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# The crystal structure of (Z)-4-ethyl-2-((4-ethyl-3,5-dimethyl-1H-pyrrol-2-yl)methylene)-3,5-dimethyl-2H-pyrrol-1-ium 2,2'-spirobi[naphtho[1,8-de][1,3,2]dioxaborinin]-2-uide, $C_{37}H_{37}BN_2O_4$

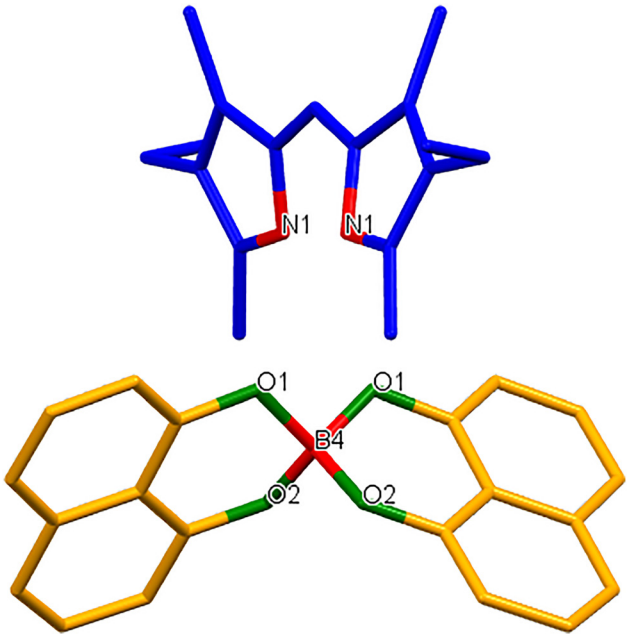


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**Table 1:** Data collection and handling.

| | |
|---|---|
| Crystal: | Orange plate |
| Size: | 0.43 × 0.08 × 0.05 mm |
| Wavelength: | Cu *K*α radiation (1.54184 Å) |
| $\mu$: | 0.65 mm$^{-1}$ |
| Diffractometer, scan mode: | Xcalibur, $\omega$ |
| $\theta_{max}$, completeness: | 66.9°, >99 % |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$, $R_{int}$: | 10,896, 2696, 0.027 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\sigma(I_{obs})$, 2410 |
| $N(param)_{refined}$: | 206 |
| Programs: | CrysAlis$^{Pro}$ [1], SHELX [2, 3], Olex2 [4] |

**Abstract**

$C_{37}H_{37}BN_2O_4$, monoclinic, *I*2/*a* (no. 15), $a$ = 13.8030(3) Å, $b$ = 17.6109(2) Å, $c$ = 14.1059(3) Å, $\beta$ = 117.524(3)°, $V$ = 3040.83(11) Å$^3$, $Z$ = 4, $R_{gt}(F)$ = 0.0340, $wR_{ref}(F^2)$ = 0.0867, T = 150 K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

## 1 Source of materials

The 2,6-diethyl-3,5-dimethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (50 mg, 0.16 mmol) and TMSOTf (0.11 mL, 0.57 mmol) were dissolved in toluene (5 mL) and the mixture was heated under reflux for 30 min. The solution was cooled to room temperature, and 1,8-dihydroxynaphthalene (132 mg, 0.82 mmol) was added followed by diisopropylethylamine (0.10 mL, 0.57 mmol). The reaction mixture was stirred for 2 h at room temperature, the solvent was removed under reduced pressure, and the crude product was purified by column chromatography to give the title compound in 20 % yield. Good quality single crystal suitable for single crystal diffraction

