

Fusion of Aza- and Oxadiborepins with Furans in a Reversible Ring-Opening Process Furnishes Versatile Building Blocks for Extended π -Conjugated Materials

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Dedicated to Professor Anthony J. Arduengo III on the occasion of his 70th birthday.

Abstract: A modular synthesis of both difurooxa- and difuroazadiborepins from a common precursor is demonstrated. Starting from 2,2'-bifuran, after protection of the positions 5 and 5' with bulky silyl groups, formation of the novel polycycles proceeds through opening of the furan rings to a dialkyne and subsequent re-cyclization in the borylation step. The resulting bifuran-fused diborepins show pro-

nounced stability, highly planar tricyclic structures, and intense blue light emission. Deprotection and transformation into dibrominated building blocks that can be incorporated into π -extended materials can be performed in one step. Detailed DFT calculations provide information about the aromaticity of the constituent rings of this polycycle.

Introduction

π -Conjugated organic materials are subject of continuing tremendous research activities due to their versatile applications in various fields ranging from energy storage and conversion to sensors to biomedical uses.^[1] Recent focus in organic electronic materials' design has shifted towards the development of electron-deficient building blocks.^[1] Therein, the strongly electron-withdrawing dicarboximide functional group, $-\text{C}(=\text{O})-\text{NR}-\text{C}(=\text{O})-$, appears as a ubiquitous structural feature.^[2,3] 2,2'-Bithiophene-3,3'-dicarboximide (BTI, A, Figure 1) can be quoted as a representative example.^[2] Through the readily addressable α -positions of its thiophene moieties, this tricyclic building block is easily incorporated in π -extended conjugated scaffolds with applications as n-type semiconducting materials.

In recent times, the doping of π -conjugated frameworks with trivalent boron atoms has emerged as a versatile novel approach for the construction of strongly electron-deficient

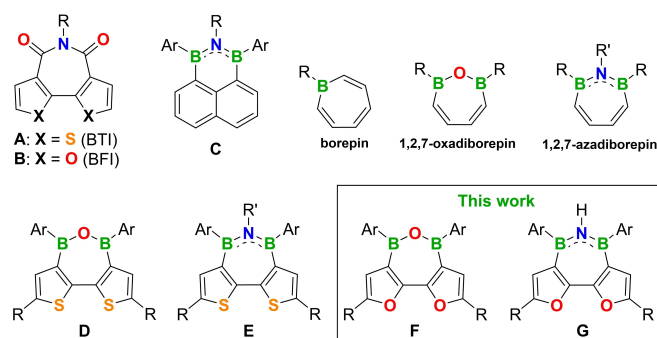


Figure 1. 2,2'-Bithiophene- (BTI, A) and 2,2'-bifuran-3,3'-dicarboximide (BFI, B) as well as the diborepins D–G derived from them; BNB-doped phenalenyl C, and generic structures of borepin, 1,2,7-oxadiborepin, and 1,2,7-azadiborepin.

materials.^[4,5] In this case, the effect comes from the expansion of the π system with an empty p orbital. Replacement of the carbonyl ($>\text{C}=\text{O}$) units in a dicarboximide group with borylene ($>\text{B}-\text{Ar}$) units gives a diborylene-amine fragment, $-\text{BAr}-\text{NR}-\text{BAr}-$ (DBA), which is an efficient π -acceptor group (with 3-center 2- π -electron bonding) that resembles the dicarboximide moiety also structurally. In contrast to the latter, the DBA group offers the additional opportunity to fine-tune its electronic properties through the variable Ar groups. Recently, Wagner's and our group independently explored the BNB-doped phenalenyl system C,^[6] whereby we introduced the use of DBA as a substitute for the imide group as a concept to generate new electron-deficient electronic materials. Thus, compound C can be regarded as an analogue of naphthalene dicarboximide.

