5b,7b-Diaza-3b,9b-diborabenzo[ghi]perylenes

Michael J.D. Bosdet, Warren E. Piers, Ted S. Sorensen, and Masood Parvez

Abstract: Treatment of a precursor to the chelating Lewis acid 2,2'-diborabiphenyl with 2,6-bisalkynyl-substituted pyridazines, leads to elimination of 2 equiv. of ClSiMe₃; subsequent treatment of the mixture with PtCl₂ catalyzes the cyclization of observable intermediates to the title 5b,7b-diaza-3b,9b-diborabenzo[*ghi*]perylene compounds in low isolated yields. The compounds were characterized by NMR and UV–vis spectroscopies, and in one case, by X-ray crystallography. NICS(1) computations indicate that the inner ring is less aromatic than the outer rings.

Key words: polycyclic aromatic hydrocarbons, boron heterocycles, nitrogen heterocycles, X-ray structure.

Résumé : Le traitement d'un précurseur de l'acide de Lewis chélatant 2,2'-diborabiphényle avec des pyridazines substituées dans les positions 2,6 par des groupes bisalkynyles conduit à l'élimination de deux équivalents de ClSiMe₃; le traitement subséquent du mélange avec du PtCl₂ catalyse la cyclisation des intermédiaires observables et à la formation des composés 5b,7b-diaza-3b,9b-diborabenzo[*ghi*]pérylènes mentionnés dans le titre qui sont isolés avec de faibles rendements. Les composés ont été caractérisés par spectroscopies RMN et UV–vis et, dans un cas, par diffraction des rayons-X. Des calculs NICS(1) indiquent que le noyau interne est moins aromatique que les cycles externes.

Mots-clés : hydrocarbures aromatiques polycycliques, hétérocycles du bore, hétérocycles de l'azote, structure par diffraction des rayons X.

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Introduction

Transposition of C–C units for isoelectronic B–N modules in polycyclic aromatic hydrocarbons offers a means of altering opto-electronic, redox, and chemical properties of these important organic materials without dramatically affecting their gross structural features.^{1–3} One of the most elementary examples is the BN-biphenyl analog I (Chart 1), the pyridine adduct of borabenzene, which has been known for many years.⁴ Unlike biphenyl, I is susceptible to protonation by Brønsted acids at the carbon alpha to boron,^{5,6} and facile Diels–Alder addition with moderately active dienophiles,⁷ demonstrating the more reactive nature of the BN analog; indeed, I is quite air- and moisture-sensitive and needs to be handled accordingly.

We have been interested in this strategy as a means of producing novel organic electronic materials and have been developing synthetic methods to novel B_xN_x hetercyclic analogs of various PAH frameworks. For example, the BN-phenanthrene⁸ and BN-pyrene^{9,10} derivatives **II** and **III** (Chart 1) can be prepared via formation of borabenzene pyridine adducts wherein the pyridine unit is functionalized with al-kynyl groups alpha to nitrogen. This buttressing of the B–N bond has a stabilizing effect, in that compounds **II** can be handled briefly in air, while pyrene analogs **III** can be stored under ambient atmosphere indefinitely; indeed, they are even unperturbed by treatment with aqueous HCl.

The B_2N_2 -triphenylenes IV (Chart 1) are another class of

compounds we have studied extensively.^{11,12} While they exhibit favorably modified redox and photophysical properties relative to the all-carbon triphenylenes, they do not have long-term stability to ambient conditions, limiting the scope of their utility. We thus sought to implement the buttressing strategy that was successful in stabilizing the BN-pyrenes **III** and protect the bay region of the triphenylenes **IV**. Herein, we report the synthesis of two examples of a 5b,7b-diaza-3b,9b-diborabenzo[*ghi*]perylene framework, albeit in low yields. The limitations of the approach will be discussed along with the characterization of these intriguing compounds.

