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Synthesis, structure and anion binding properties of 1,8bis(dimesitylboryl)anthracene and its monoborylated analog

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Two boranes, 1-(dimesitylboryl)anthracene (1) and 1,8bis(dimesitylboryl)anthracene (2), have been synthesized with the spectrophysical properties showing how the inclusion of one or two boron atoms progressively perturbs the π -system of the anthracene. This is caused by conjugation of the π * orbitals with the vacant p-orbital on boron. Additionally, both 1 and 2 display effective fluoride and cyanide complexation in a 1:1 guest-host ratio, with the mono-borane 1 being particularly potent for cyanide binding, displaying a binding constant of 3 x 10⁷. Furthermore, both 1 and 2 possess interesting fluorescence properties as a result of the disrupted π -system leading to a blue shift of 1 and a red shift of 2 upon fluoride coordination.

Bifunctional boranes have attracted interest because of their ability to chelate anions¹ or activate small molecules.² The separation between the boron atoms influences the binding selectivity of these systems. The chelation of small monoanions is typically favoured in the case of diboranes that are based on the ortho-phenylene³ or 1,8-naphthalenediyl⁴ backbone. Such compounds have been used in a number of applications including anion sensing, ^{4b, c, 4e-g, i} small molecule activation^{2d, 3h,} $^{4h,\,5}$ and catalysis. $^{2a,\,3c,\,d,\,6}\,$ In the past few years, the synthesis of diboranes featuring a larger separation has attracted renewed interest. Building on the pioneering studies of Katz who investigated several decades ago the synthesis of 1,8anthracenediethynyl-bis(catechol boronate) (I) as a bidentate Lewis acid for the chelation of pyrimidines,⁷ several groups including ours have investigated the synthesis and properties of systems where two Lewis acidic diarylboryl moieties are separated by more than 4 Å.⁸ The Mitzel group recently described an analog of Katz's compound (II) in which the two boronate units are replaced by diphenylboryl moieties.⁹ This

simple permutation affords more Lewis acidic boron moieties as demonstrated by the formation of isolable complexes with tetramethylethylene diamine and pyrimidine. In parallel to these efforts, we have reported on the synthesis of related large-bite diboranes based on the 1,8-triptycenediyl and 1,8biphenylenediyl backbone.¹⁰ Our investigations of these systems have revealed that they are particularly well-suited for the complexation of the cyanide anion in a μ -1,2 fashion.^{10b} While carrying out these studies, it occurred to us that the related diborane based on the 1,8-anthracenediyl scaffold had not been considered.¹¹ In this paper, we fill this knowledge gap by describing the synthesis and properties of 1.8bis(dimesitylboryl)anthracene (2). We also report on the properties of 1-(dimesitylboryl)anthracene (1).



Figure 1. Selected examples of known large-bite diboranes.

To begin, 1,8-dibromoanthracene was targeted as the building block for further functionalisation, which could be synthesised in two steps in accordance with previously established literature methods.¹² From this point, both mono- and bifunctionalised anthracene derivatives **1** and **2** could be readily synthesised through functionalisation of one or both sites through lithiation and quenching with dimesitylboron fluoride in the necessary stoichiometries (Scheme 1). These compounds could be readily characterised by multinuclear NMR spectroscopy with the prevailing ¹¹B resonance appearing for both **1** and **2** as a broad singlet centred at $\delta \approx 75$ ppm as usually

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observed for such triarylboranes.^{8a, b, 10} Additionally the ¹H NMR spectrum of 1 features resonances at δ = 2.00 (12H) and 2.31 (6H) ppm for the methyl groups of the mesityl moiety, with the aryl mesityl protons appearing at δ = 6.80 (4H) ppm. Similar shifts are observed for $\boldsymbol{2}$ (δ = 1.83 (24H), 2.27 (12H) and 6.70 (8H) ppm however, the ortho-Me and meta-H groups show extensive line broadening as a result of restricted rotation about the juxtaposed boranes which is evident in the solid-state. Solid-state structures of both 1 and 2 could be measured using X-ray diffraction which confirmed the expected formulation (Figure 2). 1, which crystallises in the C2/c space group, adopts a propeller configuration as expected with angles about the central boron atom measuring between 116.1(3) and 122.5(3)° in a trigonal planar geometry. In the solid-state, 2 also crystallises in the C2/c space group with half of the molecule in the asymmetric unit. There is slightly more variation in the bond angles about the boron centre, between 114.8(2) and 123.9(2)° with the interstitial separation between the two boron atoms measuring 5.576(4) Å. This boron-boron separation is close to that observed in the triptycene-based system IV (5.559(4) Å).



