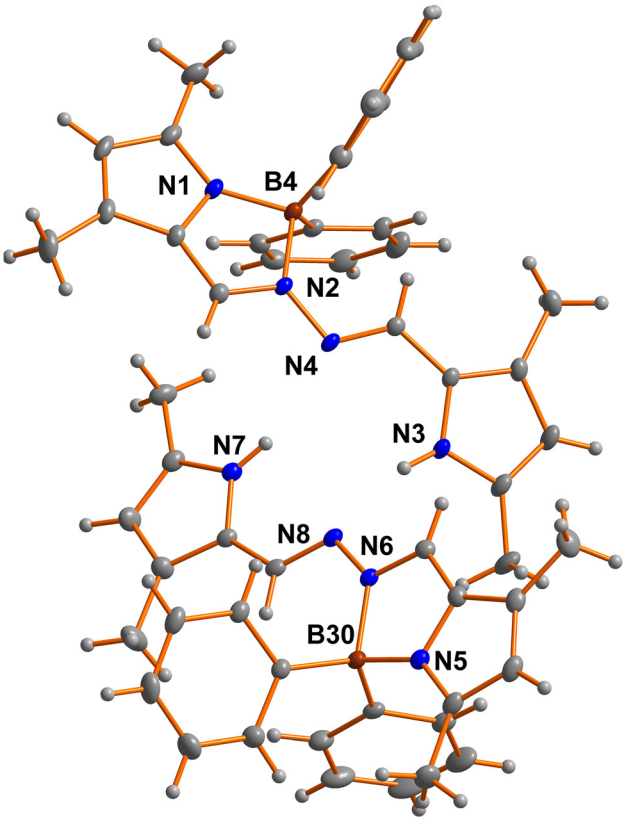
Ghaferah H. Al-Hazmi, Moamen S. Refat, Rabia Usman* and Arshad Khan*

The crystal structure of unsymmetrical BOPHY $C_{26}H_{27}BN_4$



https://doi.org/10.1515/ncrs-2024-0061
Received February 12, 2024; accepted March 24, 2024;
published online April 5, 2024

Abstract

$C_{26}H_{27}BN_4$, monoclinic, $C2/c$ (no. 15), a = 38.716(3) Å, b = 9.2723(6) Å, c = 27.3977(18) Å, β = 113.4790(10)°, V = 9021.1(11) Å^3, Z = 16, $R_{gt}(F)$ = 0.0520, $wR_{ref}(F^2)$ = 0.1440, T = 100 K.

CCDC no.: 2342739

***Corresponding authors: Arshad Khan**, Nanomedicine Department, King Abdullah International Medical Research Center (KAIMRC), King Saud Bin Abdulaziz University for Health Sciences, Ministry of National Guard Health Affairs, Riyadh 11426, Kingdom of Saudi Arabia; and **Rabia Usman**, School of Chemistry and Environmental Engineering, Sichuan University of Science & Engineering, Zigong, Sichuan 643000, China, E-mail: khanar@kaimrc.edu.sa (A. Khan), arshaibar@gmail.com (R. Usman). https://orcid.org/0000-0001-8716-4312 (A. Khan). https://orcid.org/0000-0002-1387-3519 (R. Usman)
Ghaferah H. Al-Hazmi, Department of Chemistry, College of Science, Princess Nourah bint Abdulrahman University, P. O. Box 84428, Riyadh 11671, Saudi Arabia
Moamen S. Refat, Department of Chemistry, College of Science, Taif University, P. O. Box 11099, Taif 21944, Saudi Arabia

Table 1: Data collection and handling.

Crystal:	Yellow plate
Size:	0.05 × 0.01 × 0.01 mm
Wavelength:	Synchrotron radiation (0.6889 Å)
μ:	0.07 mm^{-1}
Diffractometer, scan mode:	Fluid film devices, φ and ω with 0.1° frames
θ_{max}, completeness:	29.5°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	64,902, 13,737, 0.066
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 10,590
$N(param)_{refined}$:	573
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], Olex2 [4]

1 Source of materials

Treatment of the tetramethyl bis-(pyrrole imine) hydrazine with one equivalent of BPh3 in toluene for 1 h resulted in formation of the titled compound *N*-(4,6-dimethyl-1,1-diphenyl-1l^4,7l^4-pyrrolo[2,1-e][1,3,2]diazaborol-2(1*H*)-yl)-1-(3,5-dimethyl-1H-pyrrol-2-yl)methanimine. This was isolated by column chromatography in 54 % yield. Good quality single crystals were obtained by slow evaporation from a DCM/hexane mixtures (1:2).

