

1-Heteroaromatic-Substituted Tetraphenylboroles: $\pi - \pi$ Interactions Between Aromatic and Antiaromatic Rings Through a B–C Bond

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Supporting Information



ABSTRACT: A series of 2,3,4,5-tetraphenylboroles substituted with different aromatic heterocycles (thiophene, furan, pyrrole, and dithiophene) in the 1-position were synthesized and characterized by means of NMR, elemental analysis, and X-ray crystallography. In contrast to known 2,3,4,5-tetraphenylboroles, X-ray diffraction revealed a nearly coplanar arrangement of the aromatic heterocycles and the antiaromatic borole scaffold as a result of π -conjugation, which could be substantiated by DFT calculations. Furthermore, the 2,2'-dithiophene-bridged bisborole (14) exhibits a large bathochromic shift in the absorption spectrum, demonstrating the exceptional Lewis acidity of the nonannulated borolyl moiety.

INTRODUCTION

Conjugated organic systems have been established as an important class of materials because of their interesting applications in a range of technological areas.¹ In particular, dimesitylboryl-substituted heterocyclic compounds reported by Marder, Lequan, and Shirota demonstrated the versatile properties of boron-modified π -conjugated systems, such as strong photoluminescence, electroluminescence, and nonlinear optical qualities.² With its empty p_z orbital, the threecoordinated boron atom is able to interact with organic π systems leading to planar conjugated frameworks.^{3,4} For instance, Jäkle and co-workers reported on diborylated 2,2'dithiophenes with different aryl substituents on boron featuring a planarized geometry between the p_z orbital of boron and the organic spacer, enabling these compounds to display interesting electron transfer phenomena.⁵ Investigations by Weber and coworkers on the synthesis and characterization of 1,3,2diazaborolyl-functionalized thiophenes and dithiophenes revealed desirable electrochemical and optical properties for functional materials.⁶

Boroles are unsaturated, extremely electron-deficient, pentacyclic molecules with four π -electrons. Due to their photophysical characteristics and isoelectronic relationship to the cyclopentadienyl cation, boroles are of fundamental interest. Up to date, several differently substituted, nonannulated borole derivatives have been isolated and characterized by X-ray crystallography.⁷ The substitution pattern of the C₄R₄ backbone is mainly limited to phenyl (**1a**–**i**),⁸ but examples with perfluorophenyl (**2**)⁹ or thienyl groups (**3**) are known.¹⁰ In contrast, the substituent at the boron atom has been varied over a much wider range, including phenyl derivatives (1a-d, 1g), halogens (1f), ferrocenyl (1h), cymantrenyl (1i), or platinum groups (1j) (Chart 1).

The metallocene-substituted boroles (1h, 1i) display a boron-metal through-space interaction, which induces the π -

Chart 1. Several Nonannulated Boroles^a



^aMes = 2,4,6-trimethylphenyl; Fc = ferrocenyl; Cym = cymantrenyl; Cy = cyclohexyl.

Received: October 8, 2012 Published: November 21, 2012 systems of the cyclopentadienyl and borole ring to lie in the same plane. In contrast, the metal-free boroles share as a common feature a propeller-like arrangement of the aryl substituents around the BC₄ scaffold. The phenyl substituent on boron in pentaphenylborole (**1a**) features a torsion angle of $-32.9(2)^{\circ}$, thus not allowing an effective π -stabilization of the boron atom. Some degree of π -conjugation was suggested in tetrathienylborole (**3**), in which the thienyl groups in 2 and 5 position showed smaller dihedral angles (10.7° and 38.2°). However, direct conjugation between a nonannulated borolyl boron atom and an organic π -system has not been observed so far.

Given our interest in borole chemistry, we attempted to combine the highly Lewis acidic borolyl group (BC_4Ph_4) with heteroaromatic π -conjugated systems. Herein, we disclose the syntheses of the first 1-heteroaromatic-substituted 2,3,4,5-tetraphenylboroles (heterocycles: 7 = thiophene, 8 = 5-trimethylsilylthiophene, 9 = 5-methylfuran, 11 = N-methylpyrrole, 14 = 2,2'-dithiophene) and provide a rationale for the interactions between the two different types of five-membered rings.

RESULTS AND DISCUSSION

Two different routes to prepare 1-heteroaromatic-substituted boroles can be envisaged. The possible salt-elimination reaction of 1-chloroborole (1f) with the respective lithiated heterocycles was not followed, as the preparation and handling of 1f is rather cumbersome. Instead, we used the established tin-boron exchange reaction to synthesize the target compounds. The boron dihalide precursors 4, 5, and 6 have been prepared via a silicon-boron exchange reaction by treating the corresponding trimethylsilyl-substituted compounds with neat BCl₃.¹¹ Hence, compounds 7, 8, and 9 were successfully obtained by reaction with 1,1-dimethyl-2,3,4,5-tetraphenylstannole and the respective boron dihalides (Scheme 1).

