

Communication

# 2-(4-(Dimethylamino)phenyl)-3,3-difluoro-4,6-diphenyl-3,4-dihydro-1,2,4,5,3-tetrazaborinin-2-ium-3-ide

Ida A. Lupanova, Dzhamilya N. Konshina, Nikita A. Elkov and Valery V. Konshin \* 

Department of Chemistry and High Technology, Kuban State University, Stavropolskayast 149, 350040 Krasnodar, Russia; konovalova\_ida@mail.ru (I.A.L.); jfox@list.ru (D.N.K.); nikitaelkov1@gmail.com (N.A.E.)

\* Correspondence: organotin@mail.ru; Tel.: +7-(953)-104-3352

**Abstract:** Reaction of 1-(4-(dimethylamino)phenyl)-3,5-diphenylformazane with boron trifluoride diethyl etherate (5 equiv) in the presence of triethylamine (3 equiv) in toluene medium gave “boratetrazine”—2-(4-(dimethylamino)phenyl)-3,3-difluoro-4,6-diphenyl-3,4-dihydro-1,2,4,5,3-tetrazaborinin-2-ium-3-ide in a 58% yield.

**Keywords:** formazane; boron trifluoride; boron chelate



**Citation:** Lupanova, I.A.; Konshina, D.N.; Elkov, N.A.; Konshin, V.V. 2-(4-(Dimethylamino)phenyl)-3,3-difluoro-4,6-diphenyl-3,4-dihydro-1,2,4,5,3-tetrazaborinin-2-ium-3-ide. *Molbank* **2022**, *2022*, M1312. <https://doi.org/10.3390/M1312>

Academic Editor: R. Alan Aitken

Received: 9 December 2021

Accepted: 24 December 2021

Published: 29 December 2021

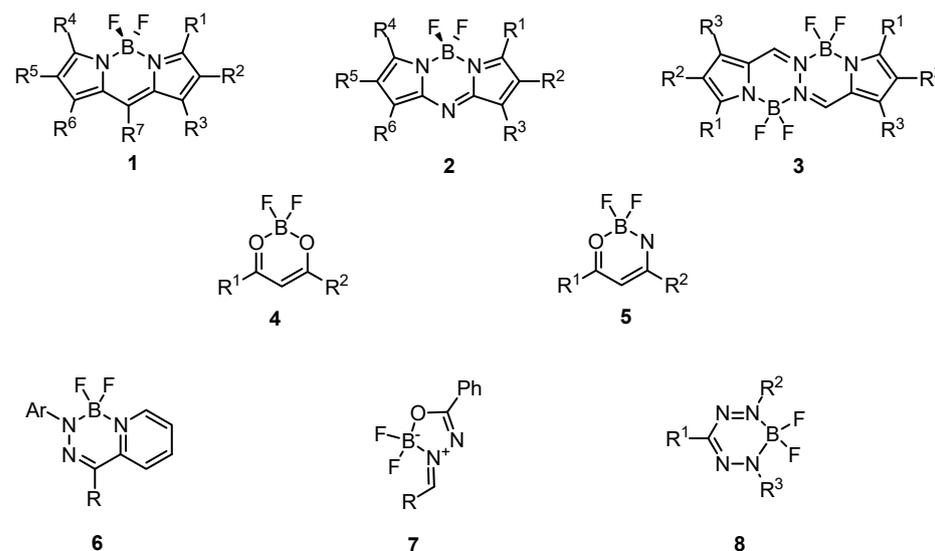
**Publisher’s Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