2 Experimental details

The structure of the title compound was solved using SHELXT [2] and refined by SHELXL program [3] through the Olex2 interface [4]. All hydrogen atoms were positioned at calculated coordinates and refined isotropically.

3 Comment

In recent years BOPHY dyes have rapidly found utility in various applications due to their outstanding photophysical

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
N1	0.24611 (3)	0.65896 (11)	0.34685 (4)	0.0152 (2)
N2	0.29702 (3)	0.49726 (11)	0.36972 (4)	0.01283 (18)
N3	0.40315 (3)	0.28595 (11)	0.45073 (4)	0.01446 (19)
H3	0.3986 (4)	0.2773 (18)	0.4173 (7)	0.017*
N4	0.33091 (3)	0.42149 (11)	0.39098 (4)	0.01341 (19)
N5	0.44494 (3)	−0.15216 (11)	0.34661 (4)	0.01451 (19)
N6	0.41447 (3)	0.06758 (11)	0.34683 (4)	0.01264 (18)
N7	0.36810 (3)	0.50307 (11)	0.31231 (4)	0.01367 (19)
H7A	0.3627 (4)	0.4751 (18)	0.3378 (6)	0.016*
N8	0.39911 (3)	0.20513 (11)	0.34230 (4)	0.01326 (18)
C1	0.21925 (3)	0.65083 (14)	0.25624 (5)	0.0183 (2)
C2	0.19963 (3)	0.74828 (14)	0.27487 (5)	0.0205 (3)
H2	0.1788	0.8024	0.2537	0.025*
C3	0.21657 (3)	0.75088 (14)	0.33079 (5)	0.0187 (2)
C4	0.27923 (3)	0.50295 (13)	0.31761 (5)	0.0149 (2)
H4	0.2863	0.4515	0.2940	0.018*
C5	0.24814 (3)	0.59657 (13)	0.30217 (5)	0.0153 (2)
C6	0.39737 (3)	0.33212 (13)	0.52766 (5)	0.0162 (2)
C7	0.43388 (3)	0.27923 (14)	0.53864 (5)	0.0203 (2)
H7	0.4528	0.2653	0.5723	0.024*
C8	0.43682 (3)	0.25154 (14)	0.49081 (5)	0.0188 (2)
C9	0.34281 (3)	0.39855 (12)	0.44186 (5)	0.0130 (2)
H9	0.3273	0.4239	0.4591	0.016*
C10	0.37858 (3)	0.33624 (12)	0.47234 (4)	0.0130 (2)
C11	0.21126 (4)	0.61055 (17)	0.19984 (5)	0.0276 (3)
H11A	0.1864	0.5700	0.1836	0.041*
H11B	0.2294	0.5409	0.1993	0.041*
H11C	0.2128	0.6950	0.1805	0.041*
C12	0.20565 (4)	0.83487 (16)	0.36880 (6)	0.0271 (3)
H12A	0.1968	0.7701	0.3887	0.041*
H12B	0.1860	0.9015	0.3494	0.041*
H12C	0.2271	0.8871	0.3928	0.041*
C13	0.38282 (4)	0.38196 (15)	0.56799 (5)	0.0223 (3)
H13A	0.3925	0.3204	0.5987	0.033*
H13B	0.3558	0.3781	0.5528	0.033*
H13C	0.3909	0.4793	0.5783	0.033*
C14	0.46908 (4)	0.19499 (18)	0.47990 (6)	0.0269 (3)
H14A	0.4664	0.0926	0.4744	0.040*
H14B	0.4922	0.2154	0.5097	0.040*
H14C	0.4694	0.2405	0.4486	0.040*
C15	0.30577 (3)	0.72302 (13)	0.43400 (5)	0.0145 (2)
C16	0.32840 (3)	0.71257 (14)	0.48853 (5)	0.0183 (2)
H16	0.3265	0.6307	0.5069	0.022*
C17	0.35365 (4)	0.82052 (15)	0.51619 (5)	0.0232 (3)
H17	0.3683	0.8095	0.5523	0.028*
C18	0.35698 (4)	0.94472 (15)	0.48990 (6)	0.0227 (3)
H18	0.3740	1.0166	0.5081	0.027*