Scheme 1. Synthetic overview for mono- and bis-boranes 1 and 2 adapted in part from literature methods.¹²⁻¹³ (a) KBr (4.5 equiv.), CuCl₂ (0.1 equiv.), H₃PO₄/PhNO₂ (1:4), reflux, 2 d; (b) Al(O*i*Pr)₃ (7 equiv.), cyclohexanol, reflux, 3 d; (c) *n*-butyllithium (2 equiv.), TMEDA (2.5 equiv.), THF, Mes₂BF (1 equiv.) 18 h; (d) *n*-butyllithium (2 equiv.), TMEDA (2.5 equiv.) THF, Mes₂BF (2 equiv.), 18 h.



Figure 2. Solid-state structures of 1 (top) and 2 (bottom). Hydrogen atoms omitted for clarity. Thermal ellipsoids drawn at 50%.

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electron reduction corresponding to the Pornation/6Paboroni centred radical.¹⁴ A prototypical example of such a behaviour is displayed by Mes₃B which is reduced at -2.73 V vs Fc⁺/Fc in THF.¹⁵ In the case of diboranes such as **III** and **IV**, two distinct waves are observed in line with the successive reduction of the two boron centers.¹⁰ We note in passing that a related behaviour is observed for 9,10-bis(dimesitylboryl)anthracene which is cleanly reduced into an isolable dianion.^{11b} The cyclic voltammograms of 1 and 2 show a much more complicated behaviour characterised by the absence of reversible processes. The first reduction wave appears at E_{1/2} -2.23 V and -2.31 V for 1 and 2, respectively. The potential measured for both compounds are close to one another which may appears surprising at first but which is consistent the fact that calculated LUMO energies are also virtually identical, differing by only 0.05 ev. For both compounds, the first reduction wave is quasireversible; it also appears at a potential that is substantially more anodic than that of simple triaryl boranes and close to the redox potential of simple anthracene derivatives.¹⁶ Hence, we assigned this first reduction to an anthracene-based process. This assignment is consistent with the LUMO of these derivatives which shows extensive participation of the backbone, with a contribution from the boron atoms. Scanning to more negative potentials indicates several subsequent irreversible processes that have not been assigned. The UV-vis spectrum of compound **1** displays two main low energy bands. The first one, centred at 328 nm is reminiscent of that observed for simple triaryl boranes such as trimesityl borane¹⁷ and is thus assigned to the boron centred chromophore, with the main transition having ligand-to-element-charge-transfer character. The second band centred at 407 nm shows three vibronic features that closely resemble the 0-0, 0-1 and 0-2 vibronic bands of anthracene both in terms of respective intensity and energy spacing (1203-1624 cm⁻¹ vs. 1478 cm⁻¹ for anthracene). On this basis, this band is assigned to the $S_0 \rightarrow S_1$ transition of the anthryl chromophore which has π -to- π^* character. However, the energy of this band is redshifted with respect to that of anthracene. This redshift can be quantitatively analysed based on the 0-0 vibronic band which is centred at 407 nm in 1 vs 378 nm in anthracene. We rationalise this 1885 cm⁻¹ redshift is due to the presence of the boron atom, the empty p-orbital of which conjugates with the π^* of the anthryl group, lowering its energy. The spectrum of 2 again features a low energy band whose vibronic features are less distinct but suggests an assignment to the $S_0 \rightarrow S_1$ transition of the anthryl chromophore. This band is further redshifted with respect to that of the pure hydrocarbon (419 nm (2) vs 378 nm (anthracene)), as could be expected with additional $p\text{-}\pi^*$ conjugation arising from the presence of a second chromophore. The features observed at higher energy, past 370 nm, are less readily assignable than in the case of 1 but probably involve the boron-centred chromophores.