Scheme 1. Synthesis of Various 1-Heteroaromatic-Substituted 2,3,4,5-Tetraphenylboroles (4, 7 (E = S; R = H); 5, 8 (E = S; R = SiMe₃); 6, 9 (E = O; R = Me))



After workup and recrystallization from toluene, 7, 8, and 9 were isolated as air- and moisture-sensitive deep purple solids in moderate to good yields (7: 70%, 8: 77%, and 9: 39%). The identity of 7, 8, and 9 was confirmed by means of NMR spectroscopy and elemental analysis. The ¹¹B NMR resonances of 7 (58.2 ppm), 8 (58.1 ppm), and 9 (52.3 ppm) are, compared to the known pentaphenylborole (1a) (65.4 ppm), shifted to lower frequency, due to the higher π -donor strength of the heterocycles.¹²

Crystallization of 7 and 8 from CH_2Cl_2 /hexane solutions yielded dark purple crystals that were suitable for X-ray analysis. In compound 7 (monoclinic, $P2_1/c$), two independet molecules were found in the unit cell, and the thiophene rings were disordered over two positions (occupancies: 85:15; 79:21). The unit cell of 8 (monoclinic, $P2_1/c$) contains two molecules and

reveals no disorder in the thiophene unit due to the SiMe₃ substituent. In comparison to 1-aryl-2,3,4,5-tetraphenylboroles (1a-d), the most striking feature of the thiophene-functionalized boroles 7 and 8 is the nearly coplanar alignment of the two five-membered rings. Although 7 shows some disorder, the interplanar torsion angles are found in a range between $6.4(2)^{\circ}$ and $13.0(2)^{\circ}$. In 8 we found a similar coplanar arrangement of the borolyl moiety and the 5-trimethylsilylthiophene ring with even smaller interplanar torsion angles $(5.7(2)^{\circ}, 10.1(2)^{\circ})$. This indicates that some degree of π -conjugation and electronic interaction is operative in these systems. With the exception of tetrathienyl-substituted borole (3), which features a π interaction between two thienyl moieties and the borole scaffold,¹⁰ all known nonannulated boroles display a propellerlike arrangement throughout all substituents.7 The B1-C5 bond length of 8 (av. 1.527 Å) lies in the same range compared to other 1-aryl-2,3,4,5-tetraphenylboroles (1c = 1.537(7) Å, 1d = 1.513(8) Å) but is shorter than the B1-C5 bond in 1g (1.560(2) Å) or 3 (1.552(6) Å) with a sterically demanding mesityl group.^{8d,m,10} Compound 9 was crystallized from a saturated benzene solution as dark purple needles. Similar to the solid state structures of 7 and 8, the borolyl substituent and the aromatic furan ring in 9 are coplanar in the solid state, suggesting π -bonding interactions. The interplanar torsion angle of $17.4(2)^{\circ}$ is slightly larger compared to the thiophene derivatives 7 and 8. The B1–C5 bond length of 9 (1.515(4) Å) is comparable to those of 8 (Table 1).





To extend this series of 2-borolyl heterocycles, we attempted the synthesis of 1-pyrrolyl-2,3,4,5-tetraphenylborole. However, the required dichloro-*N*-methylpyrrol-2-ylborane could not be isolated according to the literature procedure.¹¹ Instead, we found the selective formation of dichloro-*N*-methylpyrrol-3ylborane (**10**) in good yields. Comparable migrations are known for 2-(arylsulfinyl)pyrroles and 2-(acyl)pyrroles, which are reported to be acid-induced transpositions.¹³ Unlike the thiophene- and furan-substituted boroles, no reaction was observed by treatment of dihaloborane (**10**) with 1 equiv of 1,1-dimethyl-2,3,4,5-tetraphenylstannole even at elevated temperatures (50 °C). Accordingly, the synthesis could only be accomplished via a salt-elimination reaction of **10** with 1,4dilithio-2,3,4,5-tetraphenylbuta-1,3-diene (Scheme 2). As ex-

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	7^b	8^b	9	11
$^{11}B [ppm]^a$	58.2	58.1	52.3	57.5
B1-C1	1.576(3)/1.574(3)	1.577(3)/1.589(3)	1.587(4)	1.579(4)
B1-C4	1.576(3)/1.577(3)	1.587(3)/1.589(3)	1.574(4)	1.580(4)
B1-C5	C	1.528(3)/1.525(3)	1.515(4)	1.509(6)
C1=C2	1.352(3)/1.352(3)	1.353(3)/1.353(3)	1.358(4)	1.357(4)
C2-C3	1.535(3)/1.529(3)	1.532(3)/1.528(3)	1.521(4)	1.516(5)
C3=C4	1.361(3)/1.360(3)	1.347(3)/1.352(3)	1.352(4)	1.357(4)
borole/heterocycle [°]	C	10.1(2)/5.7(2)	17.4(2)	6.7(4)
^a Referenced against external [Et ₂ O	·BF ₃]. ^b Two independent molec	cules in the unit cell. ^c Not discus	ssed, due to disorder.	

Table 1. ¹¹B NMR Chemical Shifts δ [ppm], Bond Lengths [Å], and Interplanar Torsion Angles [°] of 7, 8, 9, and 11



Figure 1. Molecular structures and side views of (a) 7, (b) 8, (c) 9, and (d) 11. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are set at 50% probability.

pected, the ¹¹B NMR resonance of 11, detected at 57.2 ppm, is comparable to those observed for the thiophene derivatives 7 and 8.

Single crystals of **11** could be obtained from a saturated toluene solution as dark red crystals. Despite the fact that the borolyl group resides in the 3-position, the solid structure features a similar coplanar arrangement with torsion angles of $6.77(4)^{\circ}$. The B1–C5 distance of **11** (1.509(6) Å) is slightly shortened compared to **8** and **9**, which arises from the better π -donor ability of the nitrogen atom.¹² It is noteworthy that **7**, **8**,

9, and **11** exhibit an intermolecular interaction between the boron atom of the borole and a phenyl group of a neighboring molecule as previously reported for related 1-aryl-2,3,4,5-tetraphenylboroles.^{8b,d} Moreover, the enhanced π -conjugation in 7, 8, 9, and **11** (Figure 1) does not affect the degree of bond alternation in the borolyl moiety (Table 1).

