beta$  = 91.7200 (8)°

*V* = 1720.33 (6) Å<sup>3</sup>

*Z* = 4

*F*(000) = 752

*D<sub>x</sub>* = 1.406 Mg m<sup>-3</sup>

Mo *K* $\alpha$  radiation,  $\lambda$  = 0.71073 Å

Cell parameters from 9889 reflections

$\theta$  = 2.8–32.5°

$\mu$  = 0.21 mm<sup>-1</sup>

*T* = 100 K

Plate, colourless

0.27 × 0.15 × 0.04 mm

##### Data collection

Bruker D8 QUEST PHOTON-III area detector diffractometer

Radiation source: fine-focus sealed X-ray tube  $\varphi$  and  $\omega$  scans

Absorption correction: analytical (SADABS; Krause *et al.*, 2015)

*T<sub>min</sub>* = 0.702, *T<sub>max</sub>* = 0.746

64200 measured reflections

6292 independent reflections

5312 reflections with *I* > 2 $\sigma$ (*I*)

*R<sub>int</sub>* = 0.041

$\theta_{\max}$  = 32.7°,  $\theta_{\min}$  = 2.8°

*h* = -11→11

*k* = -17→18

*l* = -28→28

##### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.034

*wR*(*F*<sup>2</sup>) = 0.090

*S* = 1.03

6292 reflections

235 parameters

0 restraints

Primary atom site location: difference Fourier map

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

*w* = 1/[ $\sigma^2(F_o^2) + (0.0403P)^2 + 0.7409P$ ]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

( $\Delta/\sigma$ )<sub>max</sub> = 0.001

$\Delta\rho_{\max}$  = 0.45 e Å<sup>-3</sup>

$\Delta\rho_{\min}$  = -0.30 e Å<sup>-3</sup>

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.84161 (3)	0.77669 (2)	0.66905 (2)	0.01507 (6)
F1	0.37533 (8)	0.47800 (5)	0.87911 (4)	0.02186 (13)
F2	0.44409 (9)	0.62246 (6)	0.95338 (3)	0.02200 (13)
N1	0.42895 (10)	0.65968 (7)	0.82742 (4)	0.01540 (15)
N2	0.67101 (10)	0.54855 (7)	0.88026 (4)	0.01384 (14)
C1	0.28040 (13)	0.71956 (9)	0.81925 (6)	0.02002 (19)
H1	0.191765	0.724323	0.853302	0.024*
C2	0.27586 (13)	0.77380 (9)	0.75314 (6)	0.0224 (2)
H2	0.186268	0.821940	0.735087	0.027*
C3	0.42703 (13)	0.74382 (9)	0.71911 (6)	0.01876 (18)
H3	0.459250	0.766234	0.672925	0.023*
C4	0.52415 (12)	0.67355 (8)	0.76622 (5)	0.01446 (16)
C5	0.69134 (12)	0.62665 (8)	0.76159 (5)	0.01292 (15)
C6	0.76540 (12)	0.56795 (8)	0.81948 (5)	0.01312 (15)
C7	0.93860 (12)	0.53056 (8)	0.83257 (5)	0.01448 (16)
H7	1.031418	0.533229	0.800315	0.017*
C8	0.94721 (13)	0.48929 (8)	0.90137 (5)	0.01685 (17)
H8	1.047172	0.458677	0.925277	0.020*
C9	0.77969 (13)	0.50136 (8)	0.92910 (5)	0.01684 (17)
H9	0.748065	0.479417	0.975450	0.020*
C10	0.79423 (12)	0.64260 (8)	0.69795 (5)	0.01341 (15)
C11	0.86597 (12)	0.56204 (8)	0.65512 (5)	0.01466 (16)
C12	0.96116 (13)	0.61169 (8)	0.59931 (5)	0.01747 (17)
H12	1.019220	0.569191	0.564492	0.021*
C13	0.96074 (13)	0.72614 (9)	0.60079 (5)	0.01759 (17)
H13	1.019433	0.772085	0.567917	0.021*
C14	0.83518 (14)	0.43748 (8)	0.66102 (5)	0.01752 (17)
H14A	0.792936	0.420093	0.708926	0.021*
H14B	0.946934	0.397354	0.655200	0.021*
C15	0.70289 (13)	0.39605 (8)	0.60560 (5)	0.01605 (17)
C16	0.52988 (14)	0.43302 (10)	0.60547 (6)	0.0230 (2)
H16	0.494303	0.484795	0.640544	0.028*
C17	0.40940 (15)	0.39469 (11)	0.55446 (7)	0.0277 (2)
H17	0.292221	0.420597	0.554866	0.033*
C18	0.45901 (16)	0.31889 (11)	0.50298 (7)	0.0277 (2)
H18	0.376319	0.292630	0.468269	0.033*
C19	0.63037 (16)	0.28183 (10)	0.50265 (6)	0.0261 (2)
H19	0.665301	0.229907	0.467558	0.031*
C20	0.75163 (14)	0.32035 (9)	0.55354 (6)	0.01976 (18)