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The substitution of particular C=C units in aromatic hydrocarbons with their isoelectronic and isosteric B=N units (“BN/CC isosterism”) has evolved to a viable concept for expanding the chemical space of conjugated organic frameworks. This has led to a considerable number of mono- and polycyclic aromatic compounds known to date that contain one or more BN units.^[7,8] On the other hand, relatively few BNB-doped aromatics have been developed and investigated for their optoelectronic properties so far.^[6,9–11] The same is true for compounds featuring the structurally and electronically related BOB fragments.^[6a,12–15] In 2018, Yan et al. reported on the synthesis of dithieno[3,2-c:2',3'-e][1,2,7]oxadiborepin derivatives (**D**).^[12] They obtained the tricyclic system serendipitously in an attempt to prepare a dithienoborole. In parallel, we developed a modular approach for the synthesis of both dithieno[3,2-c:2',3'-e][1,2,7]oxa- (**D**) and -azadiborepins (**E**) from a common precursor,^[13] both of them being relatives of BTI (**A**). Only few further compounds featuring 1,2,7-oxadiborepin as a substructure have been reported,^[14] and the 1,2,7-azadiborepin ring system had been previously unknown. The latter is formally derived from the 6 π -electron-heteroaromatic borepin^[16] by replacing a C=C unit adjacent to the boron center with a B=N unit. According to our DFT calculations, both 1,2,7-azadiborepin and -oxadiborepin are weakly aromatic. This is a good prerequisite for extended π -conjugation over the bithiophene moiety of tricyclic **D** and **E**. Our synthetic route to build up the dithienodiborepin system, however, required blocking of the α -positions of the thiophene moieties to prevent undesired side reactions, which would otherwise occur at some point. We did this by attaching methyl groups in these positions (i. e., R = Me).^[13]

While thiophene components have been dominating the spectrum of organic electronic materials for a long time,^[17] the involvement of furan-containing components is currently of sharply growing interest.^[18] Furan rings can be derived from lignocellulosic biomass, and they are biodegradable, hence, they provide a sustainable alternative. In addition, furan-based materials often have several favorable (opto)electronic features such as effective inter-ring conjugation due to lower aromaticity, increased luminescence properties, as well as better solubility. Their broader application though has been to some extent hampered by their reduced stability towards oxidative degradation. However, it has recently been recognized that this issue can be effectively overcome by the combination of the furan rings with electron-withdrawing molecule parts.^[18] In that regard, Gidron as well as Guo and their colleagues have independently developed 2,2'-bifuran-3,3'-dicarboximide (BFI, **B**, Figure 1) as a new, robust electron-deficient building block.^[19] Our group has demonstrated that the combination of furan rings with trivalent boron can lead to highly stable materials with strong luminescence properties.^[20]

Herein, we present the synthesis and characterization of the first difuro[3,2-c:2',3'-e][1,2,7]oxa- (**F**) and -azadiborepins (**G**), which are relatives of BFI (**B**). As with their thiophene congeners, **D** and **E**, we had to block the α -positions of the furan rings to prevent side reactions. In this case, however, we used bulky silyl groups as protecting groups, which we succeeded in deprotecting afterwards and installing bromide as