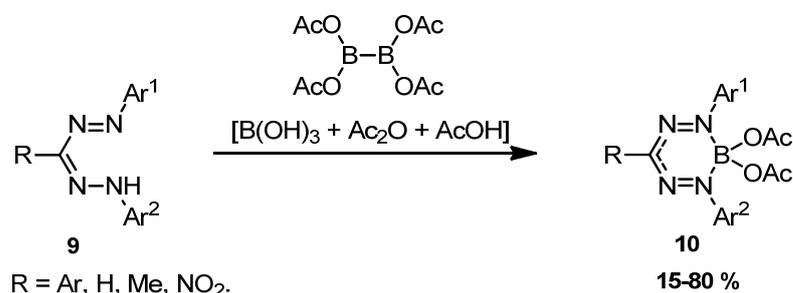
Various boron chelates are some of the most common fluorophores, finding widespread practical application in bioimaging [1], as molecular reporters and chemodosimeters [2,3], in sensors [4–6], in optoelectronic applications [7–9] and others. The most studied are BODIPY **1** [10–12] and their structural analogs **2** [13], BOPHY **3** [14], boron difluoride 1,3-diketonates **4** [15] and 1,3-ketoiminates **5** [16]. Difluoroboron derivatives of different types of hydrazones **6** [17], such as N-acylhydrazones **7** [18] and azohydrazones (formazanes) **8** [19] (Figure 1), are also of interest and are being extensively studied at the present time.



**Figure 1.** Examples of various boron chelates.

The pioneering work on the reaction of formazans with boron trifluoride diethyl etherate showed it to afford triphenyltetrazolium tetrafluoroborate [20]. Later, the first representatives of boron formazanate complexes, “boratetrazines” **10**, were obtained by the

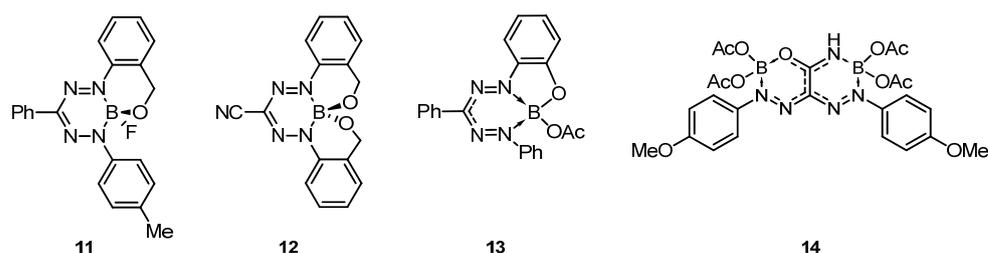
reaction of formazans with diboron tetraacetate (in situ synthesized from boric acid, acetic acid and acetic anhydride) (Scheme 1) [21].



**Scheme 1.** Examples of preparation “boratetrazines”.

The purposeful study of boron formazanates was started in 2007 by Gilroy et al. [22]. Later, efficient synthesis of them was proposed in toluene medium in the presence of triethylamine [23]. Different derivatives based on cyano- [24], nitro- [25] and triarylformazans [19,26–29] have been obtained.

The reaction between boron trifluoride etherate and more complex substrates containing additional groups, which can coordinate to the boron, proceeds nontrivially, as in the case of **11–14** (Figure 2), where coordination is realized through the oxygen atom [30–33].

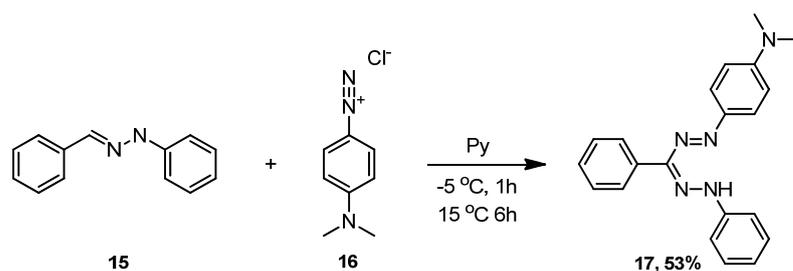


**Figure 2.** Examples of various boron formazanates.

To date, only one representative of “boratetrazines” having a donor *N,N*-dialkylamino group has been described [34]. It was prepared from cyanoformazan containing the 4-(dimethylamino)phenyl fragment in the N<sup>1</sup> and N<sup>5</sup> positions. The aim of the present work was to study the reaction of triarylformazan containing the *N,N*-dialkylamino group in the N<sup>1</sup> position with boron trifluoride etherate.

