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Introduction

Over the past two decades, organic electronic materials have attracted increasing attention owing to their applications as diverse as sensors,¹ field-effect transistors,² photovoltaics,^{3,4} lasers⁵ and light-emitting diodes.^{6,7} Plastic electronics possess the major advantage over silicon-semiconductor technology that organic compounds are highly tuneable. Research into structure–property relationships is therefore the key to the improvement of critical features both of the underlying molecular species and of the (semi)conducting bulk systems, *viz.* optical absorption and emission characteristics or charge generation, recombination and transport issues. The field has consequently developed into a wide academic and industrial playground for many interacting research disciplines including

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Effects of boron doping on the structural and optoelectronic properties of 9,10-diarylanthracenes†

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Key structural and optoelectronic properties of 9,10-dihydro-9,10-diboraanthracene (DBA) derivatives carrying mesityl (2a), 2-methylnaphthyl- (2b) and 9-phenyl-2,7-di-tert-butylanthryl (2c) substituents at the boron atoms have systematically been compared with the properties of their all-carbon congeners 4a-c. The experimental investigations have been augmented by guantum-chemical calculations. Steric repulsion leads to large dihedral angles between the aryl substituents and the DBA (2a-c) or anthrylene (4a-c) cores; as a result, the B-C bonds of 2a-c are kinetically shielded from hydrolysis and oxidative degradation. Lithium metal reduces the mesityl derivative 2a to the inverse sandwich complexes $[Li(OR_2)_n]_2$ [2a] (X-ray crystallography; OR₂ = THF, n = 2; Et₂O, n = 1). In line with the nodal structures of the LUMO of 2a/HOMO of $[Li(THF)_2]_2[2a]$, the C–C bond lengths of the anionic fragment $[2a]^{2-}$ show characteristic differences to those of 2a and come close to the C-C bond lengths of the isoelectronic species 4a. X-ray crystallography on anti-2b \times 2 C₆H₆ and anti-4b \times 2 C₆H₆ reveals an essentially identical packing of the main molecules. The benzene solvate molecules, however, interact in a very different manner with anti-2b or anti-4b, which can be traced down to subtle disparities between the electron density distributions of the two compounds. 2a-c undergo a photoinduced aryl-to-DBA charge transfer; the back electron transfer results in blue (2a), green (2b) and red (2c) emission, albeit with low quantum yields. 4a-c are characterised by a local π - π^* photoexcitation of the central 9,10-anthrylene fragments and corresponding blue emission. Each of the compounds 2a-c gives rise to two reversible DBA-centred one-electron transitions in the cyclic voltammogram.

> preparative and computational chemistry, materials science and device physics. From a chemist's view, particularly exciting perspectives are offered by the incorporation of main-group elements, like B,8 Si,9 N,10 P11 or S,12 into the carbon frameworks of functional molecular building blocks. Detailed studies, however, in which the optoelectronic properties of a specific all-carbon system have been thoroughly characterised and compared with those of an isostructural/isoelectronic organo-element congener are lacking. The objective of this paper is therefore to provide a quantitative evaluation of the crystal-structure changes and the modifications in the optoelectronic behaviour experienced by a series of oligoacenes upon boron doping. Our aim is to systematically identify the ingredients available for the rational design of molecular building blocks in order to develop optimised materials for a given purpose.

> We have selected anthracene derivatives for our investigations as those have become benchmark materials for organic light-emitting devices (OLEDs) due to their high oxidation potential, small π surface and good fluorescence quantum yield ($\phi_{\rm F}$).¹³ While $\phi_{\rm F}$ of pristine anthracene is only moderate (0.27; C₆H₆),¹⁴ an introduction of phenyl rings into

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the 9,10-position of the molecular scaffold results in a dramatically improved performance ($\phi_{\rm F} = 0.96$; C₆H₆).¹⁵ In fact, 9,10diphenylanthracene is frequently used as a reference standard in chemiluminescence studies.^{16,17}