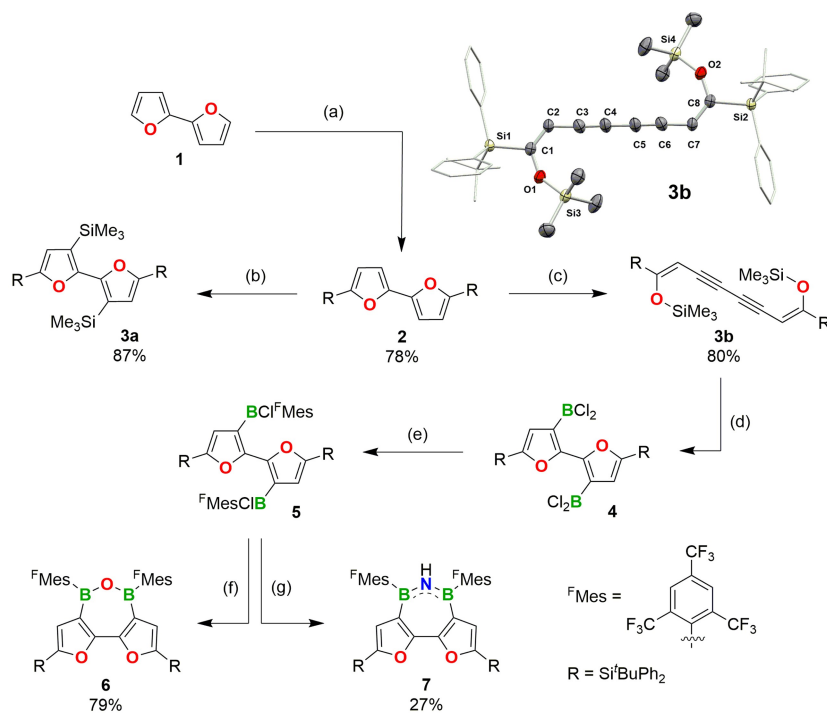
a leaving group in one step. We furthermore demonstrate that the system is easily transformed into effectively π -extended molecular arrays.

Results and Discussion

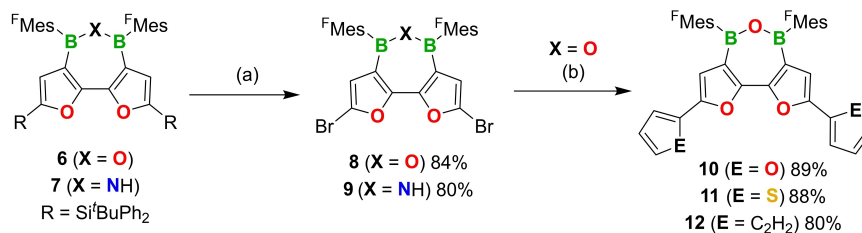
In the first step of the synthesis the sterically demanding *tert*-butyldiphenylsilyl (TB DPS) protecting groups were introduced at positions 5 and 5' of 2,2'-bifuran (**1**) to give **2** (Scheme 1). Following our procedure for the synthesis of the diborepins **D** and **E**,^[13] our initial plan was then to introduce TMS groups at positions 3 and 3' of **2**, and to transform them subsequently into boryl groups by Si/B exchange. Surprisingly, upon lithiation and silylation, besides the expected tetrasilylated building block **3a**, compound **3b**, which is an acyclic isomer of **3a**, was formed in addition. By adjusting the reaction conditions we were able to shift the product ratio to either side. While treatment of **2** with *n*BuLi (~2.2 equiv.) at 0 °C in THF and addition of Me₃SiCl after 1 h afforded **3a** in 87% isolated yield, complete opening of the furan rings^[21] occurred if the reaction mixture was stirred at ambient temperature for 16 h before Me₃SiCl was added (isolated yield of **3b**: 80%). Both **3a** and **3b** can be handled in air, and they show no sign of interconversion, even at 90 °C.

Compound **3a** can be selectively diborylated in positions 3 and 3' with BBr₃ in a Si/B exchange reaction involving the SiMe₃ groups. To our delight, its acyclic isomer **3b** is selectively diborylated as well, even with the milder BCl₃ and within only 40 min at low temperature. This reaction affords compound **4**, wherein the original bifuran structure is reconstituted. As this route proved advantageous, we decided to follow it in the further procedure. After solvent exchange to toluene and without further purification, the dichloroboryl species **4** was converted with ^tMesLi (^tMes = 2,4,6-tris(trifluoromethyl)phenyl) to compound **5**. The latter was then subjected to hydrolysis, resulting in cyclization to difurooxadiborepin **6**. To prepare the difuroazadiborepin **7**, compound **5** was refluxed with HN-(SiMe₃)₂ in a toluene/chloroform mixture. The difurodiborepins **6** and **7** were obtained in good (79%) or moderate yields (27% from **3b**) after column-chromatographic work-up.

