Electronic Supplementary Information

Heteroarene-Fused Boroles: What Governs the Antiaromaticity and Lewis Acidity of the Borole Skeleton?

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1. Experimental Details

General. Melting points (mp.) were determined with a Stanford Research Systems MPA100 OptiMelt instrument. ¹H, ¹³C, and ¹¹B NMR spectra were measured with a JEOL AL-400 spectrometer (400 MHz for ¹H, 100 MHz for ¹³C, and 128 MHz for ¹¹B) in CDCl₃ or CD₂Cl₂. Mass spectrometry was measured with a Bruker Daltonics micrOTOF-focus. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thickness of Silica Gel 60F-254 (Merck). Column chromatography was performed using silica gel PSQ 60B (Fuji Silysia Chemical). Dry THF and ether was purchased from Kanto Chemicals and used as received. Dibutyl ether was distilled over sodium. Pentane, hexane, and dichloromethane were distilled over calcium hydride and degassed by Freeze-Pump-Thaw cycles. 2-(2-Bromophenyl)-1-methylindole,¹ 1-bromo-2-[(2-methoxyphenyl)ethynyl]-benzene,²

2-(2-bromophenyl)-3-bromobenzo[b]thiophene (7),³ and 2,2'-dibromobiphenyl⁴ were prepared as described in the literature. All reactions were carried out under an argon atmosphere.

Electrochemical Properties. Cyclic voltammograms were recorded with an ALS/chi-617A electrochemical analyzer using degassed and dried THF under an argon atmosphere. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and a Ag/AgNO₃ reference electrode. All measurements were performed using THF solutions of samples with a concentration of 1 mM and 0.1 M $Bu_4N^+PF_6^-$ as a supporting electrolyte with a scan rate of 50 mVs⁻¹. Potentials were determined against a ferrocene/ferrocenyl ion couple (Fc/Fc⁺).

Photophysical Properties. UV-visible absorption spectra were recorded on a Shimadzu UV-3510 spectrometer with a resolution of 0.5 nm. Degassed and dried spectral grade CH_2Cl_2 was used for the measurements.

3-Bromo-2-(2-bromophenyl)-1-methylindole (5). To a solution of 2-(2-bromophenyl)-1-methylindole (4.58 g, 16.0 mmol) in CHCl₃ (100 mL) was added *N*-bromosuccinimide (2.85 g, 16.0 mmol) and the mixture was stirred for 20 h. After concentrated under reduced pressure, the mixture was dissolved into CH₂Cl₂ and the resulting solution was washed with water and brine. The organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The resulting brown solid was purified by silica gel column chromatography ($R_f = 0.40$, hexane/CH₂Cl₂ 3:1) to

afford 5.36 g (14.7 mmol) of **5** in 92% yield as colorless solids: mp. 95.5–96.0 °C; ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.78 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.50 (dt, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.44–7.39 (m, 3H), 7.32 (dt, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.23 (dt, 7.4 Hz, 0.8 Hz, 1H), 3.56 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 137.0, 136.2, 133.2, 132.9, 132.1, 130.9, 127.4, 126.7, 125.4, 122.9, 120.4, 119.4, 109.7, 90.7, 31.2; HRMS (APCI): 365.9316 ([M+H]⁺); Calcd for C₁₅H₁₂Br₂N: 365.9304.

2-(2-Bromophenyl)-3-iodobenzo[b]furan solution of (6). То а 1-bromo-2-[(2-methoxyphenyl)ethynyl]benzene (4.32)15 mmol) g, in 1,2-dichloroethane (45 mL) was added I₂ (7.59 g, 30 mmol) and the mixture was stirred at 80 °C for 4 h. After cooling, the excess I₂ was removed by washing with a saturated Na₂SO₃ aqueous solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting mixture was purified by silica gel column chromatography ($R_{\rm f} = 0.60$, hexane) to afford 5.35 g (13.4 mmol) of **6** in 89% yield as yellow oil: ¹H NMR (400 MHz, CDCl₃): $\delta = 7.75$ (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.58 (dd, J = 7.6 Hz, 1.6 Hz, 1H), 7.54–7.49 (m, 2H), 7.47– 7.41 (m, 2H), 7.40–7.35 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 154.8, 154.4, 133.3, 132.9, 131.4, 131.3, 131.1, 127.1, 125.8, 124.0, 123.6, 121.8, 111.5, 66.2; HRMS (APCI): 397.8803 (M⁺); Calcd for C₁₄H₈BrIO: 397.8803.

