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Crystal structure of 2-bromo-1,3,6,8-tetramethylBOPHY (BOPHY = bis(difluoroboron)-1,2-bis((1*H*-pyrrol-2-yl)methylene)hydrazine), $C_{14}H_{15}B_2BrF_4N_4$

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Abstract

$C_{14}H_{15}B_2BrF_4N_4$, orthorhombic, *Pbca* (no. 61), $a = 11.970(1) \text{ \AA}$, $b = 10.049(1) \text{ \AA}$, $c = 27.847(1) \text{ \AA}$, $V = 3349.6 \text{ \AA}^3$, $Z = 8$, $R_{\text{gt}}(F) = 0.0697$, $wR_{\text{ref}}(F^2) = 0.1585$, $T = 296 \text{ K}$.

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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

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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.

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

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.30 × 0.23 × 0.17 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	2.50 mm ⁻¹
Diffraction, scan mode:	Xcalibur, φ and ω
$\theta_{\max}$, completeness:	28.3°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	66,122, 4156, 0.088
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 2757
$N(\text{param})_{\text{refined}}$:	240
Programs:	CRYSTALIS ^{PRO} [1], OLEX2 [2], SHELX [3, 4], DIAMOND [5]

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 temperature. The mixture was stirred for about 12 h in the dark. Reaction progress was monitored by TLC methodology. Once BOPHY 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 $d(\text{C-H}) = 0.93$ Å (aromatic), 0.96 Å ($-\text{CH}_3$). $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ for CH or $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$ 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 established fluorescent dyes, such as coumarin, rhodamine,

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1 ^a	0.88323 (7)	0.11819 (9)	0.32237 (3)	0.0583 (3)
Br1A ^b	0.8956 (2)	0.1305 (3)	0.77722 (7)	0.0749 (9)
F1	0.7733 (3)	−0.1147 (3)	0.51179 (10)	0.0497 (7)
F2	0.6626 (2)	0.0665 (3)	0.50726 (11)	0.0519 (8)
F3	1.0896 (2)	0.2477 (3)	0.59149 (11)	0.0522 (8)
F4	0.9340 (3)	0.3742 (3)	0.59566 (11)	0.0545 (8)
N1	0.8334 (3)	0.0671 (4)	0.46243 (14)	0.0373 (9)
N2	0.8341 (3)	0.0834 (4)	0.55227 (14)	0.0354 (9)
N3	0.9272 (3)	0.1692 (4)	0.55015 (14)	0.0351 (8)
N4	0.9367 (3)	0.1716 (4)	0.64030 (14)	0.0407 (9)
C1	0.9624 (4)	0.1770 (5)	0.41647 (18)	0.0395 (11)
C2	0.8877 (4)	0.1092 (5)	0.38792 (17)	0.0426 (11)
H2 ^b	0.889841	0.107987	0.354539	0.051*
C3	0.8084 (4)	0.0426 (5)	0.41569 (17)	0.0385 (11)
C4	0.9268 (4)	0.1487 (4)	0.46382 (16)	0.0354 (10)
C5	0.9678 (4)	0.1967 (4)	0.50714 (18)	0.0386 (11)
H5	1.029286	0.253244	0.505775	0.046*
C6	0.7992 (4)	0.0483 (5)	0.59532 (17)	0.0387 (11)
H6	0.737803	−0.008248	0.596666	0.046*
C7	0.8447 (4)	0.0871 (5)	0.63847 (17)	0.0402 (11)
C8	0.9656 (5)	0.1867 (6)	0.68679 (19)	0.0504 (13)
C9	0.8910 (6)	0.1140 (6)	0.7155 (2)	0.0624 (16)
H9 ^a	0.892074	0.110233	0.748832	0.075*
C10	0.8163 (5)	0.0495 (6)	0.6863 (2)	0.0532 (14)
C11	0.7241 (6)	−0.0427 (8)	0.7002 (2)	0.081 (2)
H11A	0.653595	0.001763	0.696621	0.122*
H11B	0.733569	−0.069270	0.733096	0.122*
H11C	0.725754	−0.119962	0.679961	0.122*
C12	0.7139 (4)	−0.0415 (5)	0.40104 (19)	0.0490 (13)
H12A	0.714879	−0.122735	0.419146	0.074*
H12B	0.719844	−0.061425	0.367423	0.074*
H12C	0.645116	0.004912	0.406976	0.074*
C13	1.0568 (4)	0.2623 (6)	0.40167 (19)	0.0520 (13)
H13A	1.117360	0.251840	0.423967	0.078*
H13B	1.033305	0.353636	0.401287	0.078*
H13C	1.081203	0.236908	0.370127	0.078*
C14	1.0607 (5)	0.2729 (7)	0.7020 (2)	0.076 (2)
H14A	1.050319	0.360990	0.689408	0.113*
H14B	1.129352	0.236601	0.689836	0.113*
H14C	1.063735	0.276505	0.736381	0.113*
B1	0.7705 (4)	0.0220 (5)	0.5066 (2)	0.0378 (12)
B2	0.9757 (4)	0.2453 (6)	0.5953 (2)	0.0385 (12)

^aOccupancy: 0.7049(17), ^bOccupancy: 0.2951(17).

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]. Structurally, BOPHY is similar to BODIPY. Both of them have a BF₂ unit. However, BOPHY has two BF₂ units. Interestingly, the emission of BOPHY shifts towards shorter wavelength in contrast to BODIPY and one can observe bright blue-green color when excited the BOPHY derivatives 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 BF_2 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 (C_{2h} symmetry), following that of BODIPY. The bonds length demonstrates furtherly 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 BF_2 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 hydrogen 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].

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