Next, we accomplished to remove the Si^tBuPh₂ protecting groups from **6** and **7** by reaction with an excess of iodine bromide, thus affording the dibrominated diborepins **8** and **9** (Scheme 2). The respective diiodinated species, which likely occur as intermediates in this transformation, were not accessible through this procedure due to the required excess of IBr.^[22] Compounds **6–9** were characterized unambiguously by multinuclear NMR spectroscopy, high-resolution mass spectrometry (HRMS), and single-crystal X-ray diffraction (Figure 2). Compounds **6** and **7** feature largely planar tricyclic skeletons in the solid state. The boron centers are trigonal planar coordinated (360°), and the seven-membered rings have an interior angle sum close to the ideal value of 900° (**6**: 899.68°, **7**: 899.97°). The angles between the furan units (**6**: 0.99°, **7**: 1.12°) and the angles between the plane of the respective B–X–B unit and the best plane through the bifuran moiety are small (**6**: 0.77°, **7**: 1.05°). The B–O–B binding angle of 136.7(2)° for **6** is



Scheme 1. Synthesis of difuro[3,2-c:2',3'-e][1,2,7]oxa- and -azadiborepins **6** and **7**, plus molecular structure of **3b** in the solid state according to single-crystal X-ray diffraction (H-atoms omitted for clarity; ellipsoids drawn at the 70% probability level). a) $n\text{BuLi}$, THF, -78°C to 25°C , 1.5 h, then $\text{Si}^t\text{BuPh}_2\text{Cl}$, 25°C , overnight; b) $n\text{BuLi}$, THF, 0°C , 1 h, then SiMe_3Cl , 25°C , overnight; c) $n\text{BuLi}$, THF, 25°C , 16 h, then SiMe_3Cl , 25°C , overnight; d) BCl_3 , CH_2Cl_2 , -78°C to 25°C , 40 min; e) $^f\text{MesLi}$, toluene, 25°C , overnight; f) H_2O ; g) $\text{HN}(\text{SiMe}_3)_2$, toluene/ CHCl_3 , 110°C , 3 d.



Scheme 2. Desilylation of **6** and **7** to building blocks **8** and **9**, and syntheses of compounds **10–12**. a) exc. IBr , CH_2Cl_2 , 25°C , overnight; b) Ar-SnMe_3 , $\text{Pd}(\text{PPh}_3)_4$, toluene, 100°C , 24–72 h.