C19	0.33456 (3)	0.95978 (14)	0.43616 (5)	0.0204 (2)
H19	0.3362	1.0429	0.4182	0.024*
C20	0.30948 (3)	0.85026 (14)	0.40885 (5)	0.0169 (2)
H20	0.2948	0.8622	0.3728	0.020*
C21	0.25614 (3)	0.49982 (13)	0.42871 (5)	0.0153 (2)
C22	0.24846 (4)	0.55218 (15)	0.47120 (5)	0.0201 (2)
H22	0.2590	0.6395	0.4868	0.024*
C23	0.22553 (4)	0.47721 (16)	0.49090 (6)	0.0248 (3)
H23	0.2208	0.5149	0.5191	0.030*
C24	0.20988 (4)	0.34677 (17)	0.46852 (6)	0.0264 (3)
H24	0.1945	0.2967	0.4815	0.032*
C25	0.21726 (4)	0.29067 (16)	0.42660 (6)	0.0255 (3)
H25	0.2069	0.2027	0.4115	0.031*
C26	0.24024 (4)	0.36678 (14)	0.40731 (5)	0.0202 (2)
H26	0.2451	0.3280	0.3794	0.024*
C27	0.43375 (3)	−0.28913 (13)	0.40831 (5)	0.0175 (2)
C28	0.45615 (3)	−0.36608 (14)	0.38775 (5)	0.0196 (2)
H28	0.4653	−0.4590	0.3975	0.023*
C29	0.46249 (3)	−0.27972 (13)	0.34988 (5)	0.0174 (2)
C30	0.40967 (3)	−0.02301 (13)	0.38073 (5)	0.0144 (2)
H30	0.3961	−0.0015	0.4013	0.017*
C31	0.42742 (3)	−0.15553 (13)	0.38206 (5)	0.0148 (2)
C32	0.38975 (4)	0.50208 (13)	0.24742 (5)	0.0181 (2)
C33	0.37060 (4)	0.63201 (14)	0.24531 (5)	0.0205 (2)
H33	0.3672	0.7062	0.2210	0.025*
C34	0.35765 (3)	0.63074 (13)	0.28564 (5)	0.0169 (2)
C35	0.40286 (3)	0.28191 (13)	0.30507 (5)	0.0133 (2)
H35	0.4162	0.2411	0.2868	0.016*
C36	0.38830 (3)	0.42279 (12)	0.28997 (5)	0.0134 (2)
C37	0.41910 (4)	−0.33688 (15)	0.44863 (6)	0.0249 (3)
H37A	0.4000	−0.4088	0.4332	0.037*
H37B	0.4086	−0.2557	0.4596	0.037*
H37C	0.4393	−0.3767	0.4789	0.037*
C38	0.48429 (4)	−0.31359 (16)	0.31717 (6)	0.0250 (3)
H38A	0.4675	−0.3172	0.2803	0.038*
H38B	0.4965	−0.4053	0.3278	0.038*
H38C	0.5029	−0.2402	0.3224	0.038*
C39	0.40815 (5)	0.45668 (17)	0.21104 (6)	0.0298 (3)
H39A	0.4037	0.5284	0.1839	0.045*
H39B	0.3978	0.3662	0.1948	0.045*
H39C	0.4348	0.4463	0.2311	0.045*
C40	0.33591 (4)	0.74289 (14)	0.30055 (6)	0.0216 (3)
H40A	0.3094	0.7282	0.2804	0.032*
H40B	0.3429	0.8369	0.2929	0.032*
H40C	0.3414	0.7357	0.3379	0.032*
C41	0.48072 (3)	0.08365 (13)	0.34137 (5)	0.0149 (2)
C42	0.48956 (3)	0.19336 (15)	0.31307 (6)	0.0208 (2)
H42	0.4733	0.2115	0.2780	0.025*
C43	0.52218 (4)	0.27609 (16)	0.33629 (7)	0.0286 (3)
H43	0.5272	0.3493	0.3169	0.034*
C44	0.54701 (4)	0.24960 (18)	0.38809 (7)	0.0351 (4)
H44	0.5684	0.3063	0.4038	0.042*
C45	0.53984 (4)	0.13815 (19)	0.41650 (6)	0.0311 (3)
H45	0.5568	0.1177	0.4510	0.037*
C46	0.50701 (3)	0.05686 (16)	0.39314 (5)	0.0210 (3)
H46	0.5024	−0.0175	0.4126	0.025*
C47	0.41858 (3)	−0.01123 (12)	0.25487 (5)	0.0137 (2)
C48	0.43772 (4)	−0.04160 (15)	0.22195 (5)	0.0200 (2)

