Synthesis and Properties of 2-(Dimesitylboryl)benzylideneamines

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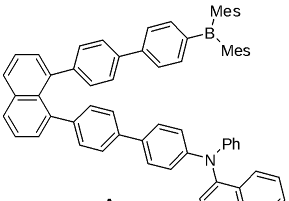
Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

Lithiation of 2-(2-bromophenyl)-dioxolane (**1**) followed by reaction with dimesitylboron fluoride afforded 2-(2-dimesitylborylphenyl)-dioxolane (**2**) which was deprotected to afford 2-dimesitylboryl-benzaldehyde (**3**). Compound **3** reacts with aliphatic amines such as *n*-butylamine and ethanolamine to afford the corresponding imines 2-(dimesitylboryl)benzylidenebutylamine (**4**) and 2-(dimesitylboryl)benzylideneethanolamine (**5**), respectively. Structural studies indicate coordination of the imine-nitrogen atom to the boron center. Imines **4** and **5** emit a green fluorescence near 510 nm with quantum yields approaching 10 %. TD-DFT calculations suggest that this emission arises from an intramolecular charge-transfer excited state.

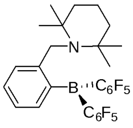
Key words: Boron, Fluorescence, Imine, Aldehyde

Introduction

The chemistry of triarylboranes has experienced a surge of interest because of the discovery of applications in the domain of optoelectronic and sensing [1 – 9]. The development of such applications often necessitates the combination of a triarylboron unit with another functionality. This point can be illustrated by recent efforts in the chemistry of boron-nitrogen compounds such as **A**, **B** and **C** [10 – 12] which have been used as fluoride turn-on sensors in the case of **A** [10], H_2 activating catalysts in the case of **B** [11], or fluorescent dyes in the case of **C** [12]. These advances have only been made possible by the discovery of high-yield synthetic routes that facilitate the incorporation of the triarylboron unit in the target derivatives. As part of our contribution to this area of synthetic chemistry, we have now decided to synthesize 2-dimesitylboryl-benzaldehyde and investigate its reactivity with primary amines. These investigations were further motivated by the fact that 2-diarylboryl-benzaldehyde derivatives have never been reported in the literature.



A



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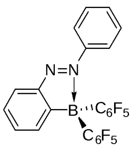
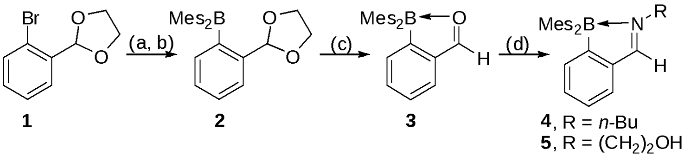


C

Results and Discussion

Lithiation of 2-(2-bromophenyl)-dioxolane (**1**) followed by reaction with dimesitylboron fluoride afforded 2-(2-dimesitylborylphenyl)-dioxolane (**2**) in 94 % yield (Scheme 1). Deprotection of the aldehyde functionality could be achieved by addition of concentrated HCl_{aq} to a THF solution of **2** to afford 2-dimesitylboryl-benzaldehyde (**3**) in 98 % yield (Scheme 1). Compound **3** is stable and can be stored at r. t. for extended periods of time. It has been characterized by NMR spectroscopy and mass spectrometry which allowed detection of the molecular peak at m/z = 355.8593 for $[M+H]^+$. The ^1H NMR spectrum features all expected resonances including a signal at δ = 9.69 ppm corresponding to the hydrogen atom of the aldehyde functionality. The ^{11}B NMR resonance detected at 25 ppm is significantly upfield when compared to that of **2** (75 ppm), thus suggesting that the oxygen atom of the aldehyde functionality is coordinated to the boron atom. A similar conclusion could be derived from the IR spectrum of **3** which displays a ν(co) at 1671 cm^{-1}, significantly shifted to lower energy when compared to that of benzaldehyde (ν(co) =



Scheme 1. a: *n*-BuLi, OEt_2; b: Mes_2BF; c: HCl, THF, H_2O; d: RNH_2.