H2O	0.868880	0.294677	0.552698	0.024*
B1	0.47484 (14)	0.57533 (9)	0.88759 (6)	0.01587 (18)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.01764 (10)	0.01170 (10)	0.01596 (10)	−0.00004 (7)	0.00183 (7)	0.00133 (7)
F1	0.0164 (3)	0.0159 (3)	0.0335 (3)	−0.0049 (2)	0.0042 (2)	−0.0008 (2)
F2	0.0260 (3)	0.0227 (3)	0.0179 (3)	−0.0011 (2)	0.0099 (2)	−0.0029 (2)
N1	0.0126 (3)	0.0151 (3)	0.0186 (4)	−0.0003 (3)	0.0032 (3)	−0.0024 (3)
N2	0.0145 (3)	0.0149 (3)	0.0123 (3)	−0.0024 (3)	0.0025 (3)	−0.0006 (3)
C1	0.0131 (4)	0.0194 (4)	0.0277 (5)	0.0001 (3)	0.0023 (3)	−0.0045 (4)
C2	0.0142 (4)	0.0228 (5)	0.0298 (5)	0.0031 (4)	−0.0031 (4)	−0.0019 (4)
C3	0.0168 (4)	0.0191 (4)	0.0202 (4)	0.0011 (3)	−0.0031 (3)	0.0002 (3)
C4	0.0137 (4)	0.0140 (4)	0.0157 (4)	−0.0001 (3)	0.0010 (3)	−0.0019 (3)
C5	0.0141 (4)	0.0115 (4)	0.0133 (4)	−0.0009 (3)	0.0015 (3)	−0.0012 (3)
C6	0.0133 (3)	0.0137 (4)	0.0125 (3)	−0.0014 (3)	0.0026 (3)	−0.0003 (3)
C7	0.0131 (4)	0.0147 (4)	0.0157 (4)	−0.0009 (3)	0.0006 (3)	−0.0003 (3)
C8	0.0164 (4)	0.0184 (4)	0.0156 (4)	−0.0013 (3)	−0.0020 (3)	0.0010 (3)
C9	0.0188 (4)	0.0185 (4)	0.0132 (4)	−0.0035 (3)	0.0004 (3)	0.0006 (3)
C10	0.0152 (4)	0.0121 (4)	0.0130 (4)	0.0003 (3)	0.0013 (3)	0.0015 (3)
C11	0.0175 (4)	0.0135 (4)	0.0131 (4)	0.0021 (3)	0.0013 (3)	0.0010 (3)
C12	0.0200 (4)	0.0180 (4)	0.0146 (4)	0.0024 (3)	0.0042 (3)	0.0010 (3)
C13	0.0186 (4)	0.0188 (4)	0.0155 (4)	−0.0004 (3)	0.0032 (3)	0.0030 (3)
C14	0.0251 (5)	0.0124 (4)	0.0151 (4)	0.0029 (3)	0.0007 (3)	0.0004 (3)
C15	0.0208 (4)	0.0118 (4)	0.0157 (4)	0.0006 (3)	0.0027 (3)	0.0021 (3)
C16	0.0213 (5)	0.0207 (5)	0.0274 (5)	0.0029 (4)	0.0057 (4)	−0.0007 (4)
C17	0.0184 (5)	0.0273 (5)	0.0373 (6)	−0.0005 (4)	0.0006 (4)	0.0043 (5)
C18	0.0267 (5)	0.0263 (5)	0.0295 (5)	−0.0070 (4)	−0.0058 (4)	0.0023 (4)
C19	0.0308 (5)	0.0226 (5)	0.0248 (5)	−0.0022 (4)	−0.0013 (4)	−0.0066 (4)
C20	0.0225 (4)	0.0164 (4)	0.0204 (4)	0.0015 (3)	0.0014 (4)	−0.0026 (3)
B1	0.0155 (4)	0.0151 (4)	0.0173 (4)	−0.0025 (3)	0.0049 (3)	−0.0021 (3)