A typical procedure for the preparation of the boronic esters: Indolyl-3-boronic acid 2,2-dimethyl-1,3-propanediol ester 8. To a solution of 5 (1.44g, 3.94 mmol) in THF (40 mL) was added a hexane solution of *n*-BuLi (1.64 M, 2.4 mL, 3.94 mmol) dropwise at -78 °C. The mixture was stirred at the same temperature for 30 min and then trimethyl borate (0.88 mL, 7.89 mmol) was added via a syringe in one portion. The mixture was gradually warmed to room temperature and stirred for 3.5 h and then 2,2-dimethyl-1,3-propanediol (1.19 g, 11.4 mmol) was added. After stirring for 2 h, the reaction mixture was concentrated under reduced pressure. The resulting red solid was dissolved into hexane and filtered. The filtrate was concentrated under reduced pressure and purified by silica gel column chromatography ($R_f = 0.88$, hexane/EtOAc 10:1) to afford 1.21 g of 8 (2.87 mmol) in 73% yield as pale yellow solids: mp. 97.1–98.2 °C; ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 7.89$ (dd, J = 7.6 Hz, 1.6 Hz, 1H), 7.56–7.48 (m, 3H),

7.35 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.32 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.26 (dt, J = 7.6 Hz, 1.2 Hz, 1H), 7.18 (dt, J = 8.0 Hz, 1.2 Hz, 1H), 3.52 (s, 3 H), 3.48, 3.42 (ABq, 4H, $J_{AB} = 12$ Hz), 0.83 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 140.3$, 136.1, 135.5, 134.3, 131.1, 129.8, 128.2, 127.0, 121.9, 119.8, 118.8, 109.3, 89.5, 72.4, 31.6, 31.2, 21.7 (one peak for the carbon atom bonding to the boron atom was not observed due to the quadrupolar relaxation); ¹¹B NMR (128 MHz, CDCl₃): $\delta = 26.5$; HRMS (APCI): 398.0925 ([M+H]⁺); Calcd for C₂₀H₂₂BBrNO₂: 398.0927.

Benzo[b]furanyl-3-boronic acid 2,2-dimethyl-1,3-propanediol ester 9. This boronic ester was prepared essentially in the same manner as described for **8** using **6** (2.38 g, 5.98 mmol) and ether (12 mL) for solvent. The crude product was purified by silica gel column chromatography ($R_f = 0.52$, hexane/CH₂Cl₂ 1:3) to afford 799 mg of **9** (2.1 mmol) in 35% yield as yellow solids: mp. 95.1–96.8 °C; ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 7.98$ (ddd, J = 7.6 Hz, 1.6 Hz, 0.8 Hz, 1H), 7.69 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.55 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.50 (ddd, J = 8.0 Hz, 1.2 Hz, 0.8 Hz, 1H), 7.40 (dt, J = 7.6 Hz, 1.2 Hz, 1H), 7.33–7.24 (m, 3H), 3.68 (s, 4H), 1.00 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 161.4$, 154.9, 133.6, 132.8, 132.6, 131.9, 130.2, 126.6, 124.2, 123.8, 123.1, 122.8, 110.8, 72.1, 31.9, 22.0 (one peak for the carbon atom bonding to the boron atom was not observed due to the quadrupolar relaxation); ¹¹B NMR (128 MHz, CDCl₃): $\delta = 25.9$; HRMS (APCI): 384.0541 (M⁺); Calcd for C₁₉H₁₈BBrO₃: 384.0532.

Benzo[*b*]thienyl-3-boronic acid 2,2-dimethyl-1,3-propanediol ester 10. This boronic ester was prepared essentially in the same manner as described for 8 using 7 (0.89 g, 2.4 mmol). The crude product was purified by silica gel column chromatography ($R_f = 0.20$, hexane/CH₂Cl₂ 1:1) to afford 603 mg of 10 (1.50 mmol) in 63% yield as pale yellow solid: mp. 105.2–103.2 °C; ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 8.35$ (ddd, J = 8.0 Hz, 1.2 Hz, 0.8 Hz, 1H), 7.85 (ddd, J = 7.6 Hz, 1.2 Hz, 0.8 Hz, 1H), 7.65 (dd, J = 8.0 Hz, 1.2 Hz, 1H) 7.45 (dd, J = 7.6 Hz, 1.6 Hz, 1H), 7.41–7.31 (m, 3H), 7.24 (dt, J = 8.0 Hz, 1.8 Hz, 1H), 3.60 (s, 4H), 0.96 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 151.7$, 143.5, 140.6, 137.5, 132.2, 131.8, 129.2, 126.5, 125.7, 124.2, 124.1, 124.0, 121.4, 72.1, 31.6, 21.9 (one peak for the carbon atom bonding to the boron atom

was not observed due to the quadrupolar relaxation); ¹¹B NMR (128 MHz, CDCl₃): δ = 25.4; HRMS (APCI): 400.0298 (M⁺); Calcd for C₁₉H₁₈BBrO₂S: 400.0304.

