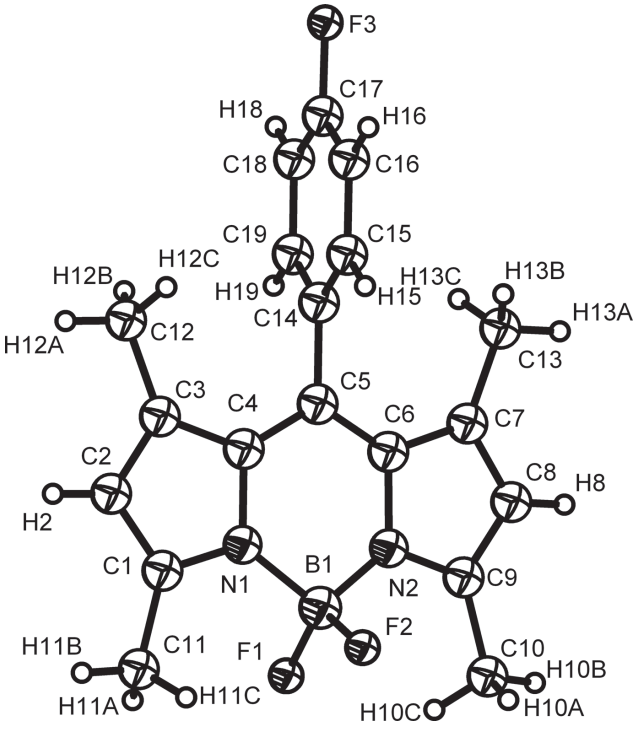
Yingfan Liu, Ming Yan, Xiaochuan Li*, Yajuan Li and Young-A Son

Crystal structure of 5,5-difluoro-10-(4-fluorophenyl)-1,3,7,9-tetramethyl-5*H*-4l4,5l4-dipyrrolo[1,2-*c*:2′,1′-*f*][1,3,2]diazaborinine - a Z′ = 3 structure, $C_{19}H_{18}B_2F_3N_2$



https://doi.org/10.1515/ncrs-2017-0143
Received June 9, 2017; accepted September 30, 2017; available online October 16, 2017

Abstract

$C_{19}H_{18}B_2F_3N_2$, triclinic, $P\bar{1}$ (no. 2), $a = 10.8885(6)$ Å, $b = 13.9767(8)$ Å, $c = 18.1330(10)$ Å, $\alpha = 79.3484(19)°$, $\beta = 86.2213(9)°$; $\gamma = 73.461(2)°$; $V = 2599.6(3)$ Å^3, $Z = 6$, $R_{gt}(F) = 0.0450$, $wR_{ref}(F^2) = 0.1105$, $T = 296$ K.

CCDC no.: 1549494

***Corresponding author: Xiaochuan Li,** College of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan, 453007, P. R. China, e-mail: lixiaochuan@htu.cn
Yingfan Liu and Ming Yan: College of Material and Chemical Engineering, Zhengzhou University of Light Industry, Henan Provincial Key Laboratory of Surface and Interface Science, Zhengzhou 450002, P. R. China
Yajuan Li: College of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan, 453007, P. R. China
Young-A Son: Department of Advanced Organic Materials and Textile System Engineering, Chungnam National University, Daejeon 305-764, South Korea

One of three crystallographically independent molecules of the title crystal structure is shown in the figure. All atoms are shown as small spheres of arbitrary radii. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Orange block
Size:	0.14 × 0.11 × 0.10 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.10 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω-scans
$2\theta_{max}$, completeness:	26.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	63046, 10788, 0.111
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4308
$N(param)_{refined}$:	689
Programs:	Bruker programs [1], SHELX [2], DIAMOND [3]

Source of material

The title compound was synthesized according to the literature procedures [4, 5]. The colorless crystals of the title compound were obtained by slow evaporation of a dichloromethane solution at room temperature.

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 $U_{iso}(H) = 1.5\ U_{eq}(C)$ for CH_3 groups.