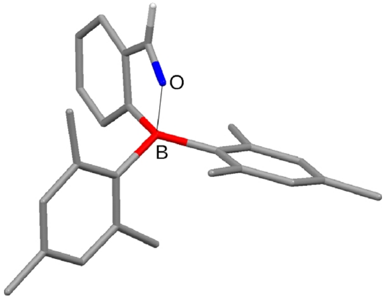


Fig. 1. DFT (B3LYP/6-31G(d)) optimized structure of **3**. H atoms (at the exception the aldehyde hydrogen) have been omitted for clarity.

Table 1. Crystal data, data collections, and structure refinements for **4** and **5**.

	4	**5**
Formula	$C_{29}H_{36}NB$	$C_{27}H_{32}NBO$
M_r	409.4	397.35
Crystal size, mm^3	$0.31 \times 0.22 \times 0.20$	$0.25 \times 0.20 \times 0.15$
Crystal system	tetragonal	monoclinic
Space group	$I4_1/a$	$P2_1$
a, Å	17.7182(2)	9.083(4)
b, Å	17.7182(2)	8.684(3)
c, Å	31.3604(8)	14.131(5)
β, deg	90	95.108(6)
V, Å^3	9845.1(3)	1110.2(7)
Z	16	2
ρ_{calcd}, g cm^{-3}	1.11	1.19
μ, mm^{-1}	0.1	0.1
$F(000)$, e	3552	428
Data collection		
T, K	173(2)	173(2)
Scan mode	ω	ω
hkl range	$-25 \le h \le 23$, $-25 \le k \le 24$, $-27 \le l \le 44$	$-11 \le h \le 11$, $-11 \le k \le 11$, $-18 \le l \le 17$
Refl. measured / unique	67367 / 7549	9325 / 4954
R_{int}	0.0818	0.0353
Reflections used for refinement	7549	4954
Parameters refined	281	271
$R1^a$, $wR2^b$ all data	0.1211/ 0.1733	0.0789/ 0.1564
GoF (F^2)	1.030	1.010
ρ_{fin} (max / min), e Å^{-3}	0.344 / −0.321	0.347 / −0.305

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [(\Sigma w(F_o^2 - F_c^2)^2) / (\Sigma w(F_o^2)^2)]^{1/2}$.

1700 cm^{-1}) [13]. While we could not obtain single crystals of this compound, a DFT geometry optimization at the B3LYP/6-31G(d) level of theory corroborates these observations and indicates the presence of a B–O dative bond of 1.66 Å length (Fig. 1). Interestingly, formation of this intramolecular dative bond does not restrict the reorientation of the mesityl groups, as indicated by the detection of a single ^{1}H NMR resonance for the *ortho*-methyl groups of the mesityl substituents.

Having confirmed the identity of **3**, we decided to survey its reaction chemistry. Compound **3** cleanly reacted with aliphatic primary amines such as *n*-butylamine and ethanolamine to afford imines **4** (96 % yield) and **5** (98 % yield), respectively (Scheme 1). By contrast, reactions with aromatic amines such as aniline failed to proceed cleanly. Imines **4** and **5** have been fully characterized. The ^{11}B NMR resonances of these two compounds are observed near 5 ppm, thus indicating coordination of the nitrogen to the boron atom. Formation of this dative bond leads to the existence of a rigid structure, as reflected by the appearance of broad multiple ^{1}H NMR resonances for the *ortho*-methyl and *para*-CH groups of the mesityl substituents. These observations suggest that, unlike in **3**, reorientation of the mesityl substituents about the C_{ipso}-boron bond of these derivatives is restricted. Presumably, the increased bulk and Lewis basicity of the imine functionality when compared to the aldehyde functionality are responsible for this difference.

The crystal structures of compounds **4** and **5** have been determined (Fig. 2, Table 1). In both cases, the imine nitrogen atom is coordinated to the boron center by N(1)–B(1) bond of 1.627(3) Å for **4** and 1.630(4) Å for **5**. These bond lengths, which can be compared to the value of 1.625 Å measured in **C**, suggest that the bulk and relative electron-richness of the Mes_2B moiety when compared to the $(C_6F_5)_2B$ moiety does not weaken the strength of the B–N dative bond. Formation of this bond leads to a noticeable pyramidalization of the boron atom, as indicated by the sum of the C–B–C angles of 340.9° for **4** and 341.2° for **5**.