In 9,10-diphenylanthracene, steric repulsion between the phenyl rings and the hydrogen atoms in the peri-positions of the anthracene core results in a dihedral angle Ph//Anth of 67.8° (solid-state structure; Anth = 9,10-anthrylene).¹⁸ Even though any significant π -conjugation between the two fragments is consequently interrupted, the presence of the two phenyl rings causes the system of singlet levels to drop in energy while the triplet levels rise such that only the $T_{\pi\pi^*}^1$ level still lies below the $S^1_{\pi\pi^*}$ level. The resulting decrease in the value of the intersystem crossing rate constant K_{st} explains the concomitant increase in $\phi_{\rm F}$ for 9,10-diphenylanthracene compared to anthracene.¹⁹ Moreover, the orthogonal phenyl substituents help to avoid π stacking in the solid state where intermolecular electronic interactions can lead to undesired fluorescence line-broadening and quenching phenomena.¹³ Further development of the field will therefore hinge on the identification of the best-suited 9,10-substituents for a given purpose, but also on an optimisation of the anthracenes' HOMO/LUMO energies.

Generally speaking, many π -electron materials are characterised by low electron affinities and thus behave as hole-transport materials (p-type semiconductors). However, for the fabrication of efficient devices, also electron-transport materials are of great significance (n-type semiconductors).²⁰ In the present context, one seeks the perfect match between the LUMO energy of an OLED emitter and the Fermi level of the cathode or between the HOMO energy and the Fermi level of the anode in order to facilitate the injection of charge carriers into the emissive layer.¹⁶

A widely used tool to increase the electron affinities of acenes is (per)fluorination.²¹⁻²³ As an added value, fluorination can lead to improved stability for devices operating under ambient conditions.²⁴ Alternatively, electron-poor heterocycles have been employed as building blocks of n-type materials (e.g., benzothiadiazoles, pyridines, quinolines).⁶ Our group uses boron heterocycles to create electron-deficient π systems, because a boron atom is isoelectronic with a carbenium ion and the vacant p orbital of a three-coordinate boron centre efficiently extends the conjugation pathway of an adjacent π -electron cloud.²⁵ In particular, we are developderivatives of 9,10-dihydro-9,10-diboraanthracene ing $(DBA),^{26-30}$ which outstanding optoelectronic possess properties.28,31-33

A challenge generally encountered with organoboranes is their sensitivity towards air and moisture. Common solutions of this problem are stabilisation of the molecules by (i) sterically demanding substituents³⁴ or (ii) incorporation of the boron atom into a rigid, planar framework.³⁵ In the first case, the access of an H₂O molecule to the vacant boron p orbital is prevented; in the second case, structural constraint energetically disfavours pyramidalisation of the boron centre in a putative R₃B–OH₂ adduct. Herein, we will be combining both approaches. On the one hand, DBA provides a comparatively rigid molecular scaffold. On the other hand, the 9,10-substituents that are needed anyway to break up undesired aggregation in the solid state (*cf.* the research on the related all-carbon systems mentioned above) can simultaneously serve to kinetically protect the organoborane from hydrolytic degradation. Moreover, we found indications that the emission colour of DBA fluorophores is influenced by the nature of 9,10-aryl substituents,³² which provides a useful set-screw for the targeted design of water-resistant 9,10-diaryl-DBA luminophores.

For the present study, we thus selected DBA derivatives bearing three different aryl groups in the 9,10-positions, *i.e.*, substituted phenyl (2a), 1-naphthyl (2b) and 9-anthryl (2c; Fig. 1) and investigated the influence of these groups on the optoelectronic properties of the materials. We then compared the DBA species 2a-c with their 9,10-anthrylene analogues 4a-c.