Time dependent density functional theory (TD-DFT) calculations reinforce the posited transitions outlined above whereby a dominant vertical excitation at 416 nm and 421 nm is noted for 1 and 2 respectively, which satisfactorily coincide with those observed experimentally for the 0-0 transitions at

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406 nm (1) and 419 nm (2). The *in silico* results also reinforce the proposed π -to- π^* (HOMO- \rightarrow LUMO) transition of the anthryl unit which is perturbed by the appended boron atoms, as seen by the mixing of the vacant p-orbital on boron and the anthracene π -system, comprising the LUMO. These TD-DFT calculations also suggest that the band at higher energy (calculated: 344 nm for 1 and 351 nm for 2, observed: 325 nm for 1 and 332 nm for 2) correspond to the HOMO-1 \rightarrow LUMO transitions which involves charge-transfer from the mesityl groups to the borylated anthracene moiety (Figure 3).



Figure 3. Depiction of LUMO, HOMO and HOMO-1 molecular orbitals of 1 (left) and 2 (right). Isosurface value = 0.03.

Building on the seminal work carried out on tris(9anthryl)borane as a fluoride receptor,¹⁸ the photophysical responses of 1 and 2 to fluoride were investigated via UV-vis. titration studies. Incremental addition of a TBAF solution to 1 in CH₂Cl₂ shows uniform conversion to a new absorbance spectrum (Figure 4). The titration data could be fitted to a 1:1 binding isotherm in both cases which is consistent with NMR spectroscopic evidence of a 1:1 binding mode. Equilibrium constants could be extracted from these data which were determined as K (F⁻) = 7 x 10⁶ M⁻¹ for **1** and 4 x 10⁶ M⁻¹ for **2**. This binding mode was further verified via mass spectrometry, particularly for 2, whereby a signal was detected at m/z = 693.4249 (calc. = 693.4245) for the parent ion of [2-F]⁻with the corresponding m/z signal at 356.2117 for the bis-functionalised $[2-F_2]^{2-}$ not being detected. With this encouraging information to hand, attention was shifted to the cyanide anion to observe as to whether diatomics could also be captured by these systems. In a similar process, addition of increasing equivalents of TBACN in THF led to a new absorbance profile in the UV-vis. spectrum for the posited complexes [1-CN]⁻ and [2-CN]⁻ closely resembling that of the fluoride adducts. Extracting equilibrium constants from these data established that 1 is particularly potent in cyanide binding with K (CN⁻) = 3 x 10^7 M⁻¹. Interestingly, the bifunctional derivative 2 was over an order of magnitude less effective at cyanide complexation with a binding constant of K (CN⁻) = 9 x 10⁵ M⁻¹ (see supporting information). This may be as a result of steric crowding about the boron centre precluding effective binding of larger diatomics. The similarity of the spectra obtained with fluoride and cyanide indicates that the cyanide anion in [**2**-CN]⁻ is not bridging the two boron centers. Bearing in mind that a bridging cyanide anion was observed in the case of [**III**-CN]⁻ and [**IV**-CN]⁻,^{10b} we propose that C-H unit at the 9 position of the anthracenediyl backbone of **2** hinders this binding mode.



Figure 4. Changes in UV-vis. absorbance spectra and cyanide binding isotherms of 1 (left) and 2 (right) upon titration with TBAF. Conducted at a concentration of 60 μ M in THF. Isotherms measured at λ_{max} = 388 nm (1) and 398 nm (2).