2-Biphenylboronic acid 2,2-dimethyl-1,3-propanediol ester 19. This boronic ester was prepared essentially in the same manner as described for **8** using 2,2'-dibromobiphenyl (320 mg, 1.02 mmol). The crude product was filtered through a plug of silica gel using hexane/CH₂Cl₂ 1:1 as an eluent to afford 165 mg of **19** (0.48 mmol) in 47% yield as colorless oil: ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.78 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.59 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.44 (dt, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.36 (dt, *J* = 7.6 Hz, 1.2 Hz, 1H) 7.32 (dt, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.24 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.19–7.15 (m, 2H), 3.51, 3.48 (ABq, 4H, *J*_{AB} = 10 Hz), 0.90 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ = 146.4, 144.7, 133.8, 131.7, 130.8, 129.5, 129.3, 127.9, 126.8, 126.5, 123.4, 72.1, 31.5, 21.9 (one peak for the carbon atom bonding to the boron atom was not observed due to the quadrupolar relaxation); ¹¹B NMR (128 MHz, CDCl₃): δ = 26.6; HRMS (APCI): 345.0658 ([M+H]⁺); Calcd for C₁₇H₁₉BBrO₂: 345.0661.

A typical procedure for the preparation of the arene-fused boroles: Pyrrole-fused borole 2. To a solution of 8 (183 mg, 0.43 mmol) in THF (5 mL) was added a THF solution of mesitylmagnesium bromide (0.86 M, 0.50 mL, 0.43 mmol) dropwise at 0 °C. The mixture was stirred at the same temperature for 30 min and refluxed for 2 h. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure. The resultant mixture was dissolved into dibutyl ether (5 mL). A pentane solution of t-BuLi (1.59 M, 0.55 mL, 0.86 mmol) was added dropwise at -78 °C and the mixture was gradually warmed to room temperature followed by stirring for 17 h and further stirring at 80 °C for 2 h. The red solution was concentrated under reduced pressure and dry hexane was added to precipitate out inorganic salts. The resultant mixture was filtered and the filtrate was concentrated under reduced pressure. Recrystallization of the crude product from hexane gave 81.1 mg (0.24 mmol) of **2** in 56% yield as red solids: mp. 124.7–126.2 °C; ¹H NMR (400 MHz, CDCl₃): δ =7.29 (d, J = 7.6 Hz, 1H), 7.20 (d, J = 7.6 Hz, 1H), 7.11 (t, J = 7.2 Hz, 1H 2H), 7.07–7.02 (m, 3H), 6.94 (t, J = 7.2 Hz, 1H), 6.90 (s, 2H), 3.94 (s, 3H), 2.36 (s, 3H), 2.30 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ = 166.5, 143.8, 142.9, 139.1, 137.6, 133.3,

130.9, 130.3, 129.5, 127.2, 122.7, 121.9, 121.8, 118.7, 110.1, 31.3, 22.4, 21.3 (three peaks for the carbon atoms bonding to the boron atom were not observed due to the quadrupolar relaxation); ¹¹B NMR (128 MHz, CDCl₃): $\delta = 61.9$; HRMS (APCI): 335.1848 (M⁺); Calcd for C₂₄H₂₂BN: 335.1845.

Furan-fused borole 3. This borole was prepared essentially in the same manner as described for **2** using **9** (114 mg, 0.30 mmol). Recrystallization of the crude product from pentane gave 17.6 mg (0.055 mmol) of **3** in 19% yield as orange solids: mp. 116.2–118.2 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.48 (d, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.19–7.10 (m, 5H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.94 (s, 2H), 2.38 (s, 3H), 2.34 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ = 184.7, 160.5, 140.7, 139.5, 138.8, 134.0, 132.1, 130.2, 128.8, 127.5, 124.4, 123.8, 121.9, 118.2, 111.9, 22.4, 21.3 (three peaks for the carbon atoms bonding to the boron atom was not observed due to the quadrupolar relaxation); ¹¹B NMR (128 MHz, CDCl₃): δ = 65.1; HRMS (APCI): 384.0541 (M⁺); HRMS (APCI): 322.1525 (M⁺); Calcd for C₂₃H₁₉BO: 322.1529.

Thiophene-fused borole 4. This borole was prepared essentially in the same manner as described for 2 using 10 (163 mg, 0.40 mmol). Recrystallization of the crude product from pentane gave 56.6 mg (0.17 mmol) of 4 in 42% yield as orange solids: mp. 114.2–116.2 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.77–7.74 (m, 1H), 7.38–7.36 (m, 1H), 7.19 (t, *J* = 5.2 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 2H), 7.05–6.98 (m, 2H), 6.93 (s, 2H), 2.38 (s, 3H), 2.27 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ = 172.1, 146.7, 144.4, 140.0, 138.7, 138.3, 133.5, 133.2, 129.3, 127.4, 125.8, 124.0, 123.7, 123.2, 119.6, 22.3, 21.3 (three peaks for the carbon atoms bonding to the boron atom were not observed due to the quadrupolar relaxation); ¹¹B NMR (128 MHz, CDCl₃): δ = 65.3; HRMS (APCI): 338.1314 (M⁺); Calcd for C₂₃H₁₉BS: 338.1314.