To finally isolate *N*-methylpyrrole with a borolyl group in the 2-position, we used 1-chloro-2,3,4,5-tetraphenylborole (1f) as a borole source since it is known that lithiation of *N*-methylpyrrole with one equivalent butyllithium in the presence



Figure 2. Migration of the borolyl moiety as followed by 1 H NMR spectroscopy for one characteristic doublet of doublets (a: reaction start; b: after 3 h; c: after 12 h; d: after 24 h).

Scheme 3. Synthesis of 12 by Direct Functionalization of the Chloroborole and Inhibition of the Migration Process by DMAP



Figure 3. Molecular structure of 12' in the solid state with hydrogen atoms and solvent molecules omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond distances [Å] and angles [°]: B1–C1 1.647(2), B1–C4 1.635(2), C1–C2 1.349(2), C2–C3 1.502(2), C3–C4 1.360(2), B1–N2 1.610(2), B1–C5 1.610(2), C5–C6 1.387(2), C6–C7 1.409(2), C7–C8 1.364(2), C8–N1 1.370(2), N1–C5 1.385(2), N1–C9 1.449(2); C1–B1–C4 99.3(1), C1–B1–C5 116.2(1), C1–B1–N2 108.3(1).

of tetramethylethylenediamine (TMEDA) occurs selectively in the 2-position.¹⁴ Immediately after addition of the lithiated *N*methylpyrrole to **1f** in benzene, two doublets of doublets at $6.04 ({}^{3}J = 4.00 \text{ Hz}, {}^{3}J = 2.24 \text{ Hz})$ and $6.78 \text{ ppm} ({}^{3}J = 4.00 \text{ Hz}, {}^{4}J$ = 1.44 Hz) and one multiplet at 6.43 ppm were found in the ¹H NMR spectrum, for the three protons of the pyrrole ring. A comparison with literature data revealed that only pyrroles substituted in the 2-position show coupling constants between 3.8 and 4.0 Hz, suggesting the formation of **12**.¹⁵ Surprisingly, we could observe a similar rearrangement reaction as found for the dihaloborane **10**. The migration of the borolyl moiety from the 2- to 3-position is slower compared to the migration of **10** and was followed by means of ¹H NMR spectroscopy. The ratio between **12** and **11** was determined to be 1:10 after one day in benzene at room temperature (Figure 2).

To prove the initial formation of **12**, we added the electronrich base 4-dimethylaminopyridine (DMAP) to block the empty p_z -orbital of the boron atom and consequently inhibit the migration process (Scheme 3). After addition, the color of the reaction mixture turned from deep red to pale yellow, and the ¹¹B NMR resonance shifted to lower frequency (0.1 ppm).

Single crystals of 12' were obtained from a saturated toluene solution. The solid state structure clearly confirms the initial formation of 12 since the boron atom (B1) is bonded to the carbon atom in the 2-position (C5) of the *N*-methylpyrrole (Figure 3). The borolyl moiety is planar, and the bond lengths within the C_4Ph_4 backbone correspond to those of an isolated diene system, such as *cis,cis*-1,2,3,4-tetraphenylbuta-1,3-diene.¹⁶ The environment of the boron center shows a distorted

Scheme 4. Synthesis of 14 via Tin-Boron Exchange and Formation of the DMAP Adduct 15



dx.doi.org/10.1021/ja309935t | J. Am. Chem. Soc. 2012, 134, 20169-20177

Journal of the American Chemical Society

tetrahedral geometry with a shorter B1–N2 distance (1.610(2) Å) as compared to the known Lewis acid–base adducts of boroles due to the electron-rich nature of DMAP.^{8l,n}

To extend the concept of borolyl-substituted π -conjugated systems, we performed the synthesis of bisborole 14 with dithiophene as a spacer between two borolyl moieties. 5,5'-Bis(dichloroboryl)-2,2'-dithiophene (13) was prepared by reaction of 5,5'-bis(trimethylsilyl)-2,2'-dithiophene with an excess of BCl₃ via the silicon-boron exchange route. In a similar manner as for the boroles 7, 8, and 9, compound 14 was obtained via a tin-boron exchange reaction and isolated in 75% yield as an orange-brown solid. The ¹¹B NMR resonance was observed as a broad signal (56.5 ppm) in a region of slightly higher frequency in comparison to 1-(thiophen-2-yl)-2,3,4,5tetraphenylborole (7). Structural characterization was achieved as its DMAP adduct (Scheme 4). To this end, 2 equiv of DMAP was added to a solution of 14 in CH₂Cl₂. The color of the solution turned from orange to yellow, and the ¹¹B NMR resonance was found at 0.3 ppm, characteristic of fourcoordinate boron. Single crystals of 15 were obtained from a saturated CH₂Cl₂/hexane solution. X-ray diffraction confirmed a distorted tetrahedral geometry at the boron center and the overall connectivity of the bisborole (Figure 4).



Figure 4. Molecular structure of **15** in the solid state with hydrogen atoms and solvent molecules omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond distances [Å]: B1–C1 1.625(3), B1–C4 1.615(4), C1–C2 1.358(3), C2–C3 1.504(3), C3–C4 1.354(3), B1–N2 1.588(3), B1–C5 1.631(4), C5–C6 1.370(4), C6–C7 1.424(4), C7–C8 1.363(4), C8–S1 1.732(3), C5–S1 1.742(2).