*Geometric parameters (Å, °)*

S1—C13	1.7093 (10)	C8—H8	0.9500
S1—C10	1.7302 (9)	C9—H9	0.9500
F1—B1	1.3948 (12)	C10—C11	1.3792 (13)
F2—B1	1.3875 (12)	C11—C12	1.4263 (13)
N1—C1	1.3488 (13)	C11—C14	1.5076 (14)
N1—C4	1.3928 (12)	C12—C13	1.3641 (14)
N1—B1	1.5477 (14)	C12—H12	0.9500
N2—C9	1.3457 (12)	C13—H13	0.9500
N2—C6	1.3921 (11)	C14—C15	1.5161 (14)
N2—B1	1.5474 (13)	C14—H14A	0.9900
C1—C2	1.4028 (16)	C14—H14B	0.9900
C1—H1	0.9500	C15—C20	1.3920 (14)
C2—C3	1.3878 (14)	C15—C16	1.3974 (15)

C2—H2	0.9500	C16—C17	1.3900 (17)
C3—C4	1.4155 (14)	C16—H16	0.9500
C3—H3	0.9500	C17—C18	1.3869 (18)
C4—C5	1.4033 (13)	C17—H17	0.9500
C5—C6	1.4015 (13)	C18—C19	1.3860 (18)
C5—C10	1.4672 (12)	C18—H18	0.9500
C6—C7	1.4151 (13)	C19—C20	1.3929 (15)
C7—C8	1.3861 (13)	C19—H19	0.9500
C7—H7	0.9500	C20—H20	0.9500
C8—C9	1.4081 (14)		
C13—S1—C10	91.91 (5)	C10—C11—C14	125.18 (9)
C1—N1—C4	107.71 (9)	C12—C11—C14	123.20 (8)
C1—N1—B1	126.85 (8)	C13—C12—C11	113.47 (9)
C4—N1—B1	124.78 (8)	C13—C12—H12	123.3
C9—N2—C6	107.79 (8)	C11—C12—H12	123.3
C9—N2—B1	127.48 (8)	C12—C13—S1	111.67 (7)
C6—N2—B1	124.72 (8)	C12—C13—H13	124.2
N1—C1—C2	110.08 (9)	S1—C13—H13	124.2
N1—C1—H1	125.0	C11—C14—C15	111.89 (8)
C2—C1—H1	125.0	C11—C14—H14A	109.2
C3—C2—C1	107.03 (9)	C15—C14—H14A	109.2
C3—C2—H2	126.5	C11—C14—H14B	109.2
C1—C2—H2	126.5	C15—C14—H14B	109.2
C2—C3—C4	107.05 (9)	H14A—C14—H14B	107.9
C2—C3—H3	126.5	C20—C15—C16	118.54 (10)
C4—C3—H3	126.5	C20—C15—C14	120.55 (9)
N1—C4—C5	120.42 (8)	C16—C15—C14	120.90 (9)
N1—C4—C3	108.10 (8)	C17—C16—C15	120.56 (10)
C5—C4—C3	131.36 (9)	C17—C16—H16	119.7
C6—C5—C4	119.99 (8)	C15—C16—H16	119.7
C6—C5—C10	119.05 (8)	C18—C17—C16	120.48 (11)
C4—C5—C10	120.90 (8)	C18—C17—H17	119.8
N2—C6—C5	120.98 (8)	C16—C17—H17	119.8
N2—C6—C7	108.20 (8)	C19—C18—C17	119.37 (11)
C5—C6—C7	130.45 (8)	C19—C18—H18	120.3
C8—C7—C6	107.02 (8)	C17—C18—H18	120.3
C8—C7—H7	126.5	C18—C19—C20	120.32 (11)
C6—C7—H7	126.5	C18—C19—H19	119.8
C7—C8—C9	107.01 (8)	C20—C19—H19	119.8
C7—C8—H8	126.5	C15—C20—C19	120.73 (10)
C9—C8—H8	126.5	C15—C20—H20	119.6
N2—C9—C8	109.97 (8)	C19—C20—H20	119.6
N2—C9—H9	125.0	F2—B1—F1	109.39 (8)
C8—C9—H9	125.0	F2—B1—N2	110.78 (8)
C11—C10—C5	128.43 (8)	F1—B1—N2	110.35 (8)
C11—C10—S1	111.57 (7)	F2—B1—N1	110.53 (8)
C5—C10—S1	119.99 (7)	F1—B1—N1	110.16 (8)