B-Mesityldibenzoborole (1a). This borole was prepared essentially in the same manner as described for 2 using 19 (146 mg, 0.42 mmol). Recrystallization of the crude product from hexane gave 44.0 mg (0.156 mmol) of 1a in 37% yield as yellow solids: mp. 130.7–132.7 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.40–7.37 (m, 4H), 7.33 (dt, *J* = 7.6 Hz, 1.2 Hz, 2H), 7.07 (t, 7.2 Hz, 2H), 6.92 (s, 2H), 2.37 (s, 3H), 2.20 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ = 153.8, 138.5, 138.0, 135.2, 134.6, 128.4, 127.2, 119.6,

22.5, 21.3 (two peaks for the carbon atoms bonding to the boron atom was not observed due to the quadrupolar relaxation); ¹¹B NMR (128 MHz, CDCl₃): δ = 71.8; HRMS (APCI): 282.1578 (M⁺); Calcd for C₂₁H₁₉B: 282.1580.

2. NMR Spectra



Figure S1a. ¹H NMR spectrum of 5 in CD₂Cl₂.



Figure S1b. The aromatic region of the 1 H NMR spectrum of **5** in CD₂Cl₂.



Figure S2. ¹³C NMR spectrum of 5 in CDCl₃.



Figure S3a. ¹H NMR spectrum of 6 in CDCl₃.



Figure S3b. The aromatic region of the ¹H NMR spectrum of 6 in CDCl₃.



Figure S4. ¹³C NMR spectrum of 6 in CDCl₃.



Figure S5a. ¹H NMR spectrum of 8 in CD₂Cl₂.



Figure S5b. The aromatic region of the ¹H NMR spectrum of **8** in CD_2Cl_2 .



Figure S6¹³C NMR spectrum of 8 in CDCl₃.



Figure S7. ¹¹B NMR spectrum of 8 in CDCl₃.



Figure S8a. ¹H NMR spectrum of 9 in CD₂Cl₂.



Figure S8b. The aromatic region of the 1 H NMR spectrum of **9** in CD₂Cl₂.



Figure S9. ¹³C NMR spectrum of 9 in CDCl₃.



Figure S10. ¹¹B NMR spectrum of 9 in CDCl₃.



Figure S11a. ¹H NMR spectrum of 10 in CD₂Cl₂.



Figure S11b. The aromatic region of the ¹H NMR spectrum of 10 in CD₂Cl₂.



Figure S12. ¹¹C NMR spectrum of 10 in CDCl₃.



Figure S13. ¹¹B NMR spectrum of 10 in CDCl₃.



Figure S14a. ¹H NMR spectrum of 19 in CD₂Cl₂.

Figure S14b. The aromatic region of the ¹H NMR spectrum of 19 in CD₂Cl₂.

Figure S15. ¹³C NMR spectrum of 19 in CDCl₃.

Figure S16. ¹¹B NMR spectrum of 19 in CDCl₃.

Figure S17a. ¹H NMR spectrum of 2 in CDCl₃.

Figure S17b. The aromatic region of the ¹H NMR spectrum of 2 in CDCl₃.

Figure S18. ¹³C NMR spectrum of 2 in CDCl₃.

Figure S19. ¹¹B NMR spectrum of 2 in CDCl₃.

Figure S20a. ¹H NMR spectrum of 3 in CDCl₃.

Figure S20b. The aromatic region of the ¹H NMR spectrum of 3 in CDCl₃.

Figure S21. ¹³C NMR spectrum of 3 in CDCl₃.

Figure S22. ¹¹B NMR spectrum of 3 in CDCl₃.

Figure S23a. ¹H NMR spectrum of 4 in CDCl₃.

Figure S23b. The aromatic region of the ¹H NMR spectrum of **4** in CDCl₃.

Figure S24. ¹³C NMR spectrum of 4 in CDCl₃.

Figure S25. ¹¹B NMR spectrum of 4 in CDCl₃.

Figure S26a. ¹H NMR spectrum of 1a in CDCl₃.

Figure S26b. The aromatic region of the ¹H NMR spectrum of 1a in CDCl₃.

Figure S27. ¹³C NMR spectrum of 1a in CDCl₃.

Figure S28. ¹¹B NMR spectrum of 1a in CDCl₃.