## 2. Results and Discussion

To begin, 1-(4-(dimethylamino)phenyl)-3,5-diphenylformazan **17** was synthesized from phenylhydrazone benzaldehyde **15** [35] and diazotized *N,N*-dimethyl-*p*-phenylenediamine in a pyridine medium (Scheme 2). The target formazan **17** was purified by flash chromatography and recrystallization from ethanol. Its physical constants and spectral data are in agreement with the literature data [36].



**Scheme 2.** Synthesis of 1-(4-(dimethylamino)phenyl)-3,5-diphenylformazan **17**.



St. Louis, MO, USA), Phenylhydrazine (for synthesis,  $\geq 97\%$ , Aldrich, St. Louis, MO, USA) and *N,N*-Dimethyl-*p*-phenylenediamine dihydrochloride ( $\geq 99\%$ , Vekton, Russia), boron trifluoride diethyl etherate (for synthesis,  $\geq 97\%$ , Aldrich, St. Louis, MO, USA). CCDC 1919508 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/or> (accessed on 29 November 2021) from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk.

### 3.1. 1-(4-(Dimethylamino)phenyl)-3,5-diphenylformazan (17)

Diazonium salt solution (obtained from 3.52 g (0.0168 mol) *N,N*-dimethyl-*p*-phenylenediamine dihydrochloride, 1.16 g  $\text{NaNO}_2$  and 4 mL conc. HCl in 30 mL water) was added to a solution of 3 g (0.0153 mol) of phenylhydrazone benzaldehyde in 100 mL pyridine at  $-5^\circ\text{C}$ . Then, a solution of 2.5 g NaOH in 6 mL water was added and stirred at  $-5^\circ\text{C}$  for 1 h. Then, the temperature was raised to  $15^\circ\text{C}$  and the reaction mixture was allowed to stand for 6 h. The reaction mixture was poured into 500 mL of cooled 2M HCl; the resulting brown precipitate was filtered off, washed on a filter with water and dried in the desiccator. It was purified by flash chromatography on alumina (neutral) eluting with a hexane–dichloromethane mixture (10:1) and subsequent recrystallization from ethanol. Yield 2.78 g (53%); violet–black microcrystalline solid; mp  $184\text{--}185^\circ\text{C}$ . IR (KBr):  $\nu = 3086, 3051$  ( $\text{Csp}^2\text{-H}$ ), 2918, 2852, 2806 ( $\text{Csp}^3\text{-H}$ ), 1595, 1510, 1494, 1438, 1377, 1307, 1234, 1147, 985, 817  $\text{cm}^{-1}$  (SI, Figure S1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 399.78 MHz):  $\delta = 3.09$  (s, 6H,  $\text{CH}_3$ ), 6.74–6.78 (m, 2H, CH), 6.98–7.04 (m, 1H, CH), 7.32–7.45 (m, 7H, CH), 7.82–7.87 (m, 2H, CH), 8.14–8.17 (m, 2H, CH), 14.92 (s, 1H, NH) (SI, Figure S2).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.5 MHz):  $\delta = 40.3$  ( $\text{CH}_3$ ), 111.8 (CH), 114.7 (CH), 122.5 (CH), 124.2 (CH), 126.0 (CH), 127.3 (CH), 128.2 (CH), 129.3 (CH), 137.9 (C), 141.0 (C), 143.3 (C), 144.0 (C), 152.4 (C) (SI, Figure S3). HRMS ESI TOF:  $m/z = 344,1875$  [ $\text{M} + \text{H}$ ] $^+$  (344,1870 calc. for  $\text{C}_{21}\text{H}_{21}\text{N}_5$ ) (SI, Figure S4).