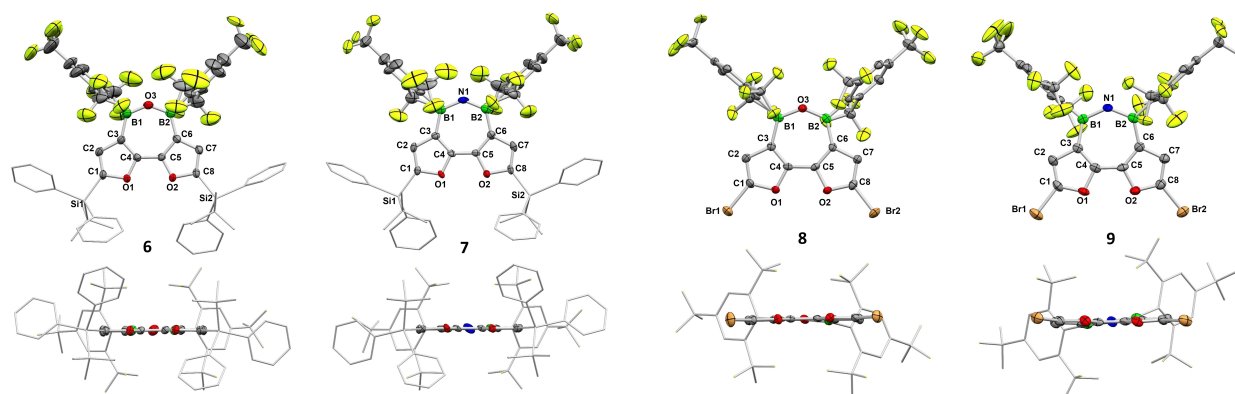


Figure 2. Molecular structures of **6–9** with views perpendicular and parallel to the polycyclic plane in the solid state by single-crystal X-ray diffraction (H-atoms and disorder of aryl groups omitted for clarity). All ellipsoids are drawn at the 70% probability level.

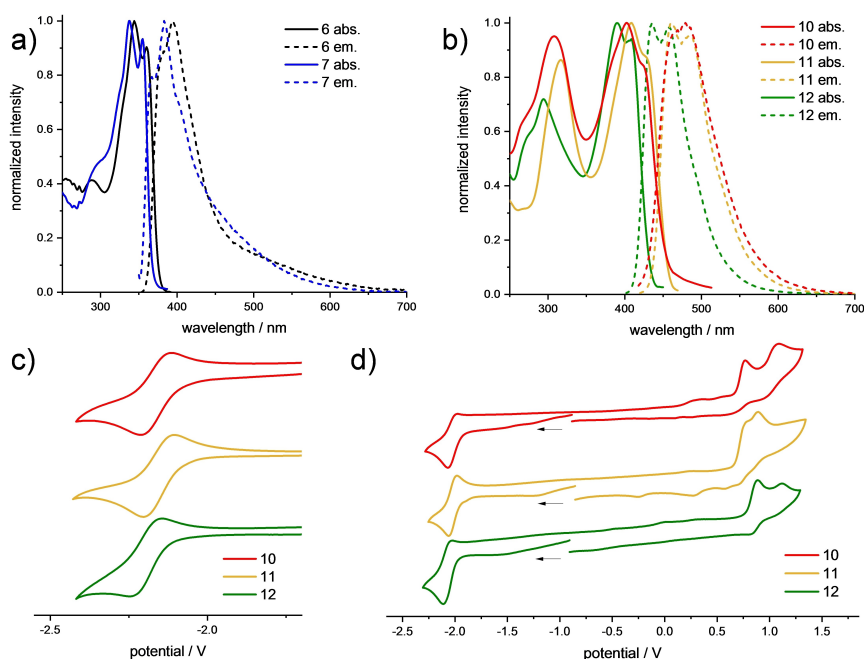


Figure 3. Absorption and emission spectra of a) **6** and **7** and b) **10–12** in CH_2Cl_2 . Cyclic voltammograms of **10–12** c) in THF (only the first reduction event) and d) in acetonitrile (vs. $[\text{Cp}_2\text{Fe}]^{0/+}$, scan rate: 250 mV s^{-1}).

slightly smaller than the B–N–B angle for the NH congener **7** ($134.9(4)^\circ$), as well as in the corresponding dithienodiborepins.^[13] Compounds **8** and **9** show slight deviation from planarity, as indicated by the larger angles between the BOB/BNB and the bifuran planes (**8**: 8.00° , 7.78° , **9**: 8.38°), as well as by the furan–furan angle (**8**: 2.59° , 4.27° , **9**: 6.93°).

Accessing the brominated compounds offers the opportunity for further derivatizations, such as incorporation into larger π -conjugated frameworks. We demonstrated this by the extension of the system with further furyl, thienyl, and phenyl groups, respectively. Compounds **10–12** were prepared in good yields (>80%) by Stille coupling of **8** with the respective aryl stannanes. They were fully characterized by NMR spectroscopy and HRMS.