3. X-ray Crystallographic Analysis

	8 () 8		
B1-C13	1.565(2)	B2-C34	1.558(2)
B1-C1	1.566(2)	B2-C25	1.566(2)
B1-C4	1.567(2)	B2-C22	1.572(2)
C1-C12	1.392(2)	C22–C33	1.387(2)
C1–C2	1.416(2)	C22–C23	1.415(2)
С2–С9	1.375(2)	C23–C30	1.387(2)
C2–C3	1.485(2)	C23–C24	1.485(2)
C3–C8	1.383(2)	C24–C29	1.381(2)
C3–C4	1.415(2)	C24–C25	1.415(2)
C4–C5	1.388(2)	C25–C26	1.389(2)
C5–C6	1.397(2)	C26–C27	1.393(3)
C6–C7	1.384(2)	C27–C28	1.380(3)
С7–С8	1.393(2)	C28–C29	1.390(3)
C9–C10	1.393(2)	C30–C31	1.393(2)
C10-C11	1.384(3)	C31–C32	1.384(3)
C11–C12	1.393(2)	C32–C33	1.394(2)
C13-B1-C1	128.13(14)	C34–B2–C25	127.00(14)
С13-В1-С4	128.17(14)	C34–B2–C22	129.54(14)
C1-B1-C4	103.70(13)	С25-В2-С22	103.44(13)
С12С1С2	118.93(14)	С33-С22-С23	118.86(14)
C12C1B1	133.00(14)	С33-С22-В2	133.16(14)
C2-C1-B1	108.04(13)	С23-С22-В2	107.96(13)
C9-C2-C1	121.34(14)	С30-С23-С22	121.15(15)
С9-С2-С3	128.70(14)	C30–C23–C24	128.62(15)
C1–C2–C3	109.96(13)	C22–C23–C24	110.22(13)
C8–C3–C4	121.15(14)	C29–C24–C25	120.89(15)
C8–C3–C2	128.40(14)	C29–C24–C23	128.86(15)
C4–C3–C2	110.44(13)	C25–C24–C23	110.25(13)
C5-C4-C3	119.07(14)	C26-C25-C24	119.02(15)
C5-C4-B1	133.13(14)	С26-С25-В2	132.86(15)
C3-C4-B1	107.78(13)	С24-С25-В2	108.11(13)
C4–C5–C6	119.99(14)	C25-C26-C27	119.91(17)
C7–C6–C5	119.89(14)	C28-C27-C26	120.18(17)

Table S1. Selected Bond Lengths (Å) and Angles (°) of Compound 1a

С6-С7-С8	121.35(14)	C27-C28-C29	121.08(17)
С3-С8-С7	118.54(14)	C24–C29–C28	118.91(17)
C2-C9-C10	118.70(15)	C23-C30-C31	118.53(16)
C11-C10-C9	121.05(15)	C32-C31-C30	121.19(15)
C10-C11-C12	120.28(16)	C31–C32–C33	119.93(15)
C1C12C11	119.69(15)	C22–C33–C32	120.33(15)

Figure S29. *ORTEP* drawings of **1a** (50% probability for thermal ellipsoids) with atom labels. Hydrogen atoms are omitted for clarity. Crystal consists of two crystallographically independent molecules, whose structures are shown.

B1-C4	1.528(3)	C5–C6	1.428(3)
B1-C15	1.575(3)	C6–C14	1.382(3)
B1-C1	1.613(3)	C6N1	1.400(3)
C1-C10	1.385(3)	N1-C24	1.461(2)
C1–C2	1.419(3)	C7–C8	1.406(3)
C2–C7	1.372(3)	C8–C9	1.380(3)
C2–C3	1.471(3)	C9–C10	1.401(3)
C3-N1	1.359(3)	C11–C12	1.386(3)

Table S2. Selected Bond Lengths (Å) and Angles (°) of Compound 2

C3–C4	1.394(3)	C12–C13	1.400(3)
C4–C5	1.433(3)	C13–C14	1.380(3)
C5-C1	1.402(3)		
C4-B1-C15	130.63(19)	C11-C5-C4	135.26(19)
C4-B1-C1	102.90(17)	C6–C5–C4	107.15(17)
C15-B1-C1	126.39(18)	C14-C6-N1	128.95(18)
C10-C1-C2	118.50(19)	C14-C6-C5	123.23(18)
С10-С1-В1	132.94(19)	N1-C6-C5	107.82(17)
C2C1B1	108.45(17)	C3-N1-C6	107.70(16)
C7–C2–C1	121.57(19)	C3-N1-C24	128.02(17)
С7–С2–С3	131.94(19)	C6-N1-C24	124.10(17)
C1–C2–C3	106.29(17)	С2-С7-С8	118.8(2)
N1-C3-C4	111.76(17)	С9–С8–С7	120.7(2)
N1-C3-C2	133.61(18)	C8-C9-C10	120.0(2)
C4–C3–C2	114.59(17)	С1-С10-С9	120.4(2)
C3–C4–C5	105.52(17)	C12-C11-C5	119.16(19)
C3-C4-B1	106.66(17)	C11-C12-C13	121.56(19)
C5-C4-B1	146.27(19)	C14-C13-C12	121.0(2)
C11–C5–C6	117.58(18)	C13–C14–C6	117.44(19)

Figure S30. *ORTEP* drawing of **2** (50% probability for thermal ellipsoids) with atom labels. Hydrogen atoms are omitted for clarity.