### 3.2. 2-(4-(Dimethylamino)phenyl)-3,3-difluoro-4,6-diphenyl-3,4-dihydro-1,2,4,5,3-tetrazaborinin-2-ium-3-ide (18)

Triethylamine 0.237 mL (1.7 mmol) was added to a solution of 0.2 g (0.58 mmol) of 1-(4-(dimethylamino)phenyl)-3,5-diphenylformazan in 15 mL of dry toluene, stirred for several minutes and 0.358 mL (2.9 mmol) boron trifluoride diethyl etherate was added. The reaction mixture, colored dark blue, was incubated at  $90^\circ\text{C}$  for 5 h. Then, it was transferred to a separating funnel, washed with water, and the toluene layer was dried with  $\text{Na}_2\text{SO}_4$ . After separation of the drying agent and concentration under vacuum, the residue was purified by flash chromatography (silica, hexane–dichloromethane 10:1), the dark blue fraction containing 18. Yield 0.132 g (88%); dark green crystalline solid (bronze reflex); mp  $189\text{--}190^\circ\text{C}$ . IR (KBr):  $\nu = 3109, 3068, 3039$  ( $\text{Csp}^2\text{-H}$ ), 2920, 2852 ( $\text{Csp}^3\text{-H}$ ), 1608, 1529, 1489, 1458, 1423, 1384, 1323, 1301, 1255, 1234, 1192, 1178, 1103, 1016, 817, 767  $\text{cm}^{-1}$  (SI, Figure S5).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 399.78 MHz):  $\delta = 3.08$  (s, 6H,  $\text{CH}_3$ ), 6.70–6.74 (m, 2H, CH), 7.31–7.35 (m, 1H, CH), 7.38–7.49 (m, 5H, CH), 7.84–7.88 (m, 2H, CH), 7.92–7.96 (m, 2H, CH), 8.11–8.15 (m, 2H, CH) (SI, Figure S6).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.5 MHz):  $\delta = 40.3$  ( $\text{CH}_3$ ), 111.7 (CH), 122.7 (CH), 125.3 (CH), 125.4 (CH), 127.9 (CH), 128.5 (CH), 128.7 (CH), 128.8 (CH), 134.1 (C), 134.5 (C), 144.3 (C), 147.7 (C), 151.4 (C) (SI, Figure S7).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376.17 MHz):  $\delta = -144.03$  (q,  $^1J_{\text{FB}} = 30$  Hz) (SI, Figure S8).  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128.27 MHz):  $\delta = -1.25$  (t,  $^1J_{\text{BF}} = 30.5$  Hz) (SI, Figure S9). HRMS ESI TOF:  $m/z = 392,1861$  [ $\text{M} + \text{H}$ ] $^+$  (392,1853 calc. for  $\text{C}_{21}\text{H}_{20}\text{BF}_2\text{N}_5$ ) (SI, Figure S10).

Crystal data for  $\text{C}_{21}\text{H}_{20}\text{BF}_2\text{N}_5$  ( $M = 391.25$  g/mol): monoclinic, space group  $\text{P}2_1/c$ ,  $a = 17.9429(15)$  Å,  $b = 13.3212(11)$  Å,  $c = 8.1555(7)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 93.752(2)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 1945.2(3)$  Å $^3$ ,  $Z = 4$ ,  $T = 120$  K,  $\mu = 0.95$   $\text{cm}^{-1}$ ,  $D_{\text{calc.}} = 1.36$   $\text{g}/\text{cm}^3$ . In total, 26,190 reflections were measured, 4241 of which were unique and used in all calculations. The final  $R_1$  was 0.0438, and the  $wR_2$  was 0.1360 (all data) (SI, Tables S1–S5).

**Supplementary Materials:** The following supporting information can be downloaded. Figure S1: IR-spectrum of 17; Figure S2:  $^1\text{H}$  NMR of 17; Figure S3:  $^{13}\text{C}$  NMR of 17; Figure S4: HRMS of 17; Figure S5: IR-spectrum of 18; Figure S6:  $^1\text{H}$  NMR of 18; Figure S7:  $^{13}\text{C}$  NMR of 18; Figure S8:  $^{19}\text{F}$  NMR of 18; Figure S9:  $^{11}\text{B}$  NMR of 18; Figure S10: HRMS of 18; Tables S1–S5: Crystal data of 18.