Discussion

4,4′-Difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) is a typical member of fluorine-boron complex, which has drawn great attention owing to its high molar extinction coefficient, narrow full width at half maximum, outstanding quantum yields, and excellent photo-/thermal resistance [6–10]. Introduction of fluorine could enhance the emission quantum yield further [5]. In this contribution, the title crystal structure was built up from $C_{19}H_{18}B_2F_3N_2$ with three title molecules in the asymmetric unit. The BODIPY core rings of the three

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
B1	0.1134(3)	0.5552(2)	0.11819(15)	0.0524(8)
C1	0.3422(2)	0.57200(16)	0.09178(12)	0.0493(6)
C2	0.4443(2)	0.57412(17)	0.13251(13)	0.0535(6)
H2	0.5226	0.5812	0.1123	0.064*
C3	0.4114(2)	0.56400(16)	0.20802(12)	0.0461(6)
C4	0.2844(2)	0.55504(16)	0.21238(12)	0.0426(6)
C5	0.2037(2)	0.53680(15)	0.27368(11)	0.0428(6)
C6	0.0874(2)	0.51881(17)	0.26411(12)	0.0472(6)
C7	−0.0076(2)	0.49321(19)	0.31604(14)	0.0611(7)
C8	−0.1007(2)	0.4820(2)	0.27369(15)	0.0721(8)
H8	−0.1741	0.4642	0.2926	0.087*
C9	−0.0682(2)	0.50140(19)	0.19805(14)	0.0597(7)
C10	−0.1429(2)	0.5004(2)	0.13194(14)	0.0775(8)
H10A	−0.1788	0.5686	0.1067	0.116*
H10B	−0.2106	0.4698	0.1487	0.116*
H10C	−0.0872	0.4621	0.0980	0.116*
C11	0.3322(2)	0.58249(19)	0.00852(11)	0.0692(8)
H11A	0.3249	0.5203	−0.0035	0.104*
H11B	0.4074	0.5974	−0.0156	0.104*
H11C	0.2579	0.6365	−0.0088	0.104*
C12	0.4982(2)	0.5619(2)	0.26959(13)	0.0682(8)
H12A	0.5793	0.5683	0.2484	0.102*
H12B	0.5110	0.4990	0.3040	0.102*
H12C	0.4599	0.6172	0.2958	0.102*
C13	−0.0116(3)	0.4823(2)	0.40002(13)	0.0903(10)
H13A	−0.0932	0.4742	0.4187	0.135*
H13B	0.0008	0.5419	0.4141	0.135*
H13C	0.0552	0.4240	0.4209	0.135*
C14	0.2452(2)	0.53514(18)	0.35024(12)	0.0454(6)
C15	0.2307(2)	0.6238(2)	0.37650(13)	0.0601(7)
H15	0.1951	0.6855	0.3458	0.072*
C16	0.2686(2)	0.6225(2)	0.44837(15)	0.0727(8)
H16	0.2586	0.6825	0.4662	0.087*
C17	0.3202(3)	0.5319(3)	0.49163(15)	0.0729(9)
C18	0.3371(3)	0.4431(3)	0.46864(15)	0.0823(9)
H18	0.3738	0.3821	0.4999	0.099*
C19	0.2984(2)	0.44484(19)	0.39692(13)	0.0669(8)
H19	0.3085	0.3841	0.3801	0.080*
F1	0.12780(14)	0.48537(12)	0.07111(7)	0.0786(5)
F2	0.04239(13)	0.64935(11)	0.08222(8)	0.0837(5)
F3	0.35646(15)	0.53097(15)	0.56242(8)	0.1155(7)
N1	0.24523(16)	0.56025(13)	0.13933(9)	0.0431(5)
N2	0.04546(17)	0.52251(14)	0.19155(10)	0.0494(5)
B2	0.4617(3)	0.1743(2)	0.67844(16)	0.0599(8)
C20	0.6907(3)	0.11108(19)	0.62774(14)	0.0633(7)
C21	0.8138(3)	0.07493(19)	0.65517(14)	0.0655(7)
H21	0.8871	0.0498	0.6275	0.079*
C22	0.8107(2)	0.08202(18)	0.72978(14)	0.0551(7)
C23	0.6797(2)	0.12492(16)	0.74796(12)	0.0477(6)
C24	0.6172(2)	0.14288(16)	0.81548(12)	0.0445(6)
C25	0.4836(2)	0.17704(17)	0.82042(12)	0.0496(6)
C26	0.3984(2)	0.20391(18)	0.88107(14)	0.0569(7)
C27	0.2773(3)	0.23071(19)	0.85270(16)	0.0697(8)
H27	0.2017	0.2520	0.8796	0.084*
C28	0.2851(3)	0.22100(19)	0.77737(16)	0.0654(7)