B1-C4	1.549(4)	C5–C6	1.405(3)
B1-C15	1.565(4)	C5-C11	1.406(3)
B1-C1	1.612(4)	C6-C14	1.356(4)
C1-C10	1.375(3)	C6-O1	1.416(3)
C1–C2	1.408(4)	С7–С8	1.430(4)
C2–C7	1.362(4)	С8–С9	1.378(4)
C2–C3	1.490(3)	C9–C10	1.404(4)
C3–C4	1.347(3)	C11–C12	1.380(3)
C3–O1	1.350(3)	C12–C13	1.403(4)
C4–C5	1.443(3)	C13–C14	1.376(4)
C4-B1-C15	130.7(2)	C6-C5-C11	117.2(2)
C4-B1-C1	102.4(2)	C6-C5-C4	106.7(2)
C15-B1-C1	126.7(2)	C11-C5-C4	136.0(2)
C10C1C2	117.8(2)	C14–C6–C5	126.2(2)
C10-C1-B1	133.1(2)	C14-C6-O1	124.3(2)
C2-C1-B1	109.1(2)	C5-C6-O1	109.5(2)
C7–C2–C1	123.2(2)	C3–O1–C6	103.29(17)
С7-С2-С3	131.6(2)	С2-С7-С8	118.2(2)
C1–C2–C3	105.2(2)	С9–С8–С7	119.4(2)
C4–C3–O1	116.6(2)	C8-C9-C10	120.6(2)
C4–C3–C2	116.5(2)	С1-С10-С9	120.8(2)
O1–C3–C2	126.9(2)	C12C11C5	117.6(2)
C3–C4–C5	103.8(2)	C11-C12-C13	122.1(2)
C3-C4-B1	106.8(2)	C14-C13-C12	121.4(2)
C5-C4-B1	149.4(2)	C6-C14-C13	115.4(2)

Table S3. Selected Bond Lengths (Å) and Angles (°) of Compound 3

Figure S31. *ORTEP* drawing of **3** (50% probability for thermal ellipsoids) with atom labels. Hydrogen atoms are omitted for clarity.

B1-C4	1.554(5)	C5–C11	1.415(5)
B1-C15	1.567(5)	C5–C6	1.417(5)
B1C1	1.595(5)	C6–C14	1.373(5)
C1C10	1.369(5)	C6–S1	1.763(4)
C1–C2	1.400(5)	С7–С8	1.414(5)
C2–C7	1.393(5)	С8–С9	1.382(5)
C2–C3	1.495(5)	C9–C10	1.400(5)
C3–C4	1.375(5)	C11–C12	1.388(5)
C3–S1	1.706(3)	C12–C13	1.402(5)
C4–C5	1.448(5)	C13–C14	1.369(5)
C4-B1-C15	130.1(3)	C11-C5-C6	117.6(3)
C4-B1-C1	102.5(3)	C11-C5-C4	130.1(3)
C15-B1-C1	127.3(3)	C6–C5–C4	112.3(3)
C10-C1-C2	118.8(3)	C14-C6-C5	122.8(3)
C10-C1-B1	132.3(3)	C14-C6-S1	126.2(3)
C2C1B1	108.9(3)	C5-C6-S1	11.0(3)
C7–C2–C1	122.6(3)	C3-S1-C6	90.52(17)
С7-С2-С3	129.7(3)	С2–С7–С8	117.4(3)

Table S4. Selected Bond Lengths (Å) and Angles (°) of Compound 4

C1-C2-C3	107.7(3)	C9–C8–C7	120.2(3)	
C4–C3–C2	112.8(3)	C8-C9-C10	120.8(3)	
C4-C3-S1	115.8(3)	C1-C10-C9	120.3(3)	
C2-C3-S1	131.4(3)	C12-C11-C5	119.3(3)	
C3–C4–C5	110.4(3)	C11-C12-C13	120.7(3)	
C3-C4-B1	108.1(3)	C14-C13-C12	121.2(3)	
C5-C4-B1	141.4(3)	C13-C14-C6	118.5(3)	

Figure S32. *ORTEP* drawing of **4** (50% probability for thermal ellipsoids) with atom labels. Hydrogen atoms are omitted for clarity.

4. Theoretical Calculations

All theoretical calculations were performed using the Gaussian 03 program.⁵ The geometry optimization (for 2–4 and 11_{opt}) and the time-dependent density functional theory (TD-DFT) calculations (for 2–4) were conducted at the B3LYP/6-31G* level of theory. The NICS calculations (for 1a–4, 11_{opt} , 11_{1a} – 11_4 , 12_{opt} , 12_{1a} – 12_4) were carried out at the B3LYP/6-311+G** level of theory using the geometries derived from the crystal structure except 11_{opt} and 12_{opt} . The single point energy calculations (for 11_{1a} – 11_4 , 11_{opt} , 12_{1a} – 12_4 , 12_{opt}) were performed at the B3LYP/6-31G* level of theory.

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atom	x	<i>y</i>	Z
С	-2.533269	0.838732	-0.924856
Н	-2.317822	1.507766	-1.752795
С	-3.782148	0.489862	-0.565377
Н	-4.709407	0.836217	-1.018985
С	-3.778627	-0.491826	0.579665
Н	-4.703126	-0.838904	1.038326
С	-2.527522	-0.839743	0.932248
Н	-2.306958	-1.508678	1.758922
В	-1.541824	0.000062	0.001153
С	0.012450	0.000505	-0.001821
С	2.860902	0.000566	-0.008249
С	0.743888	-1.213565	-0.114634
С	0.744102	1.214639	0.104793
С	2.140780	1.192849	0.105485
С	2.140252	-1.191511	-0.124764
Н	2.682961	2.132278	0.200607
Н	2.681830	-2.129901	-0.232074
С	0.046864	2.543786	0.303894
Н	-0.845448	2.641582	-0.321563
Н	0.718332	3.378350	0.076878
Н	-0.283051	2.665889	1.344344
С	0.044925	-2.541416	-0.317083
Н	-0.300060	-2.65410	-1.353658
Н	-0.838180	-2.645727	0.320398
Н	0.719967	-3.377539	-0.107212

Table S5. Coordinates of the Structure of 11_{opt} Optimized at the B3LYP/6-31G* Level.