**Author Contributions:** Conceptualization, V.V.K.; methodology, V.V.K.; software, D.N.K.; validation, V.V.K. and D.N.K.; formal analysis, D.N.K.; investigation, I.A.L. and N.A.E.; resources, I.A.L. and N.A.E.; data curation, V.V.K.; writing—original draft preparation, V.V.K. and D.N.K.; writing—review and editing, V.V.K. and D.N.K.; supervision, V.V.K.; project administration, V.V.K.; funding acquisition, V.V.K., D.N.K. and I.A.L. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was financially supported by the Ministry of Science and Higher Education of the Russian Federation (project no. FZEN-2020-0022).

**Acknowledgments:** The X-ray diffraction study was performed using the equipment (Bruker APEX DUO diffractometer) of the Center for Molecular Composition Studies of INEOS RAS, and the HRMS study was accomplished with the use of scientific equipment of the Collective Employment Centre “Ecoanalytical Centre”, Kuban State University (A. Z. Temerdashev).

**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

## References

1. Kaur, P.; Singh, K. Recent advances in the application of BODIPY in bioimaging and chemosensing. *J. Mater. Chem. C* **2019**, *7*, 11361–11405. [[CrossRef](#)]
2. Yang, Y.; Zhao, Q.; Feng, W.; Li, F. Luminescent chemodosimeters for bioimaging. *Chem. Rev.* **2013**, *113*, 192–270. [[CrossRef](#)] [[PubMed](#)]
3. Wang, H.-Y.; Zhang, H.; Chen, S.; Liu, Y. Fluorescein-inspired near-infrared chemodosimeter for luminescence bioimaging. *Curr. Med. Chem.* **2019**, *26*, 4029–4041. [[CrossRef](#)] [[PubMed](#)]
4. McNaughton, D.A.; Fares, M.; Picci, G.; Gale, P.A.; Caltagirone, C. Advances in fluorescent and colorimetric sensors for anionic species. *Coord. Chem. Rev.* **2021**, *427*, 213573. [[CrossRef](#)]
5. Wang, L.; Ding, H.; Ran, X.; Tang, H.; Cao, D. Recent progress on reaction-based BODIPY probes for anion detection. *Dyes Pigm.* **2020**, *172*, 107857. [[CrossRef](#)]
6. Møllerup, S.K.; Wang, S. Boron-based stimuli responsive materials. *Chem. Soc. Rev.* **2019**, *48*, 3537–3549. [[CrossRef](#)]
7. Li, D.; Zhang, H.; Wang, Y. Four-coordinate organoboron compounds for organic light-emitting diodes (OLEDs). *Chem. Soc. Rev.* **2013**, *42*, 8416–8433. [[CrossRef](#)]