Table 2: (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H48	0.4637	−0.0530	0.2374	0.024*
C49	0.41897 (4)	−0.05517 (16)	0.16701 (5)	0.0249 (3)
H49	0.4324	−0.0759	0.1463	0.030*
C50	0.38008 (4)	−0.03782 (16)	0.14297 (5)	0.0249 (3)
H50	0.3674	−0.0478	0.1063	0.030*
C51	0.36033 (4)	−0.00554 (14)	0.17412 (5)	0.0212 (3)
H51	0.3344	0.0077	0.1583	0.025*
C52	0.37942 (3)	0.00700 (13)	0.22923 (5)	0.0156 (2)
H52	0.3658	0.0281	0.2496	0.019*
B4	0.27685 (3)	0.59844 (14)	0.39981 (5)	0.0138 (2)
B30	0.44094 (3)	−0.00250 (14)	0.31856 (5)	0.0132 (2)

characteristics and facile synthesis [5–8], including energy-transfer cascades [9], cell imaging [10], photosensitizers for solar cells [11], photodynamic therapy [12–13], and fluorescence sensors [9–10]. Consequently, there is a need for synthetic modifications capable of modulating or enhancing the photophysical and photochemical properties of BOPHY dyes to extend their applications further [14]. There are two crystallographically independent molecules in the asymmetric unit. Single structural analysis revealed the presence of the five-membered ring. The compound showed a highly twisted conformation of the BOPHY core in solid state owing to the presence of the two phenyl rings with dihedral angles of 85.5° and 61.75° respectively. The two adjacent BOPHY molecules form a dimer structure via hydrogen-bonds.

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

Research funding: Princess Nourah bint Abdulrahman University Researchers Supporting Project number (PNURSP2024R76), Princess Nourah bint Abdulrahman University, Riyadh, Saudi Arabia. A. K thanks the support of King Abdullah International Medical Research Center (KAIMRC) through start up grant NRC23R/746/11.

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

References

1. Rigaku O. D. *CrysAlis^{PRO}*; Rigaku Oxford Diffraction Ltd: Yarnton, Oxfordshire, England, 2015.
2. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
3. Sheldrick G. M. A short history of *SHELX*. *Acta Crystallogr.* 2008, *A64*, 112–122.
4. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, *42*, 339–341.
5. Tamgho I. S., Hasheminasab A., Engle J. T., Nemykin V. N., Ziegler C. J. A new highly fluorescent and symmetric pyrrole–BF_2 chromophore: BOPHY. *J. Am. Chem. Soc.* 2014, *136*, 5623–5626.
6. Wang L., Tamgho I. S., Crandall L. A., Rack J. J., Ziegler C. J. Ultrafast dynamics of a new class of highly fluorescent boron difluoride dyes. *Phys. Chem. Chem. Phys.* 2015, *17*, 2349–2351.
7. Yu C., Jiao L., Zhang P., Feng Z., Cheng C., Wei Y., Mu X., Hao E. Highly fluorescent BF_2 complexes of hydrazine-Schiff base linked bispyrrole. *Org. Lett.* 2014, *16*, 3048–3051.
8. Huaulmé Q., Mirloup A., Retailleau P., Ziessel R. Synthesis of highly functionalized BOPHY chromophores displaying large Stokes shifts. *Org. Lett.* 2005, *17*, 2246–2249.
9. Dai C., Yang D., Zhang W., Bao B., Cheng Y., Wang L. Far-red/near-infrared fluorescent conjugated polymer nanoparticles with size-dependent chirality and cell imaging applications. *Polym. Chem.* 2015, *6*, 3962–3969.
10. Zhang C., Zhao J. Triplet excited state of diiodo BOPHY derivatives: preparation, study of photophysical properties and application in triplet-triplet annihilation upconversion. *J. Mater. Chem. C* 2016, *4*, 1623–1632.
11. Cui T.-F., Zhang J., Jiang X.-D., Su Y.-J., Sun C.-L., Zhao J.-L. Synthesis dibromo substituted BOPHY dye for the singlet oxygen generation. *Chin. Chem. Lett.* 2016, *27*, 190–194.
12. Jiang X.-D., Su Y., Yue S., Li C., Yu H., Zhang H., Sun C.-L., Xiao L.-J. Synthesis of mono-(*p*-dimethylamino)styryl-containing BOPHY dye for a turn-on pH sensor. *RSC Adv.* 2015, *5*, 16735–16739.
13. Li Y. D., Zhou H., Yin S., Jiang H., Niu N., Huang H., Shahzad S. A., Yu C. A BOPHY probe for the fluorescence turn-on detection of Cu^{2+}. *Sens. Actuators, B* 2016, *235*, 33–38.
14. Lv X., Li T., Wu Q., Yu C., Jiao L., Hao E. Polybrominated BOPHY dyes: synthesis, reactivity, and properties. *J. Org. Chem.* 2018, *83*, 1134–1145.