Results and discussion

Engagement of the buttressing strategy for the stabilization of the $C_2B_2N_2$ heterocyclic core in compounds IV (Chart 1) required first the synthesis of 3,6-di(alkynyl)pyridazines **1a–1d**, which in our hands was best-accomplished by palladium-catalyzed coupling of 3,6-dichloropyridazine with alkynylzinc compounds,¹³ as shown in Scheme 1. Terminal alkynes were first deprotonated with *n*BuLi at –78 °C, and subsequently transmetalated with ZnCl₂ to generate the required alkynylzinc reagents. The alkynylzinc compounds were transferred onto a THF solution of the aryl chloride and Pd catalyst and stirred for 24 h. After workup, the desired substrates were obtained in low but workable yields of $\approx 20\%$ –25%. Alternatively, Sonogashira coupling pro-

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Chart 1.



tocols could be employed, but dimerization of the terminal alkynes was a significant side reaction. The unsubstituted 3,6-bis(ethynyl)pyridazine (1a) was formed from the silyl derivative 1d by desilylation with $KOH_{(aq)}$ in MeOH (Scheme 1).

With substrates 1 in hand, reactions with the methylsubstituted chloroboracyclic precursor, 2^{7} , were attempted (Scheme 2). In general, these reactions were not as clean as those previously observed for pyridazine bases without the acetylenic groups. While elimination of 2 equiv. of Me₃SiCl was observed, the reactions with pyridazines 1 appear to be prone to more side reactions, particularly for the parent derivative 1a. Furthermore, the bis-acetylenic B_2N_2 -triphenylene complexes (i.e., derivatives of IV), depicted in Scheme 2, were not detected in any of these reactions. Rather, one acetylenic group underwent spontaneous cyclization, and the major products observed for R = nBu and Ph were the halfcyclized compounds 3b and 3c, presumably formed via intermediates IV. These polycyclic intermediates were not isolated in pure form, but carried forward to the fully cyclized compounds 4 using PtCl₂ catalysis as shown in Scheme 2.¹⁴ While not isolable in pure form, the nature of compounds 3 was supported by the ¹H NMR spectral features observed for the butyl-substituted derivative 3b. Two distinct methyl resonances were observed at 2.81 and 3.07 ppm in C_6D_6 solution, highlighting the averaged C_s symmetry in 3b. Further, two pairs of doublets, corresponding to H-6 and H-7 (5.97 and 6.25 ppm) and H-9 and H-10 (6.96 and 7.28 ppm) were observable, in addition to four aromatic singlets, for H-1 (9.16 ppm), H-3 (7.20 ppm), H-5 (6.56 ppm), and H-12 (8.57 ppm) (See Chart 2 for the numbering scheme).

Yields for the target heterocycles **4** were very low (trace–17%), but the compounds were isolated as moderately air- and moisture-tolerant, red-brown solids after purification via column chromatography. The majority of material loss apparently occurred in the catalyzed cycloisomerization step, since the mass balance in the production of crude **3b** was upwards of 70%. The inefficient synthesis was particularly evident in the attempted formation of **4a**; the amount

of product obtained was insufficient for NMR analysis, and while its presence may be inferred from a qualitative observation of pink–red fluorescence in solutions of the material off column, further analysis was precluded due to lack of material.

Although B₂N₂-benzo[*ghi*]perylenes¹⁵ **4b–4c** were available only in small quantities, we were able to characterize them reasonably thoroughly. Unlike the ¹H NMR spectra for compounds **3b** and **3c**, those of **4b** and **4c** were much simpler, as expected for $C_{2\nu}$ symmetric structures; the ¹H NMR spectrum of **4b** is illustrated in Fig. 1. Each derivative gave rise to four aromatic singlets between 8.0 and 9.5 ppm for the B₂N₂-benzo[*ghi*]perylene framework, corresponding to H-1, H-3, H-5, and H-6, as well as a single methyl resonance at ~3.1 ppm, and the expected resonances for the R group. The ¹¹B NMR spectrum showed a single resonance at 21 ppm, in agreement with other enclosed BN aromatic compounds (~22 ppm).