С	4.370678	-0.002206	0.020183
Н	4.782835	-0.817822	-0.583712
Н	4.746929	-0.134971	1.043719
Н	4.780672	0.941210	-0.355860

Figure S33. Comparison of the optimized structure of (a) 11_{opt} with the structures of (b) 11_{1a} , (c) 11_2 , (d) 11_3 , and (e) 11_4 , whose geometries are derived from the crystal structures of 1a-4, respectively. The selected bond lengths for the borole ring are given.

Figure S34. The optimized structures of (a) **2**, (b) **3**, and (c) **4**, together with the dihedral angles between the central borole and two terminal benzene rings, calculated at the B3LYP/6-31G* level.

atom	x	У	Ζ	
Н	0.698705	0.509046	-5.533560	
С	0.637520	1.010939	-4.572116	
С	0.506944	2.346649	-2.061000	
С	0.426356	0.308255	-3.385352	
С	0.779249	2.394728	-4.483292	
С	0.713328	3.053384	-3.241929	
С	0.362831	0.951401	-2.114355	
Н	0.946198	2.971497	-5.388710	
Н	0.826452	4.133676	-3.207853	
Н	0.454033	2.862727	-1.106464	
С	0.150207	-0.080658	-1.133705	
С	0.093270	-1.280382	-1.848763	
С	-0.113866	-2.474531	-1.003340	
С	-0.488925	-4.308218	1.063475	
С	-0.156603	-3.828748	-1.297829	
С	-0.248220	-2.005366	0.338646	
С	-0.428737	-2.928622	1.355605	
С	-0.353143	-4.747511	-0.245705	
Н	-0.028886	-4.202785	-2.309208	
Н	-0.522151	-2.590733	2.385570	
Н	-0.391128	-5.810444	-0.469543	
Н	-0.635555	-5.027469	1.864976	
В	-0.087600	-0.409062	0.344900	

Table S6. Coordinates of the Structure of 2 Optimized at the B3LYP/6-31G* Level

С	-0.154696	0.527653	1.597785
С	-0.258795	2.211728	3.885602
С	1.015125	1.158163	2.086413
С	-1.378038	0.762917	2.268190
С	-1.411705	1.598264	3.389635
С	0.945999	1.979310	3.215280
Н	-2.364267	1.776524	3.886501
Н	1.856968	2.450268	3.581853
С	-2.671314	0.167683	1.750794
Н	-2.568794	-0.900136	1.526882
Н	-2.991947	0.657692	0.821650
Н	-3.481849	0.283401	2.478028
С	2.354287	0.932909	1.414391
Н	3.138925	1.534288	1.885190
Н	2.323061	1.192882	0.349851
Н	2.664850	-0.118461	1.474995
С	-0.306192	3.079321	5.121933
Н	0.443929	3.876949	5.081479
Н	-0.105839	2.493468	6.029548
Н	-1.289564	3.545154	5.248077
Ν	0.241925	-1.069637	-3.188871
С	0.225978	-2.057369	-4.253462
Н	-0.170561	-1.600432	-5.163405
Н	-0.428387	-2.885265	-3.977124
Н	1.230622	-2.445048	-4.461663

Table S7. Coordinates of the Structure of 3 Optimized at the B3LYP/6-31G* Level

atom	x	y	Ζ
Н	0.564267	0.031530	-5.911885
С	0.550881	0.624924	-5.003533
С	0.505247	2.146660	-2.587747
С	0.365498	0.041242	-3.761676
С	0.717820	2.012217	-5.017632
С	0.694372	2.757768	-3.826822
С	0.337010	0.755246	-2.540463
Н	0.866899	2.520156	-5.966028
Н	0.825087	3.835405	-3.875091
Н	0.483217	2.735386	-1.675347