The diborepin compounds **6–8** and **10–12** were investigated by UV-vis absorption and fluorescence emission spectroscopy as well as cyclic voltammetry (Figure 3 and Table 1). Similar to the dithienodiborepin systems **D** and **E**,^[13,23] com-

pounds **6–8** give rise to a structured low-energy absorption band with two maxima, in this case between about 340 and 360 nm. On the basis of TD-DFT calculations (Table S4 and Figures S78–S80 in the Supporting Information) and the analogy with **D**^[12,13] and **E**,^[13] we assign this band to a π - π^* transition within the tricyclic system. Compounds **6–8** also show fluorescence emission with small Stokes shifts (900 – 2100 cm^{-1}) and moderate quantum efficiencies ($\Phi_{\text{fl}} = 0.19$ – 0.36).

Efficient extension of the π -conjugated system over the additional arene rings in **10–12** is clearly seen in the spectra. Compared with their precursors **6** and **8**, they show a significant red shift in both the absorption and emission features, which is most pronounced for the thienyl and furyl substituted derivatives. The absorption spectra of **10–12** display two major bands at around 390–430 nm and at 290–320 nm, respectively. Our TD-DFT calculations reveal that they are both assigned as π - π^* transitions (see Figure 4 for the orbitals of **10**; see also Figures S82–S84). The former corresponds to a HOMO–LUMO excitation. These frontier orbitals are fully delocalized over the difurodiborepin system and the aryl rings laterally attached.

No.	λ_{abs} [nm] ^[b]	λ_{em} [nm] ^[b,c]	FWHM_{em} [cm^{-1}]	Φ_{fl} ^[d]
6	344 , 360	381, ^[e] 394	3699	0.19
7	338 , 355	367, 383	3950	0.29
8	347 , 361 ^[e]	391, ^[e] 405	3484	0.36
10	308, 402 , 425 ^[e]	462, ^[e] 482	3464	0.54
11	316, 409 , 429 ^[e]	461 , 485	3029	0.42
12	295, 391 , 410	436 , 457	3107	0.45

[a] In CH_2Cl_2 . [b] Highest absorption and emission maxima in bold. [c] Excited at the wavelength of the respective absorption maximum. [d] Fluorescence quantum yield determined absolutely with an integrating sphere. [e] Shoulder.

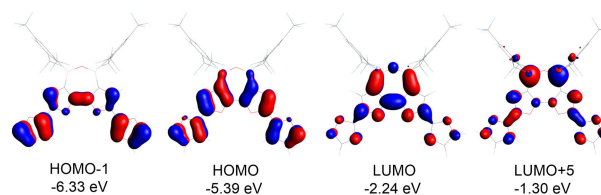


Figure 4. B3LYP-D3(BJ)/def2-SV(P)-calculated molecular orbitals involved in the strongest transitions of **10** (isovalue 0.035).

There is a nodal plane going through the oxygen atom in the HOMO, but the BOB moiety has a strong contribution to the LUMO, which demonstrates the influence of this group on the properties of the system. The higher-energy absorption band results from an excitation from the HOMO-1 to the LUMO+5. These two orbitals are delocalized over the tetraarene system as well. Here, the BOB moiety does not contribute to the HOMO-1, but in the LUMO+5 the strongest contribution comes from the boron centers, pointing to some intramolecular charge transfer character for this transition. The fluorescence spectra of **10–12** each show a narrow emission band (FWHM = 3030–3460 cm⁻¹) with fine structure and with increased quantum yields ($\Phi_f = 0.42–0.54$) compared to that of their silylated and brominated precursors **6** and **8**.