Slow evaporation of solvent from a diethyl ether solution of 4b yielded crystals suitable for analysis via X-ray crystallography. The structure of 4b is essentially planar, with a maximum dihedral angle of 1.5° within the ring system (C(18)-C(1)-B(1)-C(5)) (Fig. 2 and Table 1). The B-N bond is short, at 1.452(2) Å, consistent with BN-pyrene III (1.456(4) Å) and the B₂N₂-triphenylene **IV** (1.464(4) Å),¹² and indicative of some π -character in this bond. However, in contrast to unbuttressed IV,12 bond localization is evident throughout the carbon perimeter in 4b, with alternating long and short C-C bonds within individual rings. Thus, in the borabenzene rings, C(1)-C(2) and C(3)-C(4) are short (1.390(3) Å avg.), whereas C(2)–C(3) and C(4)–C(5) are longer (1.414(3) Å avg.). The π -electron localization in the pyridazine ring in 4b also differs from that in compounds IV, such that the short and long C-C bonds in the latter are reversed in 4b. Specifically, C(8)-C(9) and C(9')-C(8') are 1.406 Å, while C(9)-C(9') is shortened to 1.346(3) Å; the corresponding lengths in unbuttressed IV are 1.345(5) Å and 1.433(6) Å. Additionally, the C-N bonds are shortened by ~0.02 Å (to 1.381(2) Å), suggesting better overall π -electron delocalization about this ring, in contrast to the cyclohexadiene-type bonding arrangement of heterocycles IV. The longest C–C bond in 4b is C(1)-C(1)', at 1.456(3) Å, elongated by 2% relative to the same bond in B_2N_2 -triphenylene IV but of similar length to the analogous bond in the all-carbon PAH benzo[ghi]perylene, at 1.484 Å.¹⁶

Overall then, the solid-state bond-length patterns suggests that the ring system is best-represented by resonance form **A** (Chart 3), in contrast to the dominant resonance form of triphenylene analogues **IV**, best-described by resonance form **B**. This is supported by NICS(1) calculations¹⁷ performed on **4a**, which show a low aromaticity for the inner $C_2B_2N_2$ ring in **4a**, but strong aromaticity for the outer rings. This is the inverse of trends noted for **IV**, and it thus appears that the effect of buttressing the system is to lower the aromatic stabilization of the inner ring relative to the unbuttressed system. Indeed, the all-carbon PAH benzo[*ghi*]perylene exhibits this pattern as well, with the inner ring having low aromatic character relative to the outer rings.¹⁸

Unlike the all-carbon frameworks, the B_2N_2 compounds have molecular dipoles that are significant enough to influence

Scheme 1.

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Scheme 2.



Chart 2.



packing in the solid state. The molecular packing of 4b, shown in Fig. 3, features two molecules stacked with the dipoles (calculated to be 3.53 D in 4b) aligned such that a

close non-bonding B...N distance of 3.71 Å is observed. Intermolecular π -stacking distances of 3.42 Å exist between parallel sheets of **4b** molecules, which is very slightly shorter than the π - π distance in crystalline benzo[*ghi*]perylene at 3.44 Å.

The unbuttressed B_2N_2 -triphenylene compounds IV exhibit reversible one- and two-electron reduction process, and indeed the radical anion and dianions are stable and isolable.¹² It was therefore somewhat surprising to find that cyclic voltammetry on compounds **4a** and **4b** shows irreversible one-electron reductions, suggesting that the radical anions are unstable. This may be a reflection of the low aromaticity of the central rings in compounds **4** and a change in the character of the SOMO in the radical anions.

Fig. 1. ¹H NMR (400 MHz) spectrum of 4b in CD₂Cl₂.



Fig. 2. Top: X-ray structure of **4b**. Numbers are bond lengths in Å. Bottom: **4b**, viewed along the molecular plane (perpendicular to the N(1)-N(1)' bond), with butyl groups removed. Hydrogen atoms have been removed for clarity. Thermal ellipsoids are at the 50% probability level.



The absorption and emission spectra are indicative of lowered HOMO–LUMO gaps in comparison to triphenylene analogs **IV**, as may be expected by the extended conjugation afforded by the buttressing alkenyl groups. As for other B_xN_x analogs, both absorption and emission bands (621 and 630 nm for **4a** and **4b**, respectively) are red-shifted in these compounds in comparison to the all-carbon compound, but the emission quantum yields (0.023 and 0.015, respectively, relative to 9,10-diphenylanthracene in cyclohexane) are significantly lower than that of benzo[*ghi*]perylene (0.26).