Table 2 (continued)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C29	0.1775(2)	0.2391(2)	0.72467(16)	0.0979(10)
H29A	0.1906	0.2836	0.6796	0.147*
H29B	0.0979	0.2695	0.7481	0.147*
H29C	0.1750	0.1757	0.7124	0.147*
C30	0.6502(3)	0.1161(2)	0.54964(13)	0.0882(9)
H30A	0.6055	0.0660	0.5494	0.132*
H30B	0.7244	0.1033	0.5174	0.132*
H30C	0.5945	0.1822	0.5319	0.132*
C31	0.4277(2)	0.20800(19)	0.95967(13)	0.0727(8)
H31A	0.3530	0.2476	0.9824	0.109*
H31B	0.4965	0.2385	0.9590	0.109*
H31C	0.4525	0.1405	0.9881	0.109*
C32	0.9266(2)	0.0479(2)	0.77832(14)	0.0749(8)
H32A	0.9982	0.0105	0.7519	0.112*
H32B	0.9101	0.0053	0.8236	0.112*
H32C	0.9459	0.1059	0.7906	0.112*
C33	0.6933(2)	0.11820(17)	0.88506(12)	0.0470(6)
C34	0.7680(2)	0.17781(17)	0.89849(13)	0.0552(7)
H34	0.7709	0.2352	0.8639	0.066*
C35	0.8390(2)	0.1522(2)	0.96370(15)	0.0668(8)
H35	0.8898	0.1917	0.9732	0.080*
C36	0.8323(3)	0.0678(2)	1.01331(14)	0.0689(8)
C37	0.7614(3)	0.0066(2)	1.00201(14)	0.0725(8)
H37	0.7604	−0.0511	1.0367	0.087*
C38	0.6904(2)	0.03272(18)	0.93704(13)	0.0612(7)
H38	0.6401	−0.0077	0.9282	0.073*
F4	0.41987(13)	0.09900(11)	0.65645(8)	0.0809(5)
F5	0.42002(15)	0.26266(11)	0.62721(7)	0.0899(5)
F6	0.90036(16)	0.04378(13)	1.07753(8)	0.1102(6)
N3	0.60877(19)	0.14154(14)	0.68275(10)	0.0521(5)
N4	0.40927(19)	0.19032(14)	0.75727(10)	0.0523(5)
B3	1.0271(3)	−0.1890(3)	0.61241(17)	0.0631(9)
C39	1.1341(2)	−0.2214(2)	0.74012(16)	0.0721(8)
C40	1.0985(2)	−0.2320(2)	0.81577(16)	0.0729(8)
H40	1.1526	−0.2419	0.8557	0.087*
C41	0.9699(2)	−0.22514(18)	0.82146(13)	0.0556(7)
C42	0.9258(2)	−0.20962(17)	0.74699(12)	0.0494(6)
C43	0.8065(2)	−0.19639(16)	0.71764(12)	0.0450(6)
C44	0.7871(2)	−0.18185(17)	0.64087(13)	0.0513(6)
C45	0.6773(2)	−0.16952(18)	0.59787(13)	0.0575(7)
C46	0.7164(3)	−0.1608(2)	0.52409(14)	0.0732(8)
H46	0.6648	−0.1526	0.4832	0.088*
C47	0.8459(3)	−0.1661(2)	0.52064(14)	0.0714(8)
C48	0.9296(3)	−0.1581(3)	0.45221(14)	0.1106(12)
H48A	0.9914	−0.1241	0.4602	0.166*
H48B	0.8778	−0.1203	0.4099	0.166*
H48C	0.9731	−0.2248	0.4426	0.166*
C49	1.2638(2)	−0.2232(3)	0.70679(17)	0.1169(13)
H49A	1.2870	−0.2715	0.6734	0.175*
H49B	1.3254	−0.2420	0.7461	0.175*
H49C	1.2622	−0.1571	0.6795	0.175*
C50	0.5424(2)	−0.1656(2)	0.62374(13)	0.0733(8)
H50A	0.4948	−0.1719	0.5831	0.110*
H50B	0.5029	−0.1021	0.6400	0.110*
H50C	0.5434	−0.2201	0.6647	0.110*
C51	0.8959(2)	−0.23253(19)	0.89411(13)	0.0707(8)