Cyclic voltammetry (CV) of the silyl- and bromo-substituted diborepin compounds **6–8** in THF revealed a series of irreversible reduction events. The reduction onset potential of oxadiborepin **6** (−2.28 V) appears 0.10 V anodic from that of azadiborepin **7** (−2.38 V). Reduction of the brominated derivative **8** occurs even earlier (onset at ca. −2.07 V). The π -extended compounds, **10–12**, on the other hand, show each a partially reversible first reduction wave in THF at around $E_{1/2} = -2.16$ V (Figure 3c). In acetonitrile, we additionally observed (irreversible) oxidation processes (Figure 3d). This allowed us to estimate the electrochemical HOMO–LUMO gaps of **10–12**. They follow the order: **12** (2.76 eV) > **11** (2.60 eV) \approx **10** (2.58 eV), in good agreement with the optical band gaps determined by UV-vis spectroscopy (**12**: 2.86 eV, **11**: 2.68 eV, **10**: 2.70 eV). This suggests that the conjugation of the difurooxadiborepin building block is most pronounced with the hetarenes thiophene and furan.

To gain insight into the aromatic character of the difurooxa- and -azadiborepin systems, we performed NICS-scans^[24a] through the center of their boron heterocycles (see Figure 5, top, for the oxadiborepin; and Figure S90 for the azadiborepin system) and their furan rings (Figures S86 and S91) as well as NICS-X-scans^[24b] (Figures S87, S88, and S93–S95). For computational convenience we used the derivatives **13** and **14**, which are unsubstituted at the furan moieties. The NICS-scans through the furan rings show the typical features for aromatic systems. Also for the oxa- and azadiborepin rings the calculated isotropic shifts are overall negative and are mainly controlled by the out-of-plane component of the chemical shift, suggesting an aromatic character of these heterocycles. ACID calculations^[24c,d] for **13** (Figure 5, bottom) and **14** (Figure S96) corroborate this interpretation. They show an overall diatropic ring current, which is slightly more pronounced in the bifuran moiety, consistent with the results from the NICS calculations. Overall, the oxa- and azadiborepin rings with bifuran fusion show weak aromaticity, similar to their bithiophene congeners,^[13] which is a good prerequisite for extended π -conjugation over these heterocycles.

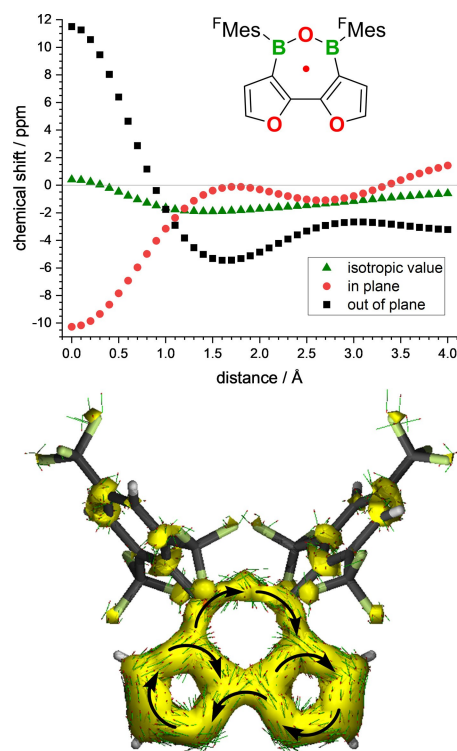


Figure 5. NICS scan of the oxadiborepin ring (top) and ACID plot (isovalue 0.02) of **13** (bottom). Calculated with B3LYP/6-31 + G*.

Conclusion

In conclusion, we have presented a modular synthesis of bifuran-fused oxa- and azadiborepins through an unexpected reversible ring-opening process. The novel tricyclic compounds exhibit strong fluorescence, highly planar tricyclic structures, and overall aromaticity, with a weakly aromatic diboron heterocycle. We have demonstrated deprotection and introduction of Br leaving groups in the α -positions in a single step, and subsequent extension of the π -conjugated system over different further arenes. In future work, we will investigate the incorporation of the new building blocks into larger π -conjugated scaffolds, including polymers, and explore the use of the resulting materials for organic optoelectronic applications.

Deposition Numbers 2179172 (for **3b**), 2179173 (for **7**), 2179174 (for **6**), 2179175 (for **9**), and 2179176 (for **8**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: aromaticity · boron · BN compounds · furan · polycycles

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