Again, mass spectrometry supports a similar 1:1 binding mode with the parent ion $[2-CN]^-$ being detected at m/z = 700.4300(calc. = 700.4291). It is also noteworthy that upon fluoride or cyanide binding to the monofunctionalised derivative 1, the resulting UV-vis. spectra closely resemble that of the native unfunctionalised anthracene backbone, confirming population of the vacant boron p-orbital by donation of an electron pair from the incoming anion. This effect is also readily detectable with the naked eye, with a distinct blue shift of the colour from deep yellow to light yellow upon conversion from 1 to [1-F]⁻. This is also supported by theoretical studies showing how addition of fluoride to 1 removes the borane from the conjugated system producing essentially idealised frontier molecular orbitals on anthracene (Figure 5). By contrast, conversion of 2 into [2-F]⁻ leads to the appearance of a redshifted absorption band. This band is assigned to an anthracene π -to-borane charge transfer band, as supported by the fact that the HOMO of the anionic complex has dominant anthracene character while the LUMO shows high boron p-orbital character (Figure 5). The spectral changes observed upon cyanide complexation are proposed to have the same origin.

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Figure 5. Depiction of frontier molecular orbitals of $[1-F]^-$ (left) and $[2-F]^-$ (right). Isosurface value = 0.03.

TD-DFT studies corroborate these findings with a dominant vertical excitation being noted at 383 nm for $[1-F]^-$ which is in approximate agreement with the 0-0 π -to- π * transition observed experimentally at 399 nm. Similarly, $[2-F]^-$ shows a theoretical excitation from TD-DFT calculations at 446 nm for the anthracene π -to-borane charge transfer band with the experimental data giving a broad absorbance band centred at 435 nm.

Finally, both 1 and 2 are fluorescent and display quantum yields (QY) of 0.41 and 0.23, respectively. The small Stokes shift measured suggest that these compounds emit from the S_0 - S_1 state which can be viewed as an anthracene π - π * excited state, perturbed by the trivalent boron atoms. In line with this view, neutralisation of the unsaturated boron centre by anion coordination as in [1-F]⁻ and [2-F]⁻, leads to some drastic changes. For 1, the emission profile and energy, becomes almost identical to that of pure anthracene as expected by removal of the boron-caused disruption. Interestingly, in the case of 2, a red shift rather than a blue shift is observed (Figure 6). The red shift of this emission is consistent with the red shift observed in the UV-vis spectrum of 2 upon anion binding. Accordingly, we assign this emission to an intramolecular electron-rich anthracene π -to-borane charge transfer excited state, the emission of which falls in the green part of the spectrum (QY = 0.31). Such a behaviour is reminiscent of that observed for related bifunctional diboranes upon coordination of an anion to one of the two boron centers.^{8b, 19}



Figure 6. Fluorescence emission spectra of 1 (left) and 2 (right) upon fluoride binding and their respective colour changes when irradiated with UV light.

Conclusions

The mono- and bis-functionalised anthracene derivatives 1- and 2 have been synthesised. UV-vis studies into these compounds reveal how progressive depletion of electron density of the anthracene backbone results in a red-shift of the $\pi-\pi*$ transition. This is achieved by virtue of increasing p- π * conjugation through the addition of one or two boryl units. These findings are supported by theoretical calculations using TD-DFT methods which confirm the HOMO-LUMO excitation of the anthracene π to π * transition which is perturbed by the inclusion of the Lewis acidic boron atoms. Anion responses of 1 and 2 show the affinity of the monofunctionalised species toward both fluoride and cyanide. Interestingly, steric crowding in 2 results in lower affinity for the diatomic cyanide anion. Subsequent fluorescence studies outline some interesting differences in the emission profiles of 1 and 2. Whereas a blueshift in the emission spectrum of 1 is observed upon fluoride association, that of 2 displays an unexpected red-shift resulting from an electron-rich anthracene π -to-borane charge transfer excited state.