ELECTROCHEMICAL STUDIES

Cyclic voltammetry was used to investigate the reduction behavior of the different boroles 7, 8, 9, and 14. Similar to pentaphenylborole (1a), 7, 8, and 9 show a quasi-reversible one-electron reduction and a second irreversible one-electron reduction event in CH₂Cl₂ with [*n*Bu₄N]PF₆ as the supporting electrolyte. As shown in our previous work, the two reduction events can be assigned to the formation of a paramagnetic 5π electron radical anion and an aromatic 6π -electron dianion.⁸¹ As a representive example of the newly synthesized boroles, Figure 5 shows the cyclic voltammogramm of 7 with the quasireversible reduction event at $E^0_{1/2} = -1.63$ V, indicating the formation of a paramagnetic monoanion. The peak potential is in the same region as that found for 1-mesityl-2,3,4,5-tetrakis(2methylthienyl)borole (3) ($E^0_{1/2} = -1.57$ V) or 1-mesityl-



Figure 5. Cyclic voltammogram of 7 at room temperature in CH_2Cl_2 . Scan rate 200 mVs⁻¹, Pt/[*n*Bu₄N][PF₆]/Ag, quasi-reversible reduction wave upon one-electron reduction (dashed lines).

2,3,4,5-tetraphenylborole (1g) ($E_{1/2}^0 = -1.69$ V) and anodically shifted compared to 1-ferrocenyl-2,3,4,5-tetraphenylborole (1h) ($E_{1/2}^0 = -1.96$ V)^{8h,l,10} The second irreversible reduction process is centered at -2.32 V and corresponds to the formation of the dianion.

Bisborole 14 is able to accept up to four electrons. Therefore, one would expect four reduction events for a fully conjugated system. The cyclic voltammogram of 14, however, shows only two broad irreversible reduction waves in THF ($E_{\rm pa} = -2.35$ V, $E_{\rm pa} = -2.97$ V) which could not be further resolved using square wave voltammetry. Due to the highly Lewis acidic boron atoms, THF readily forms a Lewis acid—base adduct with 14, resulting in a significant cathodic shift of the redox potentials compared to the measurements in noncoordinating solvents (for details, see Supporting Information).

UV-VIS SPECTROSCOPY

The π -electron donation from the heterocycles to the boron atom is also evident in the electronic absorption spectra (Figure 6). The absorption maxima of the strongly colored boroles 7



Figure 6. UV-visible spectra of compounds 7 (black), 8 (red), 9 (blue), and 11 (green) in CH_2Cl_2 at concentrations of 1 mmol L^{-1} .

 $(\lambda_{\text{max}} = 527 \text{ nm}; \varepsilon = 384 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1})$, 8 $(\lambda_{\text{max}} = 522 \text{ nm}; \varepsilon = 292 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1})$, and 9 $(\lambda_{\text{max}} = 530 \text{ nm}; \varepsilon = 462 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1})$ are blue-shifted compared to 1a $(\lambda_{\text{max}} = 567 \text{ nm}; \varepsilon = 361 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1})$. The lowest energy transition band is in the same region as the cationic 1-metalloborole (1j) $(\lambda_{\text{max}} = 524 \text{ nm}; \varepsilon = 813 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1})$, previously prepared in our group.⁸ⁱ The considerable hypsochromic shift for 11 $(\lambda_{\text{max}} = 470 \text{ nm}; \varepsilon = 507 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1})$ supports again the higher π -donor strength of the pyrrolyl substituent.¹² Calculated excitation energies for 7, 8, 9, and 11 correlate well with the experimental findings and display the same hypsochromic shift for 11 (for details, see Supporting Information).

The bisborolyl-substituted bithiophene 14 exhibits an absorption band at 456 nm ($\varepsilon = 53862 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) with a red-shifted shoulder (Figure 7). Interestingly, these data



Figure 7. UV–visible spectra of 14 in CH_2Cl_2 at concentrations of 0.1 mmol·L⁻¹.

correlate well with the diborylated bithiophenes 16, 17, and 18 reported by Jäkle et al., who observed that the absorption bands of 16 ($\lambda_{max} = 387 \text{ nm}$; $\varepsilon = 23\,890 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), 17 ($\lambda_{max} = 396 \text{ nm}$; $\varepsilon = 48\,290 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), and 18 ($\lambda_{max} = 413 \text{ nm}$; $\varepsilon = 31\,400 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) experience a bathochromic shift with increased Lewis acidity of the boryl substituents (Chart 2).^{Sb}





14 is distinctly red-shifted compared to 18, which suggests a more pronounced Lewis acidity of the borolyl moiety in comparison to the $B(C_6F_5)_2$ group. Jäkle et al. performed DFT calculations and showed that the excitations for 17 and 18 arise from the HOMO \rightarrow LUMO transitions. DFT calculations for 14 display that the HOMO is centered at the borole, and therefore the HOMO \rightarrow LUMO energy separation gives rise to a very weak absorption at 509 nm. The much more pronounced calculated absorption at 507 nm is a consequence of the HOMO-2 \rightarrow LUMO transition in 14. This correlates well with the findings of Jäkle since the molecular orbital of the HOMO-2 in 14 resembles the HOMO of 17 and 18 (for details, see Supporting Information).

THEORY

DFT calculations were performed to gain further insight into a possible π -conjugation between the borolyl moiety and the heterocycles.¹⁷ The calculated orbital plots for compounds 7, 8, 9, and 11 display a certain amount of π -conjugation in the HOMO-2 along the B–C5 bond (Figure 8). For the larger system 14, we found π -conjugation in the HOMO-4 (for details, see Supporting Information).