Conclusions

We have prepared and characterized two examples of 5b,7b-diaza-3b,9b-diborabenzo[*ghi*]perylenes with a doubly buttressed $B_2N_2C_2$ core. Although in previous work a doubly buttressed $B_2N_2C_2$ core added stability to bora-aza analogs of PAHs, here the added benefit in this regard is minimal. This may stem from the fact that the core ring is of low aromaticity and therefore more reactive towards, for example, protic reagents and oxygen. Furthermore, the synthetic route

Chart 3.



Table 1. Selected metrical parameters for 4b.

Bond lengths (Å)	
B(1) - N(1)	1.452(2)
B(1) - C(1)	1.516(2)
B(1)—C(5)	1.516(3)
C(1)—C(1)'	1.456(3)
C(1)—C(2)	1.391(2)
C(2)—C(3)	1.415(2)
N(1)—C(8)	1.381(2)
N(1)—N(1)'	1.422(2)
Bond angles (°)	
C(1)-B(1)-N(1)	122.63(14)
N(1)-B(1)-C(5)	117.23(14)
N(1)'-N(1)-B(1)	119.73(9)
B(1)–N(1)–C(8)	120.76(13)
B(1)-C(1)-C(1)'	117.63(9)
N(1)-C(8)-C(9)	119.80(14)
Torsion angles (°)	
C(8)–N(1)–B(1)–C(1)	179.74(14)

to these frameworks is inefficient (despite many attempts at improvements), and the photophysical properties are not unique enough to warrant further efforts directed towards discovery of more direct routes to the compounds. Nonetheless, the structural features and aromatic properties are of interest to add to the database of $B_r N_r$ compounds in comparison to their all-carbon counterparts.

Experimental section

General procedures have been described in detail elsewhere.¹² Celite 545[®] was purchased from Fisher Scientific and heated at 200 °C under high vacuum for 3 days prior to use. Neutral alumina (63–200 µm, 70–230 Mesh ASTM)) was purchased from EM Science and heated at 200 °C for 3 days under high vacuum prior to use. Silica-gel column chromatography was carried out on Geduran Silica 60 silica gel (particle size 40–63 μ m).

Compound 2 was prepared as described previously.¹² CuI, BCl₃, LiNMe₂, pyridazine, 9,10-diphenylanthracene, and Pd(PPh₃)₄ were purchased from Aldrich and used as re-



ceived. 3,6-Dichloropyridazine was purchased from Aldrich and sublimed prior to use. Phenylacetylene was purchased from Aldrich and passed through a column of alumina immediately prior to use. 1-Hexyne was purchased from Acros and used as received. PtCl₂ was purchased from Alfa Aesar and used as received. Trimethylsilylacetylene was purchased from Petra Research, Inc. and distilled prior to use. ¹H NMR assignments were made by comparison to known chemical shift patterns.5-9,11,12

Synthesis of 3,6-bis(1-hexynyl)pyridazine, 1b



In a microwavable reaction tube, solid $Pd(PPh_3)_4$ (8 mg, 7.1 µmol) and CuI (3 mg, 14.1 µmol) were added to a solution of 3,6-dichloropyridazine (50 mg, 0.33 mmol) in NEt₃ (2 mL). This was immediately followed by the addition of a solution of 1-hexyne (58 mg, 0.71 mmol) in NEt₃ (1 mL), and the mixture was heated in a microwave reactor (115 W, 150 °C) for 25 min. Once cooled, the crude product was extracted into Et₂O and gravity filtered. The solvent was removed in vacuo, and the orange material was dissolved in hexanes and loaded onto a column of neutral Al₂O₃. Gradient elution with hexanes/Et₂O ultimately gave the product as a yellow solid. Yield: 20 mg (25%). ¹H NMR (C₆D₆) δ (ppm): 6.62 (s, 2H, H-1), 2.12 (t, 4H, ${}^{3}J_{HH} = 7$ Hz, H-5), 1.31 (m, 2 + 2H, H-6 + H-7), 0.76 (t, 6H, ${}^{3}J_{\text{HH}}$ = 7 Hz, H–). HR-MS for C₁₆H₂₀N₂ (M⁺): 240.1626 (calcd.), 240.1624 (found).

