Weifeng He, Yingfan Liu*, Saisai Sun, Guangqian Ji and Xiaochuan Li*

Crystal structure of 2-bromo-1,3,6,8-tetramethylBOPHY (BOPHY = bis(difluoroboron)-1,2-bis((1H-pyrrol-2-yl)methylene)hydrazine), C_{14}H_{15}B_{2}BrF_{4}N_{4}

https://doi.org/10.1515/ncrs-2021-0163
Received April 26, 2021; accepted May 17, 2021; published online June 21, 2021

Abstract

C_{14}H_{15}B_{2}BrF_{4}N_{4}, orthorhombic, Pbc a (no. 61), a = 11.970(1) Å, b = 10.049(1) Å, c = 27.847(1) Å, V = 3349.6 Å³, Z = 8, R_{gt}(F) = 0.0697, wR_{ref}(F^2) = 0.1585, T = 296 K.

CCDC no.: 2080820

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

Source of material

2-Bromo-1,3,6,8-tetramethylBOPHY was synthesized according to the literature [6–9]. Firstly, 2,4-dimethylpyrrole and boron trifluoride etherate were condensed at room temperature to give 1,3,6,8-tetramethylBOPHY [6, 7]. Next, bromination of 1,3,6,8-tetramethylBOPHY would give single or double bromine substituted BOPHY derivatives by treating it with a halogenation reagent. Copper(II) bromide and N-bromosuccinimide (NBS) are all candidates for bromination of 1,3,6,8-tetramethylBOPHY. However, bromination with NBS is an economic selection, together with the advantage of an easier work-up and purification. Additionally, there are two β positions, where both the two aromatic hydrogen atoms are easy to be substituted by halogenation when subject to electrophilic attack of electrophiles. In case of

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.
bromination of 1,3,6,8-tetramethylBOPHY, the mono-
bromination is strongly dependent on the equivalent 
proportion between 1,3,6,8-tetramethylBOPHY and NBS. 
When treated with one equivalent of NBS, mono-bromo 
derivatives will be the main product, together with a small 
quantity of di-bromo derivatives. 1,3,6,8-tetramethyl-
BOPHY (338 mg) was added to dichloromethane (100 mL) 
and stirred until a complete dissolution. NBS (178 mg) was 
added in portions to the above solution at room tempera-
ture. The mixture was stirred for about 12 h in the dark. 
Reaction progress was monitored by TLC methodology. 
Once BOPPHY disappeared in the TLC plate, the mixture was 
quenched by distilled water (100 mL). After successive 
extraction, washing, drying, and condensing, the crude 
product was purified by silica gel column chromatography, 
yielding an orange powder (186 mg). Single crystals suitable 
for X-ray diffraction were obtained by evaporation of a 
saturated dichloromethane solution of the obtained orange 
powder within five 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 (–CH3). Uiso(H) = 1.2 Ueq(C) for CH or Uiso(H) = 1.5 
Ueq(C) CH3 groups. There is a disorder at the C2/C9 position 
(see the figure).

**Comment**

In dye chemistry, fluorine-boron complex (FBC) is a 
typical member of fluorescent dyes [8–13]. It is robust 
towards light and thermal influences. And its emission in 
full width at half maximum is narrower than most estab-
lished fluorescent dyes, such as coumarin, rhodamine, 
naphthalimide, etc. In the FBC family, the typical one is 
BODIPY with the emission peak in the green region, which 
is different from the emission of general FBC [8]. Struct-
urally, BOPHY is similar to BODIPY. Both of them have a 
BF2 unit. However, BOPHY has two BF2 units. Interest-
ingly, the emission of BOPHY shifts towards shorter 
wavelength in contrast to BODIPY and one can observe 
bright blue-green color when excited the BOPHY de-
rivatives in organic solvent. The chemical modification of
BOPHY could alter its photophysical properties as expected. More functional groups also can be attached to the BOPHY according to the requirement of material chemistry or biotechnology demand [10–15]. The substitution strategy of BOPHY can be copied based on that of BODIPY [14, 15]. For example, the sensor configuration of BODIPY can be transferred to BOPHY due to the identical key active position, two β hydrogen atoms and four methyl hydrogen atoms [16, 17]. Therefore, the bromine or iodine substituted BOPHY will be the key compound for the next step of advanced functionalities by copying BODIPY or introducing new groups [18, 19].

There is one molecule in the asymmetric unit. Bond lengths and angles within molecules are in the expected ranges. The frame work of BOPHY is rigid with two pyrrole rings at the periphery, which is identical to that of BODIPY. The difference to BODIPY is that the two pyrrole rings are bridged by hydrazine. The BF₂ units fix the molecule to form a closed rigid ring. Therefore, double five and six membered rings configure the basic framework of BOPHY. Also, there is an inversion center (C₂h symmetry), following that of BODIPY. The bonds length demonstrates further the regular aromaticity of the pyrrole rings. The ring of BOPHY is coplanar (RMS deviation = 0.102 Å), except the four fluorine atoms. The two plane configured by BF₂ units are perpendicular to the tetracyclic system and the dihedral angles are estimated to be 87.74° and 87.73°. The C–N (1.317, 1.322 Å) and N=N (1.410 Å) show a single and double bond character, respectively. Therefore, the conjugate system does not distribute over the whole ring. The β-substituted bromine atoms are disordered and modeled in a 70.5:29.5 ratio.

The intermolecular interactions that drive the crystallization of the dye molecules mainly include C–H⋯F and π⋯π interactions. The parallel staggered molecules are packed by intermolecular π⋯π interactions. The distance between parallel molecules is estimated to be 3.59 Å. Also, many weak C-H⋯π interactions contribute to the cohesion of molecules [20]. Adjacent molecules are connected via non-classical C–H⋯F and C–H⋯Br hydrogen bonds. Each methyl group donates one hydroxide bonds and each bromine atom accepts one of them. All Br⋯H distances are significantly below the typical van der Waals distances [21]. In contrast, each fluorine atom accepts at least one hydrogen bond. More importantly, the C–H⋯F hydrogen bonds are the stronger interactions, which stabilize the dye molecules packing. In addition, the C–H⋯F connect the molecules to zig–zag-chains along the crystallographic c axis. Whereas, the C–H⋯Br connect the molecules side by side linearly. Generally, the tight packing in the solid would lead to significant emission quench. However, some BODIPY or BOPHY emit bright light in solid. Therefore, careful analysis of the intermolecular interactions benefit to understand the aggregated induced emission [8, 9].

**Author contributions:** All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

**Research funding:** This work was supported by the National Natural Science Foundation of China (21772034).

**Conflict of interest statement:** The authors declare no conflicts of interest regarding this article.

**References**

2. OlexSys Ltd. OLEX 2, Chemistry Department; Durham University: DH1 3LE, UK.