Figure 8. Molecular orbitals (isovalue = 0.03 au) related to π -conjugation found in the studied borole compounds calculated at the PBE0/6-31+G(d,p) level.

To gain a better understanding of the π -conjugation, we carried out energy decomposition analysis (EDA) for model systems of 7', 8', 9', and 11' compared to a model of 1a'. For the model compounds we ignored the phenyl substituents at the borolyl moiety, and only the conjugated core has been taken into account. The relative energy values for the π -conjugation percentage ΔE_{π} in the model systems 7' (20.7%), 8' (20.4%), 9' (22.7%), and 11' (20.5%) are significantly larger compared to 1a' (18.2%) (see Supporting Information). In other words, the energy difference regarding the π -conjugation

between these compounds relative to 9', which shows the highest degree of π -interaction, is 4.8 (7'), 5.1 (8'), 2.9 (11'), and 10.8 (1a') kcal/mol, respectively. These results confirm the experimental findings and show that π -conjugation in 1-heteroaromatic-substituted boroles is much more pronounced compared to aryl-substituted tetraphenylboroles.

In addition, nucleus-independent chemical shift (NICS) calculations were conducted at the PBE0/6-31+g(d,p) level to evaluate the antiaromatic character of the borole ring and the aromatic nature of the heterocycles. The obtained NICS(0) values are listed in Table 2 and compared to literature data for the unsubstituted aromatic compounds.

Table 2. NICS(U) values at the PBEU/0-31+g(d,p) Leve	Table 2. NICS(0) Values	at the	PBE0/6-31+g(c	,p) Level
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"The phenyl groups around the borole moiety in the chemical drawings are omitted for clarity.

Interestingly, the comparison with literature NICS(0) values clearly displays a π -interaction of the heterocycles with the boron atom, which leads to a mutual compensation of aromaticity and antiaromaticity. While the aromaticity of the heterocycles is significantly reduced compared to literature data, the value for the benzene ring in pentaphenylborole (1a) remains unperturbed (C_6H_6 : -7.2 ppm).^{18,19} A similar behavior can be expected for boryl-substituted derivatives. In the case of borolyl substituents, however, the π -interaction of the aromatic heterocycle with the vacant p_z orbital on boron leads to a decrease in antiaromaticity of the borole ring. We believe that this effect is more pronounced in boroles 7, 8, 9, and 11 than in pentaphenylborole (1a) (+12.9 ppm) as a result of the higher π -donating abilities of the heteroaromatic groups.^{10,18}

The π -electrons of the dithiophene spacer in bisborole 14 are shared between the two borolyl moieties, which leads to an increased antiaromatic character (NICS(0): 12.1 ppm), in a region typical for pentaphenylborole 1a.

In summary, the synthesis and structural characterization of the first 1-heteroaromatic-substituted-2,3,4,5-tetraphenylboroles and a dithiophene-spaced bis-2,3,4,5-tetraphenylborole was carried out. An interesting migration process could be elucidated for the N-methylpyrrole derivative. Absorption data for bisborole 14 correlate well with known dithiophenebridged bisboryl compounds and underlines the high Lewis acidity of the 2,3,4,5-tetraphenylborolyl group. All investigations (i.e., X-ray, UV-vis, and cyclic voltammetry) support that a certain degree of π -conjugation is operative between the aromatic heterocycles and the antiaromatic borole. These findings were corroborated by DFT calculations and demonstrate that the coplanarity in these systems can be explained by an electronic interaction of the heterocycles with the empty p_z orbital of the boron atom. Studies to extend the concept of borolyl-based π -conjugated systems are currently underway.

EXPERIMENTAL DETAILS

General Information. All manipulations were performed under an inert atmosphere of dry argon using standard Schlenk techniques or in a glovebox (MBraun). Hexane, THF, and CH₂Cl₂ were dried by distillation over Na/K alloy (hexane, THF) or phosphorus pentoxide (CH₂Cl₂) under argon and stored over activated molecular sieves (4 Å). CD₂Cl₂ was degassed by several freeze-pump-thaw cycles and stored over molecular sieves. (E,E)-(1,2,3,4-Tetramethyl-1,3-butadien-1,4-ylidene)-dilithium, 1,1-dimethyl-2,3,4,5-tetraphenyl-stannole,^{8a} 2,5bistrimethylsilyl-thiophene,¹⁴ dichlorothiophene-2-ylborane, and dichloro-5-methylfurane-2-ylborane¹¹ were prepared according to known methods. The NMR spectra were recorded on a Bruker AV 500 (¹H: 500.1 MHz, ¹³C: 125.8 MHz, ¹¹B: 160.5 MHz, ²⁹Si: 99.4 MHz) FT-NMR spectrometer. ¹H and ¹³C{¹H} NMR spectra were referenced to external TMS via the residual protons of the solvent (¹H) or the solvent itself (¹³C). ¹¹B{¹H} NMR spectra were referenced to [BF3·OEt2]. Microanalyses for C, H, and N were performed on a Leco CHNS-932 Elemental Analyzer. UV-vis spectra were measured on a JASCO V-660 UV-vis spectrometer.