Experimental

General considerations

All reactions and manipulations were carried out under an atmosphere of dry, O2-free nitrogen using standard double-manifold techniques with a rotary oil pump unless otherwise stated. A nitrogen-filled glove box was used to manipulate solids including the storage of starting materials, room temperature reactions, product recovery and sample preparation for analysis. All solvents were dried by passing through an alumina column (pentane and CH₂Cl₂) or by refluxing under N₂ over Na/K (Et₂O and THF) and stored under a nitrogen atmosphere over 3 Å molecular sieves. Deuterated solvents were distilled and/or dried over molecular sieves before use. Chemicals were purchased from commercial suppliers and used as received. 1,8-dibromo-4a,9adihydroanthracene-9,10-dione and 1,8-dibromoanthracene were synthesised according to the literature with the spectral analyses being consistent with literature established values.¹² ¹H, ¹³C and ¹¹B NMR spectra were recorded on either a Bruker Avance II 400 or Bruker Avance 500 spectrometer. Chemical shifts are expressed as parts per million (ppm, δ) downfield of tetramethylsilane (TMS) and are referenced to CDCl₃ (7.26/77.16 ppm) as internal standards. NMR spectra were referenced to BF3·Et2O/CDCl3 (11B). The description of signals includes: s = singlet, d = doublet, t = triplet, m = multiplet and br. = broad. All coupling constants are absolute values and are expressed in Hertz (Hz). UV-vis spectra were recorded on a Shimadzu UV-2501PC utilising a dual halogen/deuterium light source. Mass spectrometry analyses were performed in-house at the Center for Mass Spectrometry.

Synthesis of 1-dimesitylborylanthracene (1)

n-BuLi (2.5 M in hexanes, 0.77 mL, 1.79 mmol, 2 equiv.) was added to a solution of 1,8-dibromoanthracene (0.3 g, 0.89 mmol, 1 equiv.) and TMEDA (0.34 mL, 2.23 mmol, 2.5 equiv.) in THF (5 mL) at -78 °C. After stirring for 1 hour at this temperature, the resulting mixture was treated with Mes₂BF (0.27 g, 1.02 mmol, 1 equiv.) left to warm to room temperature for 18 hrs. At this time, sat. NH₄Cl solution was added to quench the reaction and the aqueous phase was washed with CH₂Cl₂ (2 x 5 mL). The organic phases were combined, dried over MgSO₄ and

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concentrated to a yellow/orange oil. Washing this oil with MeOH (2 x 2 mL) afforded a yellow powder which was crystallised by layering a saturated CH₂Cl₂ solution with MeOH. Yield: 169 mg, 0.39 mmol, 44%. ¹H NMR (400 MHz, CDCl₃, 298 K) δ /ppm: 8.38 (d, J_{HH} = 21.1 Hz, 2H, anth-H), 8.08 (d, J_{HH} = 8.4 Hz, 1H, anth-H), 7.96 (d, J_{HH} = 8.4 Hz, 1H, anth-H), 7.59 (d, J_{HH} = 8.4 Hz, 1H, anth-H), 7.52 (d, J_{HH} = 6.4 Hz, 1H, anth-H), 7.30–7.46 (m, 3H, anth-H), 6.80 (s, 4H, Mes-H), 2.31 (s, 6H, *p*-Me), 2.00 (s, 12H, *o*-Me). ¹³C NMR (101 MHz, CDCl₃, 298 K) δ /ppm 140.8 (s), 139.1 (s), 134.8 (s), 133.7 (s), 132.4 (s), 131.8 (s), 131.8 (s), 131.5 (s), 129.0 (s), 2.33 (s), 21.4 (s). Resonances for carbons bound to boron are not observed. ¹¹B NMR (128 MHz, CDCl₃, 298 K) δ /ppm: 74.9 (br. s). HRMS (APCl⁺) *m/z* calculated for [C₃₂H₃₂B]⁺: 427.2592, found: 427.2588.

Synthesis of 1,8-bis(dimesitylboryl)anthracene (2)