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

| Atom | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.67809 (6) | 0.70100 (5) | 0.41408 (6) | 0.0275 (2) |
| O2 | 0.69001 (7) | 0.79929 (5) | 0.54066 (6) | 0.0295 (2) |
| N1 | 0.78953 (8) | 0.56589 (6) | 0.41272 (8) | 0.0238 (2) |
| H1 | 0.7457 (12) | 0.6017 (8) | 0.4184 (11) | 0.029* |
| C1 | 0.86661 (9) | 0.45483 (7) | 0.40453 (9) | 0.0237 (3) |
| C2 | 0.89341 (9) | 0.50969 (7) | 0.34997 (9) | 0.0252 (3) |
| C3 | 0.84312 (9) | 0.57779 (7) | 0.35489 (9) | 0.0251 (3) |
| C8 | 0.7500 | 0.45713 (9) | 0.5000 | 0.0232 (3) |
| H8 | 0.7500 | 0.4032 | 0.5000 | 0.028* |
| C9 | 0.79956 (9) | 0.49010 (7) | 0.44387 (9) | 0.0223 (3) |
| C10 | 0.90618 (10) | 0.37450 (7) | 0.42373 (10) | 0.0281 (3) |
| H10A | 0.8740 | 0.3467 | 0.3559 | 0.042* |
| H10B | 0.8845 | 0.3503 | 0.4736 | 0.042* |
| H10C | 0.9860 | 0.3738 | 0.4543 | 0.042* |
| C11 | 0.96002 (11) | 0.50007 (8) | 0.29149 (11) | 0.0329 (3) |
| H11A | 1.0079 | 0.4551 | 0.3202 | 0.039* |
| H11B | 1.0073 | 0.5452 | 0.3043 | 0.039* |
| C12 | 0.88885 (13) | 0.49009 (9) | 0.17155 (11) | 0.0440 (4) |
| H12A | 0.9355 | 0.4838 | 0.1368 | 0.066* |
| H12B | 0.8425 | 0.5350 | 0.1424 | 0.066* |
| H12C | 0.8427 | 0.4450 | 0.1583 | 0.066* |
| C13 | 0.84431 (11) | 0.65271 (7) | 0.30741 (10) | 0.0327 (3) |
| H13A | 0.7873 | 0.6540 | 0.2329 | 0.049* |
| H13B | 0.9158 | 0.6608 | 0.3101 | 0.049* |
| H13C | 0.8307 | 0.6928 | 0.3479 | 0.049* |
| C14 | 0.57882 (9) | 0.72763 (7) | 0.34104 (9) | 0.0239 (3) |
| C15 | 0.52492 (10) | 0.69411 (7) | 0.24262 (10) | 0.0283 (3) |
| H15 | 0.5577 | 0.6534 | 0.2237 | 0.034* |
| C16 | 0.42069 (11) | 0.72048 (8) | 0.16981 (10) | 0.0346 (3) |
| H16 | 0.3836 | 0.6975 | 0.1013 | 0.041* |
| C17 | 0.37170 (11) | 0.77857 (8) | 0.19572 (11) | 0.0365 (3) |
| H17 | 0.3008 | 0.7949 | 0.1455 | 0.044* |
| C18 | 0.37849 (11) | 0.87430 (8) | 0.32951 (11) | 0.0374 (3) |
| H18 | 0.3076 | 0.8925 | 0.2820 | 0.045* |
| C19 | 0.43468 (12) | 0.90563 (8) | 0.42898 (11) | 0.0366 (3) |
| H19 | 0.4015 | 0.9449 | 0.4500 | 0.044* |
| C20 | 0.54027 (11) | 0.88116 (7) | 0.50087 (10) | 0.0313 (3) |
| H20 | 0.5779 | 0.9041 | 0.5693 | 0.038* |
| C21 | 0.58888 (10) | 0.82405 (7) | 0.47205 (9) | 0.0257 (3) |
| C23 | 0.53162 (10) | 0.78921 (7) | 0.36981 (9) | 0.0248 (3) |
| C24 | 0.42564 (10) | 0.81482 (7) | 0.29707 (10) | 0.0304 (3) |
| B4 | 0.7500 | 0.75178 (11) | 0.5000 | 0.0268 (4) |

analysis was obtained by slow evaporation from a mixture of chloroform and hexane (1:3).

## 2 Experimental details

The structure of the as 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

Noncovalent interactions (NCIs) are ubiquitous in nature, playing a crucial role in the cohesion of chemical systems. The last decades have witnessed increased interest in the rational design of supramolecular architectures based on the self-assembly of various suitable building blocks using NCIs [5–15]. Amongst the various strategies, the utilization of intermolecular hydrogen bond interactions in the design and self-assembly of well-defined supramolecular structures has become a promising synthetic approach with potential in host–guest chemistry, gas storage, and crystal engineering [16–20]. The synthesized complex was crystallized in the monoclinic space group *I*12/*a*1. Single-crystal structure analysis revealed the product as a salt in which the boron centre had been abstracted from the diypyrromethene core followed by formation of an anion with two molecules of the naphthalene-1,8-bis(olate). The nitrogen atoms of the cation were hydrogen-bonded to the oxygen atoms of the boron containing anion.