Synthesis of 1-(Thien-2-yl)-2,3,4,5-tetraphenylborole (7). A solution of Me₂SnC₄Ph₄ (3.06 g, 6.06 mmol) in 30 mL of dichloromethane was treated dropwise with 0.60 mL of dichlorothiophene-2-ylborane (1.00 g, 6.07 mmol) at -40 °C. The reaction mixture was stirred for 3 h and subsequently allowed to warm to rt, resulting in a color change from yellow to red. All volatiles were removed in vacuo, and the side product Me₂SnCl₂ was removed quantitatively by sublimation at rt and 10^{-6} mbar within 5 h. The red residue was recrystallized from toluene/hexane to yield 7 (1.90 g, 4.22 mmol, 70%) as a purple red solid. ¹H NMR (500.1 MHz, CD₂Cl₂, 297 K): $\delta = 6.85$ (m, 4H, Ph), 7.00–7.10 (m, 6H, Ph), 7.11 (m, 1H, Hthienyl), 7.17-7.27 (m, 10H, Ph), 7.44 (m, 1H, H-thienyl), 7.90 (m, 1H, *H*-thienyl). ¹³C NMR (125.8 MHz, CD_2Cl_2 , 297 K): δ = 126.13, 127.37, 127.43, 128.01 (CH), 129.12 (C-thienyl), 129.72, 130.19 (CH), 141.37, 145.43 (C-thienyl), 136.91, 140.91, 162.25 (C_a). ¹¹B NMR (160.5 MHz, CD_2Cl_2 , 297 K): δ = 58.2 (br). Elemental analysis (%) calcd. for C32H23BS: C, 85.33; H, 5.15; S, 7.12. Found: C, 84.40; H, 5.48; S, 7.11.

Synthesis of Dichloro-5-trimethylsilylthien-2-ylborane (5). To a sample of neat BCl₃ (5.00 mL, 6.63 g, 56.6 mmol) was added 2,5-trimethylsilylthiophene (2.30 g, 10.1 mmol) at -50 °C. The mixture was allowed to warm to room temperature and stirred for 1 h. All volatiles were removed in vacuo, and the residue was distilled (1.4 mbar, 65 °C) to give **5** as a colorless liquid (2.08 g, 8.78 mmol, 87%). ¹H NMR (500.1 MHz, C₆D₆, 297 K): $\delta = 0.13$ (s, 9H, SiMe₃), 7.00 (d, ³J_{H-H} = 3.54 Hz, 1H, H-thienyl), 7.83 (d, ³J_{H-H} = 3.54 Hz, 1H, H-thienyl). ¹³C NMR (125.8 MHz, C₆D₆, 297 K): $\delta = -0.59$ (SiMe₃), 136.18, 143.91 (CH-thienyl), 158.64 (C₄). ²⁹Si NMR (99.4 MHz, CD₂Cl₂, 297 K): $\delta = -5.62$. ¹¹B NMR (160.5 MHz, C₆D₆, 297 K): $\delta = 47.8$.

Synthesis of 1-(5-Trimethylsilylthien-2-yl)-2,3,4,5-tetraphenylborole (8). A solution of $Me_2SnC_4Ph_4$ (554 mg, 1.10 mmol) in 15 mL of dichloromethane was treated dropwise with a solution of dichloro-5-trimethyl-silylthiophene-2-ylborane (260 mg, 1.10 mmol) in 5 mL of dichloromethane at -40 °C. The reaction mixture was stirred for 3 h and subsequently allowed to warm to rt, resulting in a color change from yellow to red. All volatiles were removed in vacuo, and the side product Me2SnCl2 was removed quantitatively by sublimation at rt and 10^{-6} mbar within 5 h. The red residue was recrystallized from a mixture of toluene/hexane to yield 8 as a purple solid (440 mg, 0.84 mmol, 77%). ¹H NMR (500.1 MHz, CD₂Cl₂, 297 K): $\delta = 0.24$ (s, 9H, SiMe₃), 6.83–6.86 (m, 4H, Ph), 6.99–7.08 (m, 6H, Ph), 7.14–7.16 (m, 4H, Ph), 7.18–7.26 (m, 7H, Ph & H-thienyl), 7.42 (d, ${}^{3}J_{H-H} = 3.55$ Hz, 1H, H-thienyl). ${}^{13}C$ NMR (125.8 MHz, CD_2Cl_2 , 297 K): $\delta = -0.32$ (SiMe₃), 126.04, 127.27, 127.38, 127.89, 129.72, 130.18 (s, CH), 135.49, 145.62 (CH-thienyl), 136.99, 140.85 (C_q) , 140.96 $(C_q$ -thienyl), 146.59 (C_q) , 159.23 $(C_q$ -thienyl), 162.03 (C_q) . ²⁹Si NMR (99.4 MHz, CD₂Cl₂, 297 K): $\delta = -5.61$. ¹¹B NMR (160.5 MHz, CD₂Cl₂, 297 K): δ = 58.6 (br). Elemental analysis (%) calcd for C35H31BSSi: C, 80.44; H, 5.98; S, 6.14. Found: C, 80.06; H, 5.94; S, 5.71.