Synthesis of 3,6-bis(phenylethynyl)pyridazine, 1c



To a -78 °C solution of phenylacetylene (1.33 g, 13.0 mmol) in THF (50 mL) was added a solution of *n*-butyl lithium in hexanes (1.6 mol/L, 8.12 mL, 13.0 mmol). After stirring at this temperature for 1 h, a solution of ZnCl₂ (1.77 g, 13.0 mmol) in THF (50 mL) was transferred in via canula, and this mixture was stirred for another 45 min with

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the temperature maintained at -78 °C. The reaction mixture was then warmed to 25 °C, and a solution of 3,6-dichloropyridazine (486 mg, 3.3 mmol) and Pd(PPh₃)₄ (751 mg, 0.65 mmol) in THF (50 mL) was added. The mixture was stirred for 3 days, then quenched with saturated NaHCO_{3(aq)} (75 mL), and filtered through Celite. After removing the organic layer, the aqueous layer was washed with CHCl₃ (2 \times 20 mL), and the combined organic fractions were dried with MgSO₄. The crude material obtained following gravity filtration and removal of volatiles in vacuo was purified by column chromatography, giving a white solid. Yield: 111 mg (12%). ¹H NMR (CDCl₃) δ (ppm): 7.65 (m, 4H, H-6), 7.61 (s, 2H, H-1), 7.41 (m, 2 + 1H, H-7 + H-8). ${}^{13}C{}^{1}H$ NMR (CDCl₃) δ (ppm): 146.00 (s, C-2), 132.38 (s, C-6), 129.92 (s, C-1), 129.01 (s, C-8), 128.72 (s, C-7), 121.59 (s, C-5), 95.67 (s, C-3/4), 86.10 (C-3/4). HR-MS for C₂₀H₁₂N₂ (M⁺): 280.1000 (calcd.), 280.1001 (found).

Thermal ellipsoids are at the 50% probability level.

Synthesis of 3,6-bis(trimethyl-silylethynyl)pyridazine, 1d

$$Me_3Si \longrightarrow N=N$$
 $N=N$ $SiMe_3$

To a -78 °C solution of trimethylsilylacetylene (1.151 g, 11.7 mmol) in THF (50 mL) was added a solution of *n*-butyl lithium in hexanes (1.6 mol/L, 7.3 mL, 11.7 mmol). After stirring at this temperature for 1 h, a solution of ZnCl₂ (1.60 g, 11.7 mmol) in THF (50 mL) was transferred in via canula, and this mixture was stirred for another 45 min with the temperature maintained at -78 °C. The reaction mixture was then warmed to 25 °C, and a solution of 3,6-dichloropyridazine (436 mg, 2.9 mmol) and Pd(PPh₃)₄ (338 mg, 0.29 mmol) in THF (40 mL) was added. The mixture was stirred for 3 days at 35 °C and was then quenched with saturated NaHCO_{3(aq)} (75 mL) and filtered through Celite. After removing the organic layer, the aqueous layer was washed with CHCl₃ (2 \times 20 mL), and the combined organic fractions were dried with Na₂SO₄. The crude material obtained following gravity filtration and removal of volatiles in vacuo was purified by column chromatography (5% EtOAc in hexanes), giving a white solid. Yield: 135 mg (17%). ¹H NMR (CDCl₃) δ (ppm): 7.44 (s, 2H, H-1), 0.17 (s, 18H, -SiMe₃). ¹³C{¹H} NMR (CDCl₃) δ (ppm): 145.46 (s, C-2), 129.02 (s, C-1), 102.09 (s, C-3/4), 100.42 (C-3/4), -0.53 (s, SiMe₃). HR-MS for C₁₄H₂₀N₂Si₂ (M⁺): 272.1165 (calcd.), 272.1177 (found).