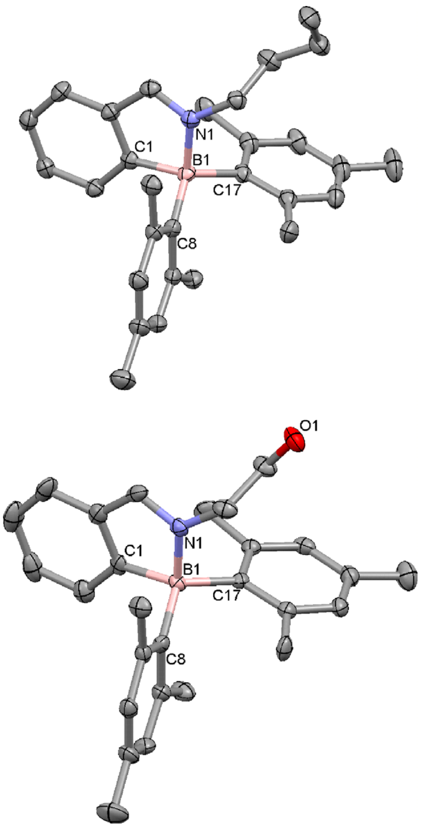
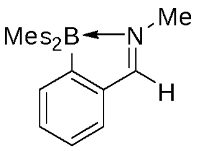


Fig. 2. Molecular structures of **4** (top) and **5** (bottom) in the crystal. Ellipsoids have been set at 50 % probability. H atoms are omitted for clarity. Pertinent metrical parameters can be found in the text and in the deposited CIF files.



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Since it is well known that rigid boron-containing heterocycles possess interesting photophysical properties [8, 12, 14 – 16], we have measured the absorption and emission spectra of **4** and **5**. The low-energy portion of both spectra features a relatively sharp absorption band near 280 nm followed by a broader feature centered around 350 nm (Fig. 3). TD-DFT calculations carried out at the B3LYP/6-31G(d) level of theory on the model compound **6** indicate that the low energy edge of the absorption spectrum is dominated by a HOMO-LUMO transition. Since the HOMO is localized on one mesityl ring while the LUMO is localized on the imine ligand (Fig. 4), this transition can be regarded as an intramolecular charge transfer (ICT) transition. This situation is reminiscent of that observed by Wang in the [2-(2-pyridyl)phenyl-*C*,*N*]dimesitylboron which features an ICT transition from the mesityl ligands to the phenyl-pyridyl ligand [17]. Under a hand-held UV lamp, both **4** and **5** display an intense green emission. Accordingly, their emission spectra display a broad band centered at 512 nm ($\lambda_{\text{excitation}}$ = 380 nm, Φ_{F} = 9.5 %) in the case of **4** and 504 nm in the case of **5** ($\lambda_{\text{excitation}}$ = 370 nm, Φ_{F} = 9.3 %; Fig. 3). Since simple benzalalkylimines are not fluorescent [18], the emissive properties of **4** and **5** are noteworthy and can most likely be assigned to the existence of this charge transfer excited state as well as the molecular rigidity arising from the chelate structure.

Experimental Section

2-(2-Bromophenyl)1,3-dioxolane (**1**) [19] was synthesized by the published procedures. 2-Bromobenzaldehyde (Alfa Aesar), ethanolamine (Alfa Aesar), ethylene glycol (EMD), *n*-butyl amine (Aldrich), 2-bromoaniline (Alfa Aesar), and a 1.9 M solution of *n*-butyllithium in hexane (Alfa Aesar) were purchased and used as received. Et_2O, THF and hexane were dried by reflux under N_2 over K. Air-sensitive compounds were handled under an argon atmosphere using standard Schlenk and glovebox techniques. IR spectra were recorded on an IR Affinity-1 FT IR spectrophotometer (Shimadzu). UV/Vis spectra were recorded on a Cary 100 Bio UV/Vis spectrophotometer, and fluorescence spectra were recorded on a Cary Eclipse spectrometer. Quantum yields were determined in reference to either anthracene or 1,4-bis(5-phenyloxazol-2-yl) benzene and corrected for solvent refractive index. Elemental analyses were performed at Atlantic Microlab (Norcross, GA). Mass spectra were obtained from the Mass Spectrometry Applications Laboratory at Texas A&M University. NMR spectra were recorded at ambient temperature on an Inova-400 FT NMR spectrometer (399.59 MHz for ^{1}H, 128.2 MHz for ^{11}B, and 100.48 MHz for ^{13}C). Spectra are internally referenced to Me_4Si (d^1H ($CDCl_3$) = 7.27; d^{13}C ($CDCl_3$) = 77.35) and externally referenced to $BF_3 \cdot OEt_2$ for $\delta^{11}B = 0$. The melting points were determined using a Melt II melting point apparatus equipped with a digital thermometer Omega (ΩE).