8. Poddar, M.; Misra, R. Recent advances of BODIPY based derivatives for optoelectronic applications. *Coord. Chem. Rev.* **2020**, *421*, 213462. [[CrossRef](#)]
9. Squeo, B.M.; Ganzer, L.; Virgili, T.; Pasini, M. BODIPY-based molecules, a platform for photonic and solar cells. *Molecules* **2020**, *26*, 153. [[CrossRef](#)]
10. Loudet, A.; Burgess, K. BODIPY dyes and their derivatives: Syntheses and spectroscopic properties. *Chem. Rev.* **2007**, *107*, 4891–4932. [[CrossRef](#)]
11. Ulrich, G.; Ziessele, R.; Harriman, A. The chemistry of fluorescent bodipy dyes: Versatility unsurpassed. *Angew. Chem. Int. Ed.* **2008**, *47*, 1184–1201. [[CrossRef](#)] [[PubMed](#)]
12. Boens, N.; Verbelen, B.; Ortiz, M.J.; Jiao, L.; Dehaen, W. Synthesis of BODIPY dyes through postfunctionalization of the boron dipyrromethene core. *Coord. Chem. Rev.* **2019**, *399*, 213024. [[CrossRef](#)]
13. Shamova, L.I.; Zatsikha, Y.V.; Nemykin, V.N. Synthesis pathways for the preparation of the BODIPY analogues: Aza-BODIPYs, BOPHYs and some other pyrrole-based acyclic chromophores. *Dalton Trans.* **2021**, *50*, 1569–1593. [[CrossRef](#)] [[PubMed](#)]
14. Bismillah, A.N.; Aprahamian, I. Fundamental studies to emerging applications of pyrrole-BF<sub>2</sub>(BOPHY) fluorophores. *Chem. Soc. Rev.* **2021**, *50*, 5631–5649. [[CrossRef](#)]
15. Collot, M. Recent advances in dioxaborine-based fluorescent materials for bioimaging applications. *Mater. Horiz.* **2021**, *8*, 501–514. [[CrossRef](#)]
16. Fedorenko, E.V.; Mirochnik, A.G.; Beloliptsev, A.Y.; Svistunova, I.V.; Tretyakova, G.O. Design, synthesis, and crystallization-induced emission of boron difluorides  $\beta$ -ketoimines. *ChemPlusChem* **2018**, *83*, 117–127. [[CrossRef](#)]
17. Cappello, D.; Therien, D.A.B.; Staroverov, V.N.; Lagugn e-Labarthet, F.; Gilroy, J.B. Optoelectronic, aggregation, and redox properties of double-rotor boron difluoride hydrazone dyes. *Chem. Eur. J.* **2019**, *25*, 5994–6006. [[CrossRef](#)]
18. Dilmann, A.D.; Arkhipov, D.E.; Levin, V.V.; Belyakov, P.A.; Korlyukov, A.A.; Struchkova, M.I.; Tartakovskiy, V.A. Trifluoromethylation of N-benzoylhydrazones. *J. Org. Chem.* **2008**, *73*, 5643–5646. [[CrossRef](#)]
19. Gilroy, J.B.; Otten, E. Formazanate coordination compounds: Synthesis, reactivity, and applications. *Chem. Soc. Rev.* **2020**, *49*, 85–113. [[CrossRef](#)]

