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Crystal structure of 2-phenylethynyl-1,3,6,8-tetramethylBOPHY (BOPHY = bis(difluoroboron)-1,2-bis((1*H*-pyrrol-2-yl)methylene)hydrazine), C₂₂H₂₀B₂F₄N₄

Table 1: Data collection and handling.

Crystal:	Red plate
Size	0.50 × 0.45 × 0.16 mm
Wavelength:	Cu Kα radiation (1.54184 Å)
μ:	0.88 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω
θ _{max} , completeness:	66.0°, >99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	10,648, 3763, 0.027
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 3240
<i>N</i> (<i>param</i>) _{refined} :	324
Programs:	CrysAlis ^{PRO} [1], Olex2 [2], SHELX [3, 4], Diamond [5]

Abstract

C₂₂H₂₀B₂F₄N₄, orthorhombic, *Pbca* (no. 61), *a* = 9.2506(2) Å, *b* = 36.1677(13) Å, *c* = 12.9475(3) Å, *V* = 4331.9 Å³, *Z* = 8, *R*_{gt}(*F*) = 0.0729, *wR*_{ref}(*F*²) = 0.1992, *T* = 294.4 K.

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The molecular structure is shown in the Figure 1 (displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

2-Phenylethynyl-1,3,6,8-tetramethylBOPHY was synthesized from commercialized 2,4-dimethylpyrrole and boron trifluoride etherate followed by multisteps of condensation and coupling according to the reported procedure [6–8]. Among the multistep reactions, the key intermediate BOPHY was obtained by the typical procedure as Ziegler and Jiao described [6, 7]. Subsequently, an iodine atom was introduced to the β position of BOPHY efficiently and gave 2-iodo-1,3,6,8-tetramethylBOPHY with 40% yield [8]. The final coupling reaction is under standard Sonogashira