Table 2 (continued)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
H51A	0.9484	−0.2318	0.9344	0.106*
H51B	0.8715	−0.2945	0.9031	0.106*
H51C	0.8205	−0.1760	0.8913	0.106*
C52	0.6942(2)	−0.19841(18)	0.76891(11)	0.0409(5)
C53	0.6065(2)	−0.10991(18)	0.78123(12)	0.0540(6)
H53	0.6204	−0.0480	0.7598	0.065*
C54	0.4985(2)	−0.11155(19)	0.82482(13)	0.0592(7)
H54	0.4392	−0.0518	0.8332	0.071*
C55	0.4813(2)	−0.2035(2)	0.85531(12)	0.0549(7)
C56	0.5651(2)	−0.2919(2)	0.84566(13)	0.0638(7)
H56	0.5507	−0.3533	0.8680	0.077*
C57	0.6734(2)	−0.28946(18)	0.80166(13)	0.0554(7)
H57	0.7324	−0.3498	0.7942	0.066*
F7	1.11273(14)	−0.26954(13)	0.58522(8)	0.0917(5)
F8	1.06157(14)	−0.10132(12)	0.58285(8)	0.0885(5)
F9	0.37333(13)	−0.20582(12)	0.89725(8)	0.0869(5)
N5	1.03099(18)	−0.20748(15)	0.69824(11)	0.0590(6)
N6	0.89033(18)	−0.17926(15)	0.59073(11)	0.0594(6)

independent molecules are planar and the mean deviations are estimated to be 0.067, 0.036, and 0.014 Å for B1N2C3—C11N12, B26N27C28—C36N37, and B51N52C53—C61N62, respectively. The dihedral angles between the 4-fluorophenyl ring and the plane of the BODIPY core varied and contributed to different configurations of the title molecules. The angles were estimated to be 99.0°, 106.1°, and 82.1° for the plane of BODIPY core and the 4-fluorophenyl ring connected with each other, which were controlled by intramolecular C—H···π interactions [11]. Totally, there exist three fluorine atoms in each molecule. And all of them seem to be involved in C—H···F interactions. For the fluorine atoms attaching to the boron atom, eight distance of C···F varied from 3.33 to 3.55 Å, which fall inside of the normal C···F interval of C—H···F interactions. Among the weak interactions mentioned above, the C—H···F interactions contribute to join the molecules into crystals. Presumably, the intramolecular C—H···π interactions were interfered by the stronger C—H···F interactions and led to three different molecules in the asymmetric unit. Owing to the various interactions observed in the crystal, the molecules were staggered layer by layer along the axis c. H···F interactions join the layers side by side.

Acknowledgements: This work was supported by the National Natural Science Foundation of China (21272060). This work was supported by the industrial Fundamental Technology Development Program (10076350) funded by the Ministry of Trade, Industry and Energy (MOTIE) of Korea.

References

1. Bruker: APEX2, SAINT and SADABS. Brucker AXS Inc., Madison, WI, USA (2009).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Brandenburg, K.; Putz, H.: Diamond-crystal and molecular structure visualization, Crystal impact. Kreuzherrenstr. 102, 53227 Bonn, Germany (2005).
4. Alamiry, M. A. H.; Benniston, A. C.; Hagon, J.; Winstanley, T. P. L.; Lemmetyinen, W. H.; Tkachenko, N. V.: The fluorine effect: photophysical properties of borondipyrromethene (bodipy) dyes appended at the meso position with fluorinated aryl groups. RSV Adv. **2** (2012) 4944–4950.
5. Bones, N.; Verbelen, B.; Dehaen, W.: Postfunctionalization of the BODIPY core: synthesis and spectroscopy. Eur. J. Org. Chem. **30** (2015) 6577–6595.
6. Li, X.; Ji, G.; Son, Y.-A.: Tunable emission of hydrazine–containing bipyrrole fluorine-boron complexes by linear extension. Dye Pigments **124** (2016) 232–240.
7. Li, X.; Ji, G.; Jung, J.-M.; Son, Y.-A.: A BODIPY based highly selective fluorescence turn-on sensor toward VIB and IIB metal ions. Mol. Cryst. Liq. Cryst. **636** (2016) 159–167.
8. Loudet, A.; Burgess, K.: BODIPY dyes and their derivatives: syntheses and spectroscopic properites. Chem. Rev. **107** (2007) 4891–4932.
9. Ulrich, G.; Ziessel, R.; Harriman, A.: The chemistry of fluorescent bodipy dyes: versatility unsurpassed. Angew. Chem. Int. Ed. **47** (2007) 1184–1201.
10. Li, X.; Son, Y.-A.: Efficient luminescence from easily prepared fluorine-boron core complexes based on benzothiazole and benzoxazole. Dye Pigments **107** (2014) 182–187.
11. Malone, J. F.; Murray, C. M.; Charlton, M. H.; Docherty, R.; Lavery, A. J.: X—H···π (phenyl) interactions theoretical and crystallographic observations. J. Chem. Soc. Faraday Trans. **93** (1997) 3429–3436.