Synthesis of 3,6-bis(ethynyl)pyridazine, 1a



Desilylation of 3,6-bis(trimethyl-silylethynyl)pyridazine was accomplished by the addition of KOH_(aq) (0.99 mol/L, 1.0 mL, 0.98 mmol) to a solution of 1d (134 mg, 0.49 mmol) in MeOH (5 mL). After stirring for 1.5 h, the mixture was extracted into CHCl3 (20 mL) and washed with 6 mol/L HCl_(aq) (2 \times 10 mL). The organic layer was dried over MgSO₄, filtered, and the solvent removed in vacuo to give 1a as white crystals. Yield: 51 mg (81%). ¹H NMR (CDCl₃) δ (ppm): 7.56 (s, 2H, H-1), 3.52 (s, 2H, H-4). ¹³C{¹H} NMR (CDCl₃) δ (ppm): 145.50 (s, C-2), 129.45 (s, C-1), 83.86 (s, C-3/4), 79.72 (C-3/4). HR-MS for C₈H₄N₂ (M⁺): 128.0374 (calcd.), 128.0376 (found).

Synthesis/characterization of 3b



A solution of 2 (55 mg, 0.14 mmol) in toluene (1 mL) was added to a solution of 1b (32 mg, 0.13 mmol) in tol-

uene (5 mL) and stirred at 25 °C for 48 h. Volatiles were removed in vacuo, and the crude product was determined to be a mixture including the intermediate **3b** via ¹H NMR spectroscopy. ¹H NMR (C₆D₆) δ (ppm): 9.16 (s, 1H, H-2), 8.57 (s, 1H, H-15), 7.28 (d, 1H, ³J_{HH} = 8 Hz, H-13), 7.20 (s, 1H, H-4), 6.96 (d, 1H, ³J_{HH} = 8 Hz, H-12), 6.56 (s, 1H, H-7), 6.25 (d, 1H, ³J_{HH} = 8 Hz, H-10), 5.97 (d, 1H, ³J_{HH} = 8 Hz, H-9), 3.25 (t, 2H, ³J_{HH} = 8 Hz, C-17), 3.07 (s, 3H, C-3-Me), 3.04 (t, 2H, ³J_{HH} = 8 Hz, C-23), 2.81 (s, 3H, C-14-Me), 2.35 (m, 2H, H-18), 2.21 (m, 2H, H-24), ~1.41 (m, H-19), ~1.38 (m, H-25), 0.99 (t, 3H, ³J_{HH} = 8 Hz, C-20), 0.90 (t, 3H, ³J_{HH} = 8 Hz, C-26).

Attempted synthesis of 4a



A solution of **2** (157 mg, 0.40 mmol) in toluene (3 mL) was added to a solution of **1a** (51 mg, 0.40 mmol) in toluene (10 mL) and stirred at 25 °C for 48 h. Volatiles were removed in vacuo and the crude material was re-dissolved in toluene and transferred onto PtCl₂ (2 mg, 7 μ mol). The mixture was stirred at 95 °C for 24 h, after which volatiles were removed, and the brown material was purified by flash chromatography through neutral Al₂O₃. The Et₂O fraction was observed to fluoresce pink–red upon irradiation at 365 nm, but an insufficient quantity for NMR characterization was obtained. Yield: trace.

Synthesis of 4b



The crude material **3b** was re-dissolved in toluene and transferred onto PtCl₂ (2 mg, 7 μ mol). The mixture was stirred at 100 °C for 24 h, after which volatiles were removed, and the brown material was purified by flash chromatography through neutral Al₂O₃. Yield: 9 mg (17%).

UV–vis (ϵ (10⁴ L mol⁻¹ cm⁻¹), cyclohexane) λ_{max} (nm): 261, 324, 413, 458, 511. Fluorescence (cyclohexane) λ_{max} (nm): 621, 667; $\phi_f = 0.023$, $\tau_f = 23$ ns. ¹H NMR (CD₂Cl₂) δ (ppm): 9.46 (s, 2H, H-1/12), 8.58 (s, 2H, H-3/10), 8.53 (s, 2H, H-5/8), 8.03 (s, 2H, H-6/7), 3.62 (t, 4H, ³J_{HH} = 8 Hz, C-13), 3.11 (s, 6H, C-2/11-Me), 2.07 (m, 4H, H-14), 1.64 (m, 4H, H-15), 1.07 (t, 6H, ³J_{HH} = 8 Hz, C-16) ppm. ¹¹B{¹H} NMR (C₆D₆) δ (ppm): 21 (br s). HR-MS for C₃₂H₂₄B₂N₂ (M⁺): 418.27516 (calcd.), 418.27679 (found).