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
B1	0.5375 (4)	0.60122 (11)	0.2250 (2)	0.0326 (8)
B2	0.4869 (4)	0.57540 (11)	0.5343 (3)	0.0338 (8)
C1	0.4024 (3)	0.54950 (9)	0.3676 (2)	0.0327 (7)
H1	0.351635	0.533723	0.411176	0.039*
C2	0.3866 (3)	0.54381 (9)	0.2630 (2)	0.0337 (7)
C3	0.3042 (4)	0.51701 (9)	0.2108 (3)	0.0379 (7)
C4	0.3290 (4)	0.52354 (11)	0.1063 (3)	0.0474 (9)
H4	0.289399	0.510084	0.052041	0.057*
C5	0.4232 (4)	0.55367 (10)	0.0962 (2)	0.0434 (8)
C6	0.6454 (3)	0.62312 (9)	0.3913 (2)	0.0332 (7)
H6	0.698263	0.638489	0.347763	0.040*
C7	0.6644 (3)	0.62787 (8)	0.4969 (2)	0.0303 (7)
C8	0.7506 (4)	0.65327 (9)	0.5519 (3)	0.0393 (8)
C9	0.7211 (4)	0.64664 (10)	0.6567 (3)	0.0391 (8)
C10	0.6210 (4)	0.61755 (9)	0.6634 (2)	0.0359 (7)
C11	0.2104 (4)	0.48843 (10)	0.2599 (3)	0.0487 (9)
H11A	0.264976	0.475215	0.311092	0.073*
H11B	0.176932	0.471463	0.208168	0.073*
H11C	0.129075	0.500202	0.292109	0.073*
C12	0.5595 (4)	0.60062 (10)	0.7581 (3)	0.0441 (8)
H12A	0.471001	0.612943	0.775908	0.066*
H12B	0.627201	0.603065	0.813911	0.066*
H12C	0.540474	0.574898	0.745870	0.066*
C13	0.4809 (5)	0.57067 (12)	0.0007 (3)	0.0556 (11)
H13A	0.476506	0.597110	0.006449	0.083*
H13B	0.424095	0.562801	−0.057369	0.083*
H13C	0.579463	0.563131	−0.009026	0.083*
C14	0.8526 (4)	0.68096 (12)	0.5086 (3)	0.0570 (11)
H14A	0.929257	0.668438	0.472871	0.086*
H14B	0.892370	0.695540	0.563613	0.086*
H14C	0.802055	0.696773	0.461219	0.086*
C15	0.7783 (4)	0.66539 (10)	0.7447 (3)	0.0472 (9)
C16	0.8236 (4)	0.67859 (11)	0.8220 (3)	0.0495 (9)
C17 ^a	0.8773 (18)	0.6944 (5)	0.9163 (7)	0.050 (4)
C17A ^b	0.8780 (18)	0.6922 (5)	0.9186 (7)	0.062 (6)
C18 ^a	0.9822 (18)	0.7216 (5)	0.9041 (12)	0.069 (4)
H18 ^a	1.009296	0.729128	0.838229	0.083*
C18A ^b	0.9792 (16)	0.7203 (4)	0.9311 (12)	0.064 (3)
H18A ^b	1.021309	0.731231	0.873507	0.076*
C19 ^a	1.0465 (17)	0.7375 (4)	0.9904 (18)	0.073 (4)
H19 ^a	1.116627	0.755694	0.982172	0.088*
C19A ^b	1.0175 (19)	0.7319 (4)	1.0297 (16)	0.078 (4)
H19A ^b	1.085236	0.750710	1.038006	0.093*
C20 ^a	1.006 (2)	0.7262 (5)	1.0888 (14)	0.074 (4)
H20 ^a	1.048953	0.736899	1.146527	0.089*
C20A ^b	0.955 (3)	0.7156 (5)	1.1157 (10)	0.083 (4)
H20A ^b	0.980183	0.723380	1.181690	0.099*
C21 ^a	0.901 (2)	0.6991 (6)	1.1011 (7)	0.076 (4)
H21 ^a	0.873945	0.691538	1.166941	0.092*
C21A ^b	0.853 (2)	0.6875 (5)	1.1033 (7)	0.082 (4)
H21A ^b	0.811201	0.676571	1.160874	0.098*
C22 ^a	0.8368 (18)	0.6832 (5)	1.0148 (10)	0.067 (4)
H22 ^a	0.766612	0.664972	1.023000	0.080*
C22A ^b	0.8150 (18)	0.6759 (5)	1.0047 (10)	0.067 (3)
H22A ^b	0.747272	0.657091	0.996374	0.080*

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
F1	0.4555 (2)	0.63232 (6)	0.20390 (15)	0.0488 (5)
F2	0.6703 (2)	0.60484 (7)	0.17962 (15)	0.0520 (6)
F3	0.3485 (2)	0.58040 (7)	0.56946 (15)	0.0583 (7)
F4	0.5373 (3)	0.54131 (6)	0.56606 (15)	0.0569 (6)
N1	0.4581 (3)	0.56611 (8)	0.19140 (18)	0.0341 (6)
N2	0.5599 (3)	0.59894 (7)	0.34759 (18)	0.0298 (6)
N3	0.4827 (3)	0.57516 (7)	0.41198 (18)	0.0300 (6)
N4	0.5873 (3)	0.60636 (7)	0.56710 (18)	0.0310 (6)

^aOccupancy: 0.48(4). ^bOccupancy: 0.52(4).

conditions. In THF 20 mL, 2-iodo-1,3,6,8-tetramethylBOPHY 100 mg (0.17 mmol), Pd(PPh₃)₄ (12 mg), CuI (12 mg), and triethylamine (10 mL) were mixed under inert atmosphere and refluxed for 12 h. The mixture was turned from dark-red to black. The reaction progress was monitored by TLC. Once 2-iodo-1,3,6,8-tetramethyl-BOPHY disappeared on the TLC plate, the reaction was quenched by adding distilled water 50 mL and extracted with dichloromethane. The collected organic phase was washed with brine (100 mL). Next, the solvent was dehydrated over anhydrous MgSO₄ and evaporated in vacuum. The residue was purified by column chromatography with dichloromethane/hexane and afforded the dark red powder (58 mg, 63%). Crystals suitable for X-ray diffraction were obtained by slow evaporation at low temperature of the title compound in dichloromethane 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 (–CH₃). *U*_{iso}(H) = 1.2 *U*_{eq}(C) for CH or *U*_{iso}(H) = 1.5 *U*_{eq}(C) for CH₃ groups.