*2-(2-Dimesitylborylphenyl)-dioxolane (**2**)*

A 1.9 M solution of *n*-butyllithium in hexane (6.5 mL, 12 mmol) was added to a solution of 2-(2-bromophenyl)-1,3-dioxolane (**1**) (2.82 g, 12.3 mmol) in diethyl ether (50 mL) at 0 °C. After 1 h of stirring at 0 °C, the resulting white suspension was cooled to −78 °C. To this cooled suspen-

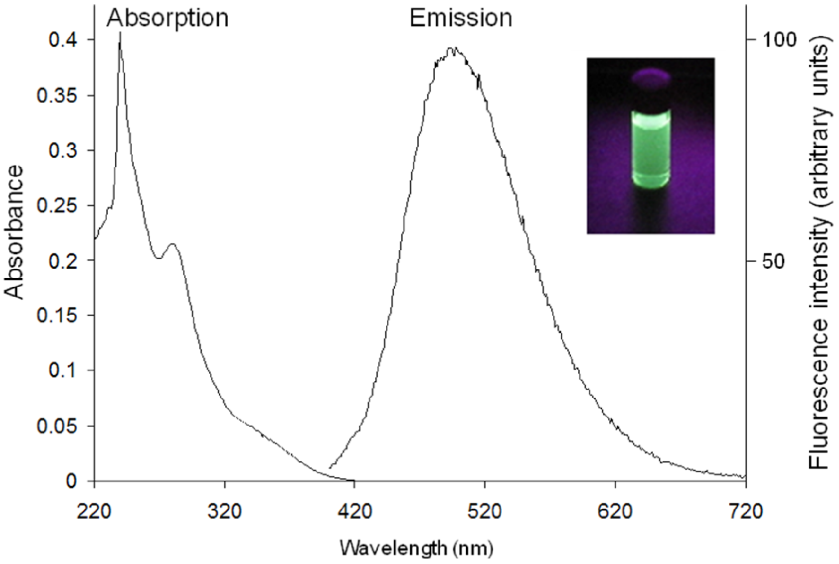

Fig. 3. UV/Vis absorption and fluorescence spectra of **4** in $CHCl_3$.

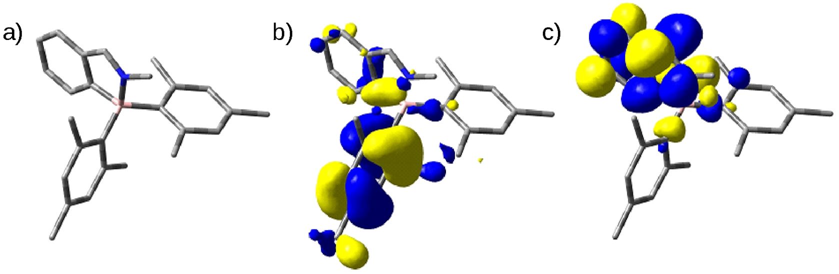

Fig. 4. Optimized structure of **6** (a), HOMO (b) and LUMO (c). Surfaces shown with an isodensity value of 0.03.

sion was added a solution of dimesitylboron fluoride (3.30 g, 12.3 mmol) in diethyl ether (30 mL). The resulting mixture was allowed to warm to r. t. and stirred overnight. The solvents were distilled off under reduced pressure leaving a solid residue which was suspended in hexane (30 mL). Filtration followed by evaporation of the solvent afforded compound **2** in a crude yield of 94 % (4.6 g). M. p. 112–114 °C. – ^{1}H NMR (399.59 MHz; $CDCl_3$): δ = 1.97 (s, 6H, CH_3-Mes), 2.25 (s, 12H, CH_3-Mes), 3.66 (br s, 2H, OCH_2), 3.82 (br s, 2H, OCH_2), 5.49 (s, 1H, O_2CH), 6.75 (s, 4H, H-Mes), 7.27 (s(b), 2H, CH), 7.41 (br s, 1H, CH), 7.60 (br s, 1H, CH). – ^{11}B{^{1}H} NMR (128.2 MHz; $CDCl_3$): δ = 73 ($w_{1/2}$ = 1282 Hz). – ^{13}C NMR (100.48 MHz; $CDCl_3$): δ = 21.5, 22.6, 23.4 (all CH_3-Mes), 64.9 (OCH_2), 102.8 (CH-O_2), 125.1, 128.6, 128.7, 128.9, 130.6 (all CH), 128.4, 134.5, 139.2, 141.2, 141.5 (all C_{ipso}). – HRMS ((+)-ESI): m/z = 398.2949 (calcd. 405.241 for $C_{27}H_{31}BO_2Li$, $[M+Li]^+$).