Synthesis of 4c



A solution of 2 (74 mg, 0.19 mmol) in toluene (1.5 mL) was added to a solution of 1c (50 mg, 0.18 mmol) in toluene (5 mL) and stirred at 45 °C for 48 h. Volatiles were removed in vacuo and the crude product was re-dissolved in toluene and transferred onto PtCl₂ (3 mg, 11 µmol). The mixture was stirred at 100 °C for 24 h, after which volatiles were removed, and the brown material was purified by flash chromatography through neutral Al₂O₃. Yield: 3 mg (3%). UV-vis (ϵ (10⁴ L mol⁻¹ cm⁻¹), cyclohexane) λ_{max} (nm): 421, 523, 625. Fluorescence (cyclohexane) λ_{max} (nm): 630, 676; $\phi_f = 0.015$, $\tau_f = 23$ ns. ¹H NMR (CD₂Cl₂) δ (ppm): 9.54 (s, 2H, H-1/12), 8.64 (s, 2H, H-3/10), 8.48 (s, 2H, H-5/8 or 6/7), 8.19 (s, 2H, H-5/8 or 6/7), 7.92 (d, 4H, ${}^{3}J_{HH} = 8$ Hz, H-14), (m, 4 + 2H, H-15 + H-16), 3.04 (s, 6H, C-2/11-Me). Cyclic voltammetry (vs. SCE) $E_{1/2}$ (THF): -1.57 (rev.) V. HR-MS for C₂₈H₃₂B₂N₂ (M⁺): 458.2126 (calcd.), 458.2109 (found).

X-ray crystallography

A deep-red – brown needle of C_{28} H_{32} B_2 N_2 was coated with Paratone 8277 oil (Exxon) and mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo K α radiation. Details of crystal data and structure refinement have been provided in Table 2. The data were collected¹⁹ using ω and ϕ scans. The data were corrected for Lorentz and polarization effects and for absorption using multi-scan method.²⁰

The structure was solved by the direct methods²¹ and expanded using Fourier techniques.²² The H atoms were included at geometrically idealized positions and were not allowed to refine. The final cycle of full-matrix least-squares refinement using SHELXL97²³ converged with unweighted

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Table 2. Crystal data and structure refinement for C₂₈H₃₂B₂N₂, 4b.

C ₂₈ H ₃₂ B ₂ N ₂
418.18
173(2) K
0.71073 Å
Monoclinic
P2/c
a = 12.473(5) Å
b = 10.189(7) Å
c = 9.339(8) Å
$\beta = 108.70(3)^{\circ}$
1124.2(13) Å ³
2
1.235 Mg/m ³
0.070 mm^{-1}
448
$0.32 \times 0.11 \times 0.10 \text{ mm}^3$
3.45 to 27.48°
$-16 \le h \le 16, -11 \le k \le 13, -12$ $\le l \le 12$
7866
2555 $[R_{(int)} = 0.0302]$
99.1%
Multi-scan method
0.9930 and 0.9779, respectively
Full-matrix least-squares on F^2
2555/0/147
1.040
$R_1 = 0.0531, wR_2 = 0.1288$
$R_1 = 0.0952, wR_2 = 0.1545$
0.270 and –0.195 e Å $^{-3}$

and weighted agreement factors, R = 0.0531 and wR =0.1545 (all data), respectively, and goodness of fit, S =1.040. The weighting scheme was based on counting statistics and the final difference Fourier map was essentially featureless. The figures were plotted with the aid of ORTEPII.24

Supplementary data

Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 5359. For more information on obtaining material, refer to cisti-icist.nrc-cnrc.gc.ca/cms/ unpub_e.shtml. CCDC 753114 (4b) contains the X-ray data in CIF format for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/ retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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