20. Acarbay, M. Über Formazyl-Verbindungen, XI. Über die reaktion von Formazyl-Verbindungen mit Bortrifluorid-ätherat. *Justus Liebigs Ann. Chem.* **1964**, *677*, 127–128. [[CrossRef](#)]
21. Stepanov, B.I.; Avramenko, G.V. Boron—nitrogen compounds I. Reactions of triarylformazans with diboron tetraacetate. Synthesis of boratetrazines. *J. Gen. Chem. (USSR)* **1980**, *50*, 292–295.
22. Gilroy, J.B.; Ferguson, M.J.; McDonald, R.; Patrick, B.O.; Hicks, R.G. Formazans as  $\beta$ -diketiminat analogues. Structural characterization of boratetrazines and their reduction to borataverdazyl radical anions. *Chem. Commun.* **2007**, *2*, 126–128. [[CrossRef](#)]
23. Barbon, S.M.; Price, J.T.; Reinkeluers, P.A.; Gilroy, J.B. Substituent-dependent optical and electrochemical properties of triarylformazanate boron difluoride complexes. *Inorg. Chem.* **2014**, *53*, 10585–10593. [[CrossRef](#)] [[PubMed](#)]
24. Barbon, S.M.; Reinkeluers, P.A.; Price, J.T.; Staroverov, V.N.; Gilroy, J.B. Structurally tunable 3-cyanoformazanate boron difluoride dyes. *Chem. Eur. J.* **2014**, *20*, 11340–11344. [[CrossRef](#)] [[PubMed](#)]
25. Barbon, S.M.; Staroverov, V.N.; Gilroy, J.B. Effect of extended  $\pi$  conjugation on the spectroscopic and electrochemical properties of boron difluoride formazanate complexes. *J. Org. Chem.* **2015**, *80*, 5226–5235. [[CrossRef](#)]
26. Kumar, C.; Agrawal, A.R.; Ghosh, N.G.; Karmakar, H.S.; Das, S.; Kumar, N.R.; Banewar, V.W.; Zade, S.S. Boron difluoride formazanates with thiophene and 3,4-ethylenedioxythiophene capping and their electrochemical polymerization. *Dalton Trans.* **2020**, *49*, 13202–13206. [[CrossRef](#)]
27. Dhindsa, J.S.; Buguis, F.L.; Anghel, M.; Gilroy, J.B. Band gap engineering in acceptor-donor-acceptor boron difluoride formazanates. *J. Org. Chem.* **2021**, *86*, 12064–12074. [[CrossRef](#)] [[PubMed](#)]
28. Maar, R.R.; Katzman, B.D.; Boyle, P.D.; Staroverov, V.N.; Gilroy, J.B. Cationic boron formazanate dyes. *Angew. Chem. Int. Ed.* **2021**, *60*, 5152–5156. [[CrossRef](#)]
29. Van Belois, A.; Maar, R.R.; Workentin, M.S.; Gilroy, J.B. Dialkynylborane complexes of formazanate ligands: Synthesis, electronic properties, and reactivity. *Inorg. Chem.* **2019**, *58*, 834–843. [[CrossRef](#)]
30. Katzman, B.D.; Maar, R.R.; Cappello, D.; Sattler, M.O.; Boyle, P.D.; Staroverov, V.N.; Gilroy, J.B. A strongly Lewis-acidic and fluorescent borenium cation supported by a tridentate formazanate ligand. *Chem. Commun.* **2021**, *57*, 9530–9533. [[CrossRef](#)]
31. Barbon, S.M.; Staroverov, V.N.; Gilroy, J.B. Structurally diverse Boron–Nitrogen heterocycles from an  $N_2O_2^{3-}$  formazanate ligand. *Angew. Chem. Int. Ed.* **2017**, *56*, 8173–8177. [[CrossRef](#)]
32. Stepanov, B.I.; Avramenko, G.V.; Khamud, S.; Mustafaeva, S.I. Boratetrazines. *J. Gen. Chem. (USSR)* **1986**, *56*, 339–341.
33. Bezuglaya, Z.V.; Naser, M.; Avramenko, G.V.; Stepanov, B.I. Influence of substitution on the path of complexation of 1, 5-diarylformazan-3-carboxylic acid amides with diobortetraacetate. *J. Gen. Chem. (USSR)* **1991**, *61*, 1758–1759.
34. Maar, R.R.; Zhang, R.; Stephens, D.G.; Ding, Z.; Gilroy, J.B. Near-infrared photoluminescence and electrochemiluminescence from a remarkably simple boron difluoride formazanate dye. *Angew. Chem. Int. Ed.* **2019**, *58*, 1052–1056. [[CrossRef](#)] [[PubMed](#)]
35. Petunin, P.V.; Martynko, E.A.; Trusova, M.E.; Kazantsev, M.S.; Rybalova, T.V.; Valiev, R.R.; Uvarov, M.N.; Mostovich, E.A.; Postnikov, P.S. Verdazyl radical building blocks: Synthesis, structure, and sonogashira cross-coupling reactions. *Eur. J. Org. Chem.* **2018**, *34*, 4802–4811. [[CrossRef](#)]
36. Kostryukov, S.G.; Balandina, A.V.; Kozlov, A.S.; Kraynov, E.V.; Pryanichnikova, M.K.; Chernyaeva, O.Y.; Akhmatova, A.A.; Lukshina, Y.I. Synthesis and electrochemical properties of 2-(4-R<sup>1</sup>-phenyl)-6-(4-R<sup>2</sup>-phenyl)-4-phenyl-3,4-dihydro-1,2,4,5-tetrazin-1(2H)-yls. *Russ. J. Gen. Chem.* **2020**, *90*, 341–351. [[CrossRef](#)]