*2-(Dimesitylborane)benzaldehyde (**3**)*

To a stirred solution of **2** (0.23 g, 0.58 mmol) in THF (10 mL)/distilled water (2 mL) was added a 10 % HCl solution (0.6 mL). After 4 h of stirring, all solvents were removed under reduced pressure affording **3** as a pale-yellow solid in a crude yield of 98 % (0.20 g). M. p. 71–72 °C. – ^{1}H NMR (399.59 MHz; $CDCl_3$): δ = 2.00 (s, 12H, CH_3-Mes), 2.23 (s, 6H, CH_3-Mes), 6.72 (s, 4H, H-Mes), 7.41 (ddd, 1H, $^{3,4}J$ = 9.8, 7.6, 1.6 Hz, CH), 7.63 (ddd, 1H, $^{3,4}J$ = 9.8, 7.6, 1.6 Hz, CH), 7.97 (d, 1H, ^3J = 9.8 Hz, CH), 7.99 (d, 1H, ^3J = 9.8 Hz, CH), 9.69 (s, 1H, HCO). – ^{11}B{^{1}H} NMR (128.2 MHz; $CDCl_3$): δ = 25 ($w_{1/2}$ = 554 Hz). – ^{13}C NMR (100.48 MHz; $CDCl_3$): δ = 21.2 (CH_3-Mes), 24.7 (CH_3-Mes), 127.3, 128.6, 128.8, 129.7, 132.6 (all CH), 128.5, 135.7, 136.6, 138.7, 139.2, 141.2 (all C_{ipso}), 198.0 (CHO). – HRMS ((+)-ESI): m/z = 354.2434 (calcd. 377.2892 for $C_{25}H_{27}BONa$, $[M+Na]^+$). – HRMS ((+)-ESI): m/z = 354.2434 (calcd. 355.8593 for $C_{25}H_{27}BO$, $[M+H]^+$).

*2-(Dimesitylboryl)benzylidenebutylamine (**4**)*

To a stirred yellow solution of **3** (0.1 g, 0.28 mmol) in toluene (10 mL) at r. t. was added *n*-butylamine (0.04 g, 0.56 mmol). After 3 h, the reaction mixture was evaporated to dryness to afford compound **4** in a crude yield of 98 %

(0.20 g). Further purification was achieved by recrystallization from $CHCl_3$. M. p. 135 – 138 °C. – UV/Vis ($CHCl_3$): $\lambda_{max}(\lg\varepsilon_{max})$ = 240 nm (4.91). – ^1H NMR (399.59 MHz; $CDCl_3$): δ = 0.80 (t, 3H, ^3J = 7.2 Hz), 1.42 (br s, 4H, $2CH_2$), 1.85 (br s, 3H, CH_3-Mes), 2.00 (br s, 3H, CH_3-Mes), 2.19 (br s, 12H, CH_3-Mes), 3.78, 3.86 (s, s, 2H, CH_2), 6.513 (s, 1H, H-Mes), 6.59 (s, 1H, H-Mes), 6.76 (s, 2H, H-Mes), 7.19 (ddd, 1H, $^{3,4,5}J$ = 8.0, 7.6, 1.2 Hz, CH), 7.31 (ddd, 1H, $^{3,4,5}J$ = 8.0, 7.6, 1.2 Hz, CH), 7.63 (d, 1H, ^3J = 7.6 Hz, CH), 7.70 (d, 1H, ^3J = 7.2 Hz, CH), 8.48 (s, 1H, N=CH). – $^{11}B\{^1H\}$ NMR (128.2 MHz; $CDCl_3$): δ = 5 ($w_{1/2}$ = 253 Hz). – ^{13}C NMR (100.48 MHz; $CDCl_3$): δ = 13.8 (CH_3-Bu), 20.5, 32.4 ($2CH_2$), 52.1 (NCH_2), 21.0 (CH_3-Mes), 25.7 (CH_3-Mes), 125.2, 125.7, 129.5, 130.5, 131.0, 132.4 (all CH), 128.7, 133.3, 134.7, 136.9, 137.1, 141.4, 141.7, 143.7 (all C_{ipso}), 166.8 (C=N). – IR (film): ν = 3556, 2960, 2929, 2867, 1607, 1549, 1442, 1374 cm^{-1}. – HRMS ((+)-ESI): m/z = 409.414 (calcd. 410.4019 for $C_{29}H_{37}BN$, $[M+H]^+$). – $C_{29}H_{36}BN$ (409.4): calcd. C 85.08, H 8.86, N 3.42; found C 84.83, H 8.85, N 3.48.