C10—C11—C12	111.37 (8)	N2—B1—N1	105.59 (7)
C4—N1—C1—C2	-0.25 (12)	C13—S1—C10—C5	178.07 (8)
B1—N1—C1—C2	-171.22 (9)	C5—C10—C11—C12	-178.38 (9)
N1—C1—C2—C3	1.12 (12)	S1—C10—C11—C12	0.69 (11)
C1—C2—C3—C4	-1.50 (12)	C5—C10—C11—C14	7.25 (16)
C1—N1—C4—C5	175.67 (9)	S1—C10—C11—C14	-173.69 (8)
B1—N1—C4—C5	-13.13 (14)	C10—C11—C12—C13	0.24 (13)
C1—N1—C4—C3	-0.70 (11)	C14—C11—C12—C13	174.74 (9)
B1—N1—C4—C3	170.50 (9)	C11—C12—C13—S1	-1.06 (12)
C2—C3—C4—N1	1.38 (11)	C10—S1—C13—C12	1.22 (8)
C2—C3—C4—C5	-174.45 (10)	C10—C11—C14—C15	100.99 (11)
N1—C4—C5—C6	-1.70 (14)	C12—C11—C14—C15	-72.74 (12)
C3—C4—C5—C6	173.70 (10)	C11—C14—C15—C20	116.03 (10)
N1—C4—C5—C10	-178.78 (8)	C11—C14—C15—C16	-63.81 (12)
C3—C4—C5—C10	-3.38 (16)	C20—C15—C16—C17	0.12 (16)
C9—N2—C6—C5	-173.72 (9)	C14—C15—C16—C17	179.97 (10)
B1—N2—C6—C5	7.51 (14)	C15—C16—C17—C18	0.16 (18)
C9—N2—C6—C7	0.03 (10)	C16—C17—C18—C19	-0.21 (19)
B1—N2—C6—C7	-178.74 (8)	C17—C18—C19—C20	-0.01 (18)
C4—C5—C6—N2	4.41 (14)	C16—C15—C20—C19	-0.34 (16)
C10—C5—C6—N2	-178.46 (8)	C14—C15—C20—C19	179.81 (10)
C4—C5—C6—C7	-167.78 (9)	C18—C19—C20—C15	0.29 (18)
C10—C5—C6—C7	9.35 (15)	C9—N2—B1—F2	43.37 (13)
N2—C6—C7—C8	-0.24 (11)	C6—N2—B1—F2	-138.11 (9)
C5—C6—C7—C8	172.72 (10)	C9—N2—B1—F1	-77.93 (12)
C6—C7—C8—C9	0.34 (11)	C6—N2—B1—F1	100.59 (10)
C6—N2—C9—C8	0.19 (11)	C9—N2—B1—N1	163.05 (9)
B1—N2—C9—C8	178.91 (9)	C6—N2—B1—N1	-18.42 (12)
C7—C8—C9—N2	-0.34 (11)	C1—N1—B1—F2	-49.37 (13)
C6—C5—C10—C11	58.94 (14)	C4—N1—B1—F2	141.13 (9)
C4—C5—C10—C11	-123.95 (11)	C1—N1—B1—F1	71.64 (12)
C6—C5—C10—S1	-120.06 (8)	C4—N1—B1—F1	-97.87 (10)
C4—C5—C10—S1	57.05 (11)	C1—N1—B1—N2	-169.22 (9)
C13—S1—C10—C11	-1.09 (8)	C4—N1—B1—N2	21.27 (12)

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

*Cg*1 and *Cg*2 are the centroids of the S1/C10–C13 and N1/C1–C4 rings, respectively.

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C9—H9 $\cdots$ F2 <sup>i</sup>	0.95	2.36	3.2017 (12)	148
C13—H13 $\cdots$ F2 <sup>ii</sup>	0.95	2.55	3.3113 (12)	137
C20—H20 $\cdots$ F2 <sup>iii</sup>	0.95	2.51	3.3221 (13)	144
C14—H14 $\cdots$ <i>Cg</i> 2 <sup>iii</sup>	0.99	2.81	3.5815 (11)	135
C18—H18 $\cdots$ <i>Cg</i> 1 <sup>iv</sup>	0.95	2.92	3.7764 (13)	151

Symmetry codes: (i)  $-x+1, -y+1, -z+2$ ; (ii)  $x+1/2, -y+3/2, z-1/2$ ; (iii)  $-x+3/2, y-1/2, -z+3/2$ ; (iv)  $-x+1, -y+1, -z+1$ .