n-BuLi (2.5 M in hexanes, 0.77 mL, 1.79 mmol, 2 equiv.) was added to a solution of 1,8-dibromoanthracene (0.3 g, 0.89 mmol, 1 equiv.) and TMEDA (0.34 mL, 2.23 mmol, 2.5 equiv.) in THF (5 mL) at -78 °C. After stirring for 1 hour at this temperature, the resulting mixture was treated with Mes_2BF (0.55 g, 2.05 mmol, 2 equiv.) left to warm to room temperature for 18 hrs. At this time, sat. NH₄Cl solution was added to quench the reaction and the aqueous phase was washed with CH_2Cl_2 (2 x 5 mL). The organic phases were combined, dried over MgSO₄ and concentrated to a yellow/orange oil. Washing this oil with MeOH (2 x 2 mL) afforded a yellow powder which was crystallised by layering a saturated CH₂Cl₂ solution with MeOH. Yield: 244 mg, 0.36 mmol, 40%. ¹H NMR (400 MHz, CDCl₃, 298 K) δ/ppm: 8.45 (d, J_{HH} = 14.6 Hz, 2H, anth-H), 8.05 (d, J_{HH} = 7.4 Hz, 2H, anth-H), 7.30–7.38 (m, 4H, anth-H), 6.70 (s, 8H, Mes-H), 2.27 (s, 12H, p-Me), 1.83 (s, 24H, o-Me). 13C NMR (101 MHz, CD₂Cl₂, 298 K) δ/ppm: 151.2 (s), 141.8 (s), 139.7 (s), 134.7 (s), 134.1 (s), 132.5 (s), 132.0 (s), 129.1 (s), 128.3 (s), 128.1 (s), 125.7 (s), 23.4 (s), 21.6 (s). ¹¹B NMR (128 MHz, CDCl₃, 298 K) δ/ppm: 74.6 (br. s). HRMS (APCI⁺) *m*/*z* calculated for [C₅₀H₅₃B₂]⁺: 675.4328, found: 675.4333.

X-ray crystallography

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The crystallographic measurements were performed at 110(2) K using a Bruker APEX-II CCD area detector diffractometer (Mo–K α radiation, λ = 0.71069 Å). For both **1** and **2**, a specimen of suitable size and quality was selected and mounted onto a nylon loop. Semi-empirical absorption corrections were applied. The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement using a difference map on F^2 using the SHELXTL/PC package (version 6.1) allowed location of the remaining non-hydrogen atoms which were refined anisotropically. H atoms were added at calculated positions using a riding model.

Theoretical

Using the X-ray solid-state structures of complexes **1** and **2**, optimizations of **1**, **2**, $[1-F]^-$ and $[2-F]^-$ using DFT methods were implemented in Gaussian 09 using the M06-2X functional and mixed basis set F/B: 6-31+G(d'), C/H: 6-31G(d'). Frequency calculations performed using the same level of theory on the optimised geometries found no imaginary frequencies. Time-dependent DFT (TD-DFT) calculations were conducted on the geometry optimised structures using MPW1PW91 functional and same basis sets as before using a polarisable continuum model with tetrahydrofuran as the solvent.

Cyclic voltammetry

Electrochemical experiments were performed with an electrochemical analyser from CH Instruments (model 610A) with a glassy-carbon working electrode and a platinum auxiliary electrode. The reference electrode was built from a silver wire inserted into a small glass tube fitted with a porous Vycor frit at the tip and filled with a THF solution containing tetrabutylammonium hexafluorophosphate (TBAPF₆, 0.1 M) and AgNO₃ (5 mM). All three electrodes were immersed in a deoxygenated THF solution (5 mL) containing TBAPF₆ (0.1 M) as a support electrolyte and the compound to be analysed. Ferrocene was used as an internal standard and all potentials are reported with respect to $E_{1/2}$ of the Fc/Fc⁺ redox couple. All voltammograms were recorded at a scan rate of 200 mv/s.

Spectroscopy

UV-vis. spectrophotometric titrations of **1** and **2** with tetrabutylammonium fluoride trihydrate and tetrabutylammonium cyanide were carried out in tetrahydrofuran. 3 mL of a 6 x 10⁻⁵ M stock solution of the borane was prepared and treated with 2 μ L aliquots of the anion at the appropriate concentrations. Fluorescence measurements were taken on samples in capped quartz cuvettes under air on a PTI QuantaMaster spectrofluorometer with entrance and exit slit widths of 2 nm. Quantum yield measurements of **1**, **2** and [**2**-F]⁻ were referenced against the emission spectra of anthracene in cyclohexane.

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Conflicts of interest

There are no conflicts to declare.

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1,8- bis(dimesitylboryl)anthracene binds the toxic fluoride and cyanide anion to afford the corresponding 1:1 complexes that display a red shifted emission in the green pact or the spectrum.