*2-(Dimesitylboryl)benzylideneethanolamine (**5**)*

Compound **5** was prepared in the same way as **4** in a crude yield of 96 %. Further purification could also be achieved by recrystallization from $CHCl_3$. M. p. 190 – 192 °C. – UV/Vis ($CHCl_3$): $\lambda_{max}(\lg\varepsilon_{max})$ = 240 nm (4.70). – ^1H NMR (399.59 MHz; $CDCl_3$): δ = 1.92 (s, 3H, CH_3-Mes), 1.98 (s, 3H, CH_3-Mes), 2.19 (s, 12H, CH_3 CH_3-Mes), 2.75, 3.48 (s, s, 2H, CH_2), 4.05 (br s, 3H, CH_2 and OH), 6.51 (s, 1H, H-Mes), 6.61 (s, 1H, H-Mes), 6.73 (s, 1H, H-Mes), 6.77 (s, 1H, H-Mes), 7.20 (ddd, 1H, $^{3,4}J$ = 7.6, 7.2, 1.2 Hz, CH), 7.33 (ddd, 1H, $^{3,4}J$ = 7.6, 7.2, 1.2 Hz, CH), 7.66 (d, 1H, ^3J = 7.6 Hz, CH), 7.72 (d, 1H, ^3J = 7.6 Hz, CH), 8.67 (s, 1H, N=CH). – $^{11}B\{^1H\}$ NMR (128.2 MHz; $CDCl_3$): δ = 5 ($w_{1/2}$ = 273 Hz). – ^{13}C NMR (100.48 MHz; $CDCl_3$): δ = 21.0 (CH_3-Mes), 25.6, 25.7 ($2CH_3$-Mes), 54.7 (NCH_2), 61.7 (OCH_2), 125.2, 126.2, 129.6, 130.5, 130.8, 132.6 (all CH), 129.3, 133.3, 135.0, 136.8, 136.9, 141.3, 141.7, 143.9 (all C_{ipso}), 170.0 (C=N). – IR (film): ν = 3551, 2916, 1547, 1609, 1454, 1438, 1374 cm^{-1}. – HRMS ((+)-ESI): m/z = 397.414 (calcd. 398.251 for $C_{27}H_{33}BNO$, $[M+H]^+$). – $C_{27}H_{32}BNO$ (397.4): calcd. C 81.60, H 8.11, N 3.52; found C 81.36, H 8.23, N 3.61.

Crystallography

Details pertinent to the crystal structure determinations are listed in Table 1. The measurements were carried out using a Bruker Apex II-CCD area detector diffractometer with a graphite-monochromated MoK_α radiation (λ = 0.71073 Å). Crystals of appropriate size were selected and mounted onto a nylon loop with Apiezon grease. Structure solution was accomplished using Direct Methods, which successfully located most of the non-H atoms. Subsequent refinement on F^2 using the SHELXTL/PC package (version 5.1) [20] allowed the location of the remaining non-H atoms.

CCDC 741373 (**4**) and 741372 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Computational details

DFT geometry optimization and TD-DFT calculations were carried out at the B3LYP/6-31G(d) level of theory using the GAUSSIAN 03 suite of programs [21]. Frequency calculations carried out on the optimized structures confirmed the absence of imaginary frequencies.

Acknowledgement

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Note added in proof

After this work was submitted, a paper describing the synthesis of closely related 2-boryl-benzylideneamines has appeared [22].

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