Synthesis of 1-(5-Methylfuran-2-yl)-2,3,4,5-tetraphenylborole (9). A solution of $Me_2SnC_4Ph_4$ (1.00 g, 1.98 mmol) in 15 mL of dichloromethane was treated dropwise with a solution of dichloro-5methylfurane-2-ylborane (322 mg, 1.98 mmol) in 5 mL of dichloromethane at -60 °C. The reaction mixture was stirred for 16 h and subsequently allowed to warm to rt, resulting in a color change from yellow to red. All volatiles were removed in vacuo, and the side product Me₂SnCl₂ was removed quantitatively by sublimation at rt and 10⁻⁶ mbar within 5 h. The red residue was recrystallized from toluene at -30 °C to yield 9 as a purple solid (348 mg, 0.78 mmol, 39%). ¹H NMR (500.1 MHz, CD_2Cl_2 , 297 K): $\delta = 2.66$ (s, 3H, CH_3), 6.11 (dd, ${}^{3}J = 3.5 \text{ Hz}, {}^{4}J = 0.8 \text{ Hz}, 1\text{H}, H\text{-furanyl}, 6.80-6.82 (m, 4\text{H}, Ph), 6.91$ $(dd, {}^{3}J = 3.5 Hz, {}^{5}J = 0.6 Hz, 1H, H-furanyl), 7.06-7.08 (m, 6H, Ph),$ 7.15-7.13 (m, 6H, Ph), 7.18-7.21 (m, 4H, Ph). ¹³C NMR (125.8 MHz, CD_2Cl_2 , 297 K): $\delta = 14.4$ (CH₃), 110.2 (CH-furanyl), 125.7, 127.2, 127.4, 127.6, 129.9, 130.1 (CH), 138.3 (CH-furanyl), 137.2 (C_q) , 140.6 (b, $C_q)$, 140.9, 161.9, 164.7 (C_q) . ¹¹B NMR (160.5 MHz, CD_2Cl_2 , 297 K): $\delta = 52.3$ (br). Elemental analysis (%) calcd for C33H25BO: C, 88.40; H, 5.62. Found: C, 88.31; H, 5.60.

Synthesis of 1-(N-Methylpyrrol-3-yl)-2,3,4,5-tetraphenylborole (11). A solution of dichloro-N-methylpyrrole-3-ylborane (0.20 g, 1.23 mmol) in 3 mL of benzene was treated dropwise with a suspension of (E,E)-(1,2,3,4-tetramethyl-1,3-butadien-1,4-ylidene)-dilithium (0.50 g, 1.23 mmol) in 10 mL of benzene at 0 $^\circ$ C. The reaction mixture was allowed to warm to rt, changing its color from light brown to dark red, and stirred for 12 h. Lithium chloride was filtered off, and all volatiles were removed in vacuo. The product was recrystallized from toluene, yielding 11 as red crystals (246 mg, 0.55 mmol, 45%). ¹H NMR (500.1 MHz, CD₂Cl₂): δ = 3.50 (s, 3H, CH₃), 6.03 (dd, ³J = 2.6 Hz, ⁴*J* = 1.6 Hz, 1H, *H*-pyrrolyl), 6.49 (dd, ³*J* = 2.6 Hz, ⁴*J* = 1.9 Hz, 1H, H-pyrrolyl), 6.83-6.85 (m, 4H, Ph), 6.71 (m, 1H, H-pyrrolyl), 6.99-7.04 (m, 6H, Ph), 7.13-7.17 (m, 6H, Ph), 7.20-7.24 (m, 4H, *Ph*). ¹³C NMR (125.8 MHz, CD_2Cl_2): δ = 36.54 (CH3), 118.55 (CHpyrrolyl), 123.87 (CH-pyrrolyl), 125.51, 126.83, 127.31, 127.72, 129.80, 129.97 (CH), 137.54 (C_q), 139.10 (C_q -pyrrolyl), 141.57, 142.22, 160.11 (C_q). ¹¹B NMR (160.5 MHz, CD_2Cl_2): $\delta = 57.5$ (br). Elemental analysis (%) calcd for C₃₃H₂₆BN: C, 88.59; H, 5.86; N, 3.13. Found: C, 88.39; H, 5.91; N, 3.30.

Synthesis of 1-(*N*-Methylpyrrol-2-yl)-2,3,4,5-tetraphenylborole-dimethylaminopyridine (12'). 2-Lithio-*N*-methylpyrrole (10.8 mg, 124 μ mol) and 1-chloro-2,3,4,5-tetraphenylborole (50.0 mg, 124 μ mol) were dissolved in 2 mL of benzene at rt. After 5 min, DMAP (15.2 mg, 124 μ mol) was dissolved in 2 mL of benzene and added slowly, resulting in a color change from red to pale yellow. Lithium chloride was filtered off, and all volatiles were removed in vacuo. The residue was recrystallized from toluene, and 12' was isolated as pale yellow solid (42 mg, 73.9 μ mol, 60%). ¹H NMR (500.1 MHz, CD₂Cl₂): δ = 3.02 (s, 6H, N(CH₃)₂), 3.83 (s, 3H, N–CH₃), 5.75 (dd, ³J = 3.4 Hz, ⁴J = 1.7 Hz, 1H, H-pyrrolyl), 6.04 (dd, ³J = 3.4 Hz, ⁴*J* = 2.4 Hz, 1H, *H*-pyrrolyl), 6.37–6.39 (m, 2H, NC₅H₄-4-NMe₂), 6.69–6.71 (m, 4H, *Ph*), 6.76–6.77 (m, 1H, *H*-pyrrolyl), 6.87–7.04 (m, 16H, *Ph*), 8.14 – 8.17 (m, 2H, NC₅H₄-4-NMe₂). ¹³C NMR (125.8 MHz, CD₂Cl₂): δ = 35.23 (N-CH₃), 39.62 (N(CH₃)₂), 106.25 (NC₅H₄-4-NMe₂), 106.98, 113.98, 123.35 (CH-pyrrolyl), 124.56, 125.58, 127.47, 127.63, 129.23, 130.47 (CH), 145.40 (NC₅H₄-4-NMe₂), 141.13 (*C*_q), 143.76 (*C*_q, NC₅H₄-4-NMe₂), 150.66, 155.85 (*C*_q). ¹¹B NMR (160.5 MHz, CD₂Cl₂): δ = 0.08. Elemental analysis (%) calcd for C₄₀H₃₆BN₃: C, 84.35; H, 6.37; N, 7.38. Found: C, 83.66; H, 6.41; N, 6.79.

