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Crystal structure of 2,7-diiodo-1,3,6,8-tetramethyl-bis(difluoroboron)-1,2-bis((1H-pyrrol-2-yl)methylene)hydrazine, $C_{14}H_{14}B_2F_4I_2N_4$

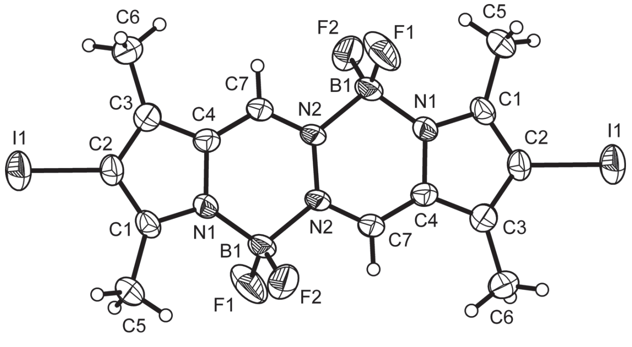

Figure 1: A view of the molecule. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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Abstract

$C_{14}H_{15}B_2F_4I_2N_4$, triclinic, $P\bar{1}$ (no. 2), $a = 7.5458(7)$ Å, $b = 8.5659(6)$ Å, $c = 8.6089(5)$ Å, $\alpha = 108.189(6)°$, $\beta = 110.492(7)°$, $\gamma = 98.678(7)°$, $V = 473.6$ Å^3, $Z = 1$, $R_{gt}(F) = 0.0334$, $wR_{ref}(F^2) = 0.0831$, $T = 296.5$ K.

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The molecular structure is shown in the Figure 1. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Red block
Size:	$0.60 \times 0.60 \times 0.40$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	3.36 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	26.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	2991, 1960, 0.042
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1785
$N(param)_{refined}$:	121
Programs:	CrysAlis^{PRO} [1], Olex2 [2], SHELX [3, 4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
B1	0.4114(8)	0.2653(5)	0.7872(6)	0.0379(10)
C1	0.2518(5)	0.2664(5)	0.4677(5)	0.0338(8)
C2	0.2067(6)	0.3913(5)	0.3997(5)	0.0355(8)
C3	0.2655(6)	0.5488(5)	0.5418(5)	0.0343(8)
C4	0.3492(5)	0.5170(5)	0.6987(5)	0.0315(8)
C5	0.2141(8)	0.0795(6)	0.3670(6)	0.0493(11)
H5A	0.3171	0.0409	0.4330	0.074*
H5B	0.2122	0.0603	0.2504	0.074*
H5C	0.0888	0.0169	0.3528	0.074*
C6	0.2426(7)	0.7148(5)	0.5322(6)	0.0457(10)
H6A	0.3278	0.7551	0.4835	0.069*
H6B	0.2773	0.7976	0.6510	0.069*
H6C	0.1077	0.6992	0.4558	0.069*
C7	0.4281(5)	0.6256(4)	0.8775(5)	0.0312(8)
H7	0.4302	0.7397	0.9022	0.037*
F1	0.2618(5)	0.1442(4)	0.7743(4)	0.0785(10)
F2	0.5609(5)	0.1966(4)	0.7722(4)	0.0695(9)
I1	0.06425(4)	0.34161(4)	0.12839(3)	0.05323(18)
N1	0.3391(5)	0.3433(4)	0.6490(4)	0.0320(7)
N2	0.5007(4)	0.5852(4)	1.0166(4)	0.0288(6)

Source of material

The title compound was synthesized from commerically available 2,4-dimethylpyrrole as the literature described [5, 6]. The key intermediate BOPHY (bis(difluoroboron) 1,2-bis((1*H*-pyrrol-2-yl)methylene)hydrazine) was obtained by three steps including Vilsmeier-Haack formylation, amidation, and complexation. The title compound was synthesized according to the following procedure [7]. In ethanol 50 mL, BOPHY 338 mg

(1.0 mmol), iodine 635 mg (2.5 mmol), and hydroiodic acid 352 mg (2.0 mmol) were mixed. Then it was heated to be refluxed in the dark, resulting in a deep-red solution. Once the BOPHY disappeared on the TLC plate, the reaction mixture was quenched by water 50 mL. After a succesive washing, extraction, concentration, and purification, a yellow powder was obtained (500 mg, 85%). Crystals were obtained by slow evaporation within 5 days.

Experimental details

The hydrogen atoms were placed geometrically and refined using a riding model with d(C—H) = 0.93 Å (aromatic), 0.96 Å ($-CH_3$). $U_{iso}(H) = 1.2\ U_{eq}(C)$ for CH or $U_{iso}(H) = 1.5\ U_{eq}(C)$ CH_3 groups. [3].

Comment

Only a limited number of BOPHY derivatives, so far, have been well documented structurally althouth its analogues BODIPY and fluorine-boron complex (FBC) are of general interest [8, 9]. The first review paper on BOPHY was published in 2018 [10]. BODIPY is a typical member of FBC, which has received great interests owing to its excellent photo-stability and thermo-stability [11–13]. As far as we know, no halogenated BOPHY derivative has been reported. This contributiion is part of our continuing interest in BOPHY and its intermolecular interactions.

The asymmetric unit of the title structure contains half of a title molecule (see Figure 1). The bond lengths and angles within these moieties are in the expected ranges.

The fluorophore is rigidly planar and composed of four rings, including two pyrrole rings at the periphery and two six-membered rings, each containing a BF_2 moiety (Figure 1). The framework has an inversion center and follows that of BODIPY core. The bond lengths support the regular aromaticity of the peripheral pyrrole rings. Except fluorine atoms, all other atoms are almost coplanar (RMS deviation = 0.022 Å). The C—N and N=N in hydrazine Schiff base units exhibit single- and double-bond character. It is attesting that the title compound does not have aromaticity extended across the tetracycles. The two planes configured by BF_2 units are perpendicular to the tetracycle system and the dihedral angles are estimated to be 89.5° (*cf.* the parent compound [6]).

The BF_2 unit donates a hydrogen bond to C—H···F interactions (C5—H5C···F1$_i$, i: $1 + x$, $2 + y$, $1 + z$), which join adjacent molecules side by side. Apart from the H···F interaction, it is the π···π interaction that joins adjacent molecules. The molecules are seperated by 3.69 Å. In addition, C—H···π interactions also contribute to the cohesion of the molecules [14]. It can be observed that the parallel displacement configuration occurs to the adjacent molecules.

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