С	0.127720	-0.239199	-1.509925
С	0.045416	-1.429802	-2.196021
С	-0.174536	-2.629595	-1.384479
С	-0.540506	-4.498123	0.626845
С	-0.265242	-3.965127	-1.730725
С	-0.269476	-2.181092	-0.034469
С	-0.443266	-3.129027	0.961114
С	-0.455593	-4.906710	-0.698131
Н	-0.189368	-4.286332	-2.765815
Н	-0.506672	-2.823713	2.003322
Н	-0.531033	-5.962174	-0.945776
Н	-0.681912	-5.236419	1.411669
Ο	0.181427	-1.319622	-3.535620
В	-0.086835	-0.583032	-0.012559
С	-0.105895	0.349427	1.239525
С	-0.103479	2.031978	3.530505
С	1.074541	1.022865	1.642808
С	-1.286510	0.543749	1.995925
С	-1.267258	1.379603	3.117390
С	1.057918	1.840529	2.775204
Н	-2.187650	1.527177	3.680304
Н	1.976253	2.341264	3.077789
С	-2.600206	-0.077520	1.568500
Н	-2.474744	-1.108541	1.221890
Н	-3.053494	0.484589	0.740688
Н	-3.323242	-0.082607	2.390931
С	2.372388	0.841351	0.882291
Н	3.164145	1.472868	1.297973
Н	2.262790	1.095400	-0.178519
Н	2.725120	-0.197381	0.925210
С	-0.091587	2.897667	4.768564
Н	0.640581	3.708195	4.684152
Н	0.173642	2.313615	5.660423
Н	-1.073735	3.345205	4.955240

atom	x	у	Z
С	-3.798719	-0.149696	-0.823723
С	-4.024787	-0.246079	1.934412
С	-2.618341	-0.122672	-0.031058
С	-5.072568	-0.225619	-0.259181
С	-5.175892	-0.274639	1.128811
С	-2.757783	-0.170198	1.368806
Н	-5.961452	-0.245238	-0.883284
Н	-6.157482	-0.333653	1.590580
Н	-1.871041	-0.142306	1.995559
Н	-4.128448	-0.281888	3.015486
С	-1.425873	-0.047343	-0.838416
С	-1.721787	-0.010779	-2.188047
С	-0.536535	0.077083	-3.062121
С	1.986542	0.212750	-4.220889
С	-0.434629	0.103319	-4.442333
С	0.614508	0.122307	-2.224457
С	1.867891	0.182680	-2.815452
С	0.849686	0.175299	-5.019199
Н	-1.316797	0.067210	-5.076903
Н	2.762850	0.207748	-2.197338
Н	0.946830	0.197520	-6.101456
Н	2.969649	0.264239	-4.681023
S	-3.417257	-0.072132	-2.553569
В	0.126229	0.044240	-0.710857
С	1.016861	0.045754	0.573679
С	2.652978	0.023567	2.896100
С	1.689011	1.217155	0.994575
С	1.170896	-1.136750	1.338270
С	1.983135	-1.129769	2.475109
С	2.486323	1.188521	2.143538
Н	2.098328	-2.049554	3.046510
Н	2.988044	2.101790	2.459603
С	1.508662	2.524874	0.251827
Н	2.262354	3.260188	0.552099
Н	0.523364	2.966016	0.454379
Н	1.580640	2.392312	-0.833485

Table S8. Coordinates of the Structure of 4 Optimized at the B3LYP/6-31G* Level

С	0.488118	-2.422721	0.919105
Н	-0.599216	-2.300651	0.844905
Н	0.685163	-3.226801	1.635453
Н	0.838939	-2.764832	-0.063279
С	3.549091	0.000996	4.112384
Н	3.630528	0.992973	4.569422
Н	4.566461	-0.321786	3.852379
Н	3.175526	-0.693434	4.873082

Figure S35. The Lowest Excitation Energies of **2–4** estimated by the TD DFT calculation at the B3LYP/6-31G* level of theory.

$\mathbf{I} \mathbf{U} \mathbf{U} \mathbf{U} \mathbf{U} \mathbf{U} \mathbf{U} \mathbf{U} U$	Table S9.	The Lowest	Excitation	Energies	of 2-4 ^a
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cmpd (w	transition energy /eV	main CL apofficient	oscillator strength
	(wavelengths / nm)	main CI coefficient	f
2	2.48 (500)	0.66872 (HOMO–LUMO)	0.0150
3	2.48 (500)	0.66806 (HOMO-LUMO)	0.0128
4	2.43 (509)	0.66487 (HOMO–LUMO)	0.0129

^{*a*}Based on the TD DFT calculations at the B3LYP/6-31G* level of theory.

Figure S36. Plots of HOMO (\blacksquare) and LUMO (\square) energy levels of the parent boroles 12_{1a} - 12_4 and 12_{opt} as a function of their NICS(1)_{zz} values.

5. Reference

- So, C. M.; Zhou, Z.; Lau, C. P.; Kwong, F. Y. Angew. Chem. Int. Ed. 2008, 47, 6402.
- Verma, A. K.; Kesharwani, T.; Singh, J.; Tandon, V.; Larock, R. C. Angew. Chem. Int. Ed. 2009, 48, 1138.
- 3. Ren, Y.; Baumgartner, T. J. Am. Chem. Soc. 2011, 133, 1328.
- 4. (a) Gilman, H.; Gaj, B. J. J. Org. Chem. 1957, 22, 447. (b) Leroux, F.; Schlosser, M. Angew. Chem. Int. Ed. 2002, 41, 4272.
- Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.;

Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J.
W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.;
Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick,
D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.;
Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.;
Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.;
Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.;
Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc.,
Wallingford CT, 2004.