Synthesis of 5,5'-Bis(dichloroboryl)-2,2'-bithiophene (13). To a sample of neat BCl₃ (4.80 g, 3.62 mL, 40.9 mmol) was added a solution of 5,5'-bis(trimethylsilyl)-2,2'-bithiophene (1.92 g, 6.18 mmol) at -20 °C. The mixture was allowed to warm to room temperature and was stirred for 2 h. All volatiles were removed in vacuo, and the residue was recrystallized from toluene at -30 °C to yield 4 as a yellow solid (1.81 g, 5.52 mmol, 89%).

¹H NMR (500.1 MHz, C₆D₆, 297 K): δ = 6.78 (m, ³J_{H-H} = 3.90 Hz, 2H, *H*-dithienyl), 7.43 (d, ³J_{H-H} = 3.90 Hz, 2H, *H*-dithienyl). ¹³C NMR (125.8 MHz, C₆D₆, 297 K): δ = 128.2 (CH-dithienyl), 144.1 (CH-dithienyl), 149.8 (C_q-dithienyl). ¹¹B NMR (160.5 MHz, C₆D₆, 297 K): δ = 47.7. Elemental analysis (%) calcd for C₈H₄B₂Cl₄S₂: C, 29.32; H, 1.23; S, 19.57. Found: C, 29.81; H, 1.24; S, 19.39.

Synthesis of 5,5'-Bis-(2,3,4,5-tetraphenylborole)-2,2'-bithiophene (14). A solution of Me₂SnC₄Ph₄ (514 mg, 1.02 mmol) in 5 mL of dichloromethane was treated dropwise with a solution of 5,5'bis(dichloroboryl)-2,2'-bithiophene (200 mg, 0.61 mmol) in 5 mL of dichloromethane at -50 °C. The reaction mixture was stirred for 3 h and subsequently allowed to warm to rt, resulting in a color change from yellow to orange. All volatiles were removed in vacuo, and the side product Me₂SnCl₂ was removed quantitatively by sublimation at rt and 10⁻⁶ mbar within 5 h. The red residue was recrystallized from toluene/hexane to yield 5 as a orange brown solid (415 mg, 4.61 mmol, 75%). ¹H NMR (500.1 MHz, CD_2Cl_2 , 297 K): $\delta = 6.82-6.84$ (m, 8H, Ph), 6.99-7.06 (m, 14H, Ph), 7.12-7.14 (m, 8H, Ph & Hdithienyl), 7.21-7.26 (m, 14H, Ph & H-dithienyl). ¹³C NMR (125.8 MHz, CD_2Cl_2 , 297 K): $\delta = 126.23$, 127.41, 127.48, 128.01 (CH), 128.03 (CH-dithienyl), 129.68, 130.05 (CH), 146.26 (CH-dithienyl), 136.80, 140.60, 150.93, 162.14 (C_q). ¹¹B NMR (160.5 MHz, CD₂Cl₂, 297 K): δ = 56.5 (br). Elemental analysis (%) calcd C₆₄H₄₄B₂S₂: C, 85.52; H, 4.93; S, 7.14. Found: C, 84.59; H, 4.84; S, 6.76.

Synthesis of 5,5'-Bis-(2,3,4,5-tetraphenylborole)-2,2'-bithiophene-bis(dimethylaminopyridine) (15). To a solution of 5 (20 mg, 22.3 μ mol) in 3 mL of dichloromethane was added DMAP (5.44 mg, 44.6 μ mol), causing an immediate color change from dark orange to yellow. All volatiles were removed in vacuo, and the residue was recrystallized in CH_2Cl_2 /hexane to give 12 (22.4 mg, 19.6 μ mol, 88%) as yellow crystals. ¹H NMR (500.1 MHz, CD_2Cl_2 , 297 K): δ = 3.10 (s, 12H, NMe₂), 6.55–6.58 (m, 4H, NC₅H₄-4-NMe₂), 6.66 (d, ${}^{3}J_{H-H}$ = 3.45 Hz, 2H, H-dithienyl), 6.73-6.76 (m, 8H, Ph), 6.87-7.04 (m, 34H, Ph & H-dithienyl), 8.24-8.27 (m, 4H, NC₅H₄-4-NMe₂). ¹³C NMR (125.8 MHz, CD_2Cl_2 , 297 K): $\delta = 39.77$ (NMe₂), 106.99 (NC₅H₄-4-NMe₂), 123.31 (CH-dithienyl), 124.43, 125.52, 127.38, 127.43, 129.36, 130.68 (CH), 131.92 (CH-dithienyl), 145.12 (NC5H4-4-NMe₂), 139.18, 140.85, 143.51, 150.04, 155.95 (C_a). ¹¹B NMR (160.5 MHz, CD_2Cl_2 , 297 K): $\delta = 0.29$. Elemental analysis (%) calcd for C₇₈H₆₄B₂N₄S₂·2(CH₂Cl₂): C, 73.18; H, 5.22; N, 4.27; S, 4.88. Found: C, 73.33; H, 5.29; N, 4.23; S, 4.81.

ASSOCIATED CONTENT

S Supporting Information

Crystallographic data of complexes 7, 8, 9, 11, 12', and 15 in cif format, cyclic voltammetry measurements, and details about DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the German Science Foundation (DFG) for financial support.

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