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

## References

1. Rigaku O. D. CrysAlisPRO; 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. Desiraju G. R. Supramolecular synthons in crystal engineering? A new organic synthesis. *Angew. Chem. Int. Ed.* 1995, *34*, 2311–2327.

6. Hosseini M. W. Molecular tectonics: from simple tectons to complex molecular networks. *Acc. Chem. Res.* 2005, *38*, 313–323.
7. Khan A., Bushnak I., Jiang Z., Usman R., Choudhari P. B., Feng C., Al-Kaysi R. O., Rahman F.-U. Novel jellyfish-shaped resorcin[4]arene macrocyclic cocrystal via collaboration of macrocyclic chemistry and co-crystal engineering: insight into structural, noncovalent interactions and computational chemistry. *J. Mol. Struct.* 2024, *1298*, 137034.
8. Feng Q., Wang M., Xu C., Khan A., Wu X., Lu J., Wei X. Investigation of molecular arrangements and solid-state fluorescence properties of solvates and cocrystals of 1-acetyl-3-phenyl-5-(9-anthryl)-2-pyrazoline. *CrystEngComm* 2014, *16*, 5820–5826.
9. Khan A., Liu M., Usman R., He N., Li R., Sayed S. M., Li S., Sun W., Chen H., Zhang L. Solid emission color tuning of organic charge transfer cocrystals based on planar p-conjugated donors and TCNB. *J. Solid State Chem.* 2019, *272*, 96–101.
10. Khan A., Usman R., Li R., Hajji M., Tang H., Ma D. Polycyclic motif engineering in cyanostilbene-based donors towards highly efficient modulable emission properties in two-component systems. *CrystEngComm* 2021, *23*, 8462–8470.
11. Khan A., Usman R., Sayed S. M., Li R., Chen H., He N. Supramolecular design of highly efficient two-component molecular hybrids toward structure and emission properties tailoring. *Cryst. Growth Des.* 2019, *19*, 2772–2778.
12. Khan A., Wang M., Usman R., Lu J., Sun H., Du M., Zhang R., Xu C. Organic charge-transfer complexes for the selective accommodation of aromatic isomers using anthracene derivatives and TCNQ. *New J. Chem.* 2016, *40*, 5277–5284.
13. Khan A., Wang M., Usman R., Sun H., Du M., Xu C. Molecular marriage via charge transfer interaction in organic charge transfer co-crystals toward solid-state fluorescence modulation. *Cryst. Growth Des.* 2017, *17*, 1251–1257.
14. Sun H., Wang M., Wei X., Zhang R., Wang S., Khan A., Usman R., Feng Q., Du M., Yu F. Understanding charge-transfer interaction mode in cocrystals and solvates of 1-phenyl-3-(pyren-1-yl) prop-2-en-1-one and TCNQ. *Cryst. Growth Des.* 2015, *15*, 4032–4038.
15. Usman R., Khan A., Sun H., Wang M. Study of charge transfer interaction modes in the mixed donor-acceptor cocrystals of pyrene derivatives and TCNQ: a combined structural, thermal, spectroscopic, and hirshfeld surfaces analysis. *J. Solid State Chem.* 2018, *266*, 112–120.
16. Usman R., Khan A., Tang H., Ma D., Alsuhaibani A. M., Refat M. S., Adnan, Ara N., Fan H.-J. S. Charge transfer and hydrogen bonding motifs in organic cocrystals derived from aromatic diamines and TCNB. *J. Mol. Struct.* 2022, *1254*, 132360.
17. Usman R., Khan A., Wang M. Study of H-bonded assemblies of the solvates of anthracene derivatives: guest effect on the crystal symmetry and spectroscopic properties. *Supramol. Chem.* 2017, *29*, 497–505.
18. Usman R., Khan A., Wang M., Luo Y., Sun W., Sun H., Du C., He N. Investigation of charge-transfer interaction in mixed stack donor-acceptor cocrystals toward tunable solid-state emission characteristics. *Cryst. Growth Des.* 2018, *18*, 6001–6008.
19. Torres-Huerta A., Velásquez-Hernández M. D. J., Martínez-Otero D., Höpfl H., Jancik V. Structural induction via solvent variation in assemblies of triphenylboroxine and piperazine-potential application as self-assembly molecular sponge. *Cryst. Growth Des.* 2017, *17*, 2438–2452.
20. Patalag L. J., Jones P. G., Werz D. B. BOIMPYs: rapid access to a family of red-emissive fluorophores and NIR dyes. *Angew. Chem. Int. Ed.* 2016, *55*, 13340–13344.