Comment

Since BOPHY was reported by Ziegler and Jiao and its co-authors, more and more BOPHY derivatives were configured in order to uncover newly photophysical properties or incorporate desired functional groups [6, 7]. Structurally, BOPHY is similar to that of the well literated BODIPY, having two β hydrogen atoms, which is easy to be substituted by nucleophilic attack. Additionally, the β position also could be efficiently attacked by a formylation by Vilsmeier–Haack reaction or amidation. Unlike the typical BODIPY's strong green emission, the emission peak of BOPHY was observed in blue-green region, which is

shorter than that of BOPHY. However, it is longer than in most other fluorine-boron complexes (FBC) [8]. In our previous work, a series of aromatic alkyne derivatives were coupled with iodine substituted BOPHY under Sonogashira conditions [9]. Due to the expansion of the conjugated system, as expected the emission was shifted to longer wavelengths. BOPHY is easy to crystallize in organic solvents and single crystal data of its simple derivatives have been well documented. However, the crystals of aromatic alkyne BOPHY derivatives must be treated carefully in saturated dichloromethane. The saturated solution of the title compound in dichloromethane was crystallized at low temperature. Finally, the suitable crystal was selected and mounted for data collection. This single crystal data would be part of our continuous research of BOPHY and its aggregate behavior. Similarly, the framework of BOPHY is another type of FBC, having excellent photo-stability and thermo-stability [10–15]. For example, the sensor configuration can be copied to BOPHY identically according to BODIPY [10, 14, 16, 17]. Also, advanced functionalities in bio-imaging and lighting materials are expected [18, 19].

In the title crystal structure, the asymmetric unit contains one molecule. Bond lengths and angles are in the expected ranges. The framework of BOPHY is rigid and coplanar with two pyrrole rings at the periphery and two six-membered rings. The two BF_2 moieties are positioned in six-membered rings. The BOPHY framework has an inversion center (C_{2h} symmetry). The bond lengths demonstrate the regular aromaticity of the pyrrole rings. The framework of BOPHY is coplanar (RMS deviation = 0.068 Å), except the four fluorine atoms distributed up and down. The B–F–B group bifurcated with an angle of 89.51°, similar to the majority of fluorine-boron molecules. The attached phenylacetylene also extended along the plane (RMS deviation = 0.077 Å). In the six-membered rings of BOPHY, the C–N (1.308, 1.320 Å) and N=N (1.394 Å) bonds have single and double bond character. Therefore, the aromaticity is not extended across the whole molecule. The phenylacetylene only extends the conjugate system in one side of BOPHY by attaching with one of the periphery pyrrole rings. Additionally, the phenyl rings of phenylacetylene are disordered and treated by two parts with free occupancy.

The intermolecular interactions between dye molecules include mainly C–H...F and $\pi\cdots\pi$ interactions. The adjacent molecules are joint by C–H...F interactions (C6–H6...F1, i : 0.5+ x , y , 0.5– z). $\pi\cdots\pi$ interactions contribute the driving force for layer packing. The plane distance of parallel BOPHY molecules is estimated to be 3.585 Å. Also, a number of weak C–H... π interactions contribute to the cohesion of molecules [20]. The dye molecules emit bright fluorescence in organic solvents.

However, the emission in solid state slightly shifts toward longer wavelengths. The interactions between the dye molecules in the solid are stronger than that between dye molecules and solvents, which lead to the energy dissipation in the excited state. Therefore, its emission behavior is highly dependent on the aggregation of dye molecules.

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