The strong general correlation between film quality/crystallinity and device performance suggests that the intermolecular interaction in the solid state is also a key parameter to consider in the development of novel organic optoelectronic



Fig. 1 DBA derivatives **2a–c** bearing substituted phenyl, 1-naphthyl and 9-anthryl groups. **2b** exists as a mixture of *syn/anti-*isomers. The methyl groups in **2a** and **2b** were attached for improved kinetic stabilisation; the *t*Bu groups and the phenyl rings in **2c** were introduced for solubility reasons and to facilitate the synthesis. The red-coloured fragments illustrate the similar degree of shielding exerted by *o*-methyl groups and annelated benzene rings.

materials.¹³ Given that **2a–c** offer the rare opportunity to put boron-doped π systems side by side with their isostructural organic congeners, we have also compared the crystal packing of *anti-***2b** and *anti-***9**,10-bis(2'-methylnaphthyl)anthracene (*anti-***4b**). We traced the observed differences to subtle disparities between the electron density distributions. Finally, the capacities of DBAs to reversibly accept electrons were explored by cyclic voltammetry as well as reduction on a preparative scale; the π -electron density distributions in **2a** and the isoelectronic couple [**2a**]^{2–}/**4a** were assessed by ¹³C{¹H}</sup> NMR spectroscopy and quantum-chemical calculations.

Results and discussion

Fig. 1 compiles the DBA derivatives under investigation here. We have used 9,10-dimesityl-DBA (2a) rather than 9,10-diphenyl-DBA to achieve optimal steric shielding of the boron p orbitals. For the same reason, 9,10-di(1'-naphthyl)-DBA was equipped with two methyl substituents (*cf.* 2b). The red-coloured fragments in Fig. 1 illustrate the similar degree of shielding that can be achieved through the introduction of *o*-methyl groups and annelated benzene rings. The *tert*-butyl groups in 2c are required for solubility reasons; the sole task of the phenyl rings was to facilitate the synthesis.^{32,36} To ensure maximum comparability, the all-carbon analogues 4a–c were equipped with precisely the same substitution patterns as 2a–c (Scheme 1).

Syntheses of the 9,10-dihydro-9,10-diboraanthracenes and their all-carbon analogues

The mesityl- (2a),³⁷ 2-methylnaphthyl- (2b) and 9-phenyl-2,7di-*tert*-butylanthryl-substituted $(2c)^{32}$ DBAs were synthesised from 9,10-dibromo-DBA $(1)^{28}$ and the respective organomagnesium (2a, 2b) or organolithium (2c) reagents through nucleophilic substitution reactions (Scheme 1). The corresponding all-carbon analogues **4a**–**c** are accessible by treating the appropriate aryllithium compound with 9,10-anthraquinone (3), followed by reduction of the resulting lithium alcoholate with SnCl₂–HCl³⁸ or H₃PO₂–HI–CH₃COOH³⁹ (Scheme 1).

Addition of excess lithium to 9,10-dimesityl-DBA (2a) in ethereal solvents yields the red-orange lithium salt $Li_2[2a]$ (Scheme 2), its dianion $[2a]^{2-}$ being isoelectronic with 9,10-dimesitylanthracene 4a.

For all the compounds **2a**, **2c**, **4a**, **4c** and Li₂[**2a**], the proton integral values as well as the number of resonances in the ¹H and ¹³C{¹H} NMR spectra are in accord with the proposed 9,10-disubstituted framework and the molecular symmetry resulting from it. A peculiarity is, however, observed for the 2-methylnaphthyl derivatives **2b** and **4b**, which give rise to *two* complete sets of ¹H and ¹³C{¹H} NMR signals. The reason lies in a hindered rotation about the exocyclic B–C or C–C bonds⁴⁰ leading to the formation of atropisomers *syn/anti-***2b** (1:1 ratio) or *syn/anti-***4b** (1:1 ratio). Isomer *syn-***2b** is expected to possess a higher dipole moment than *anti-***2b** (*cf.* a related study on 9,10-di(1'-naphthyl)anthracene).⁴⁰ Nevertheless, even



Scheme 1 Synthesis of compounds **2a–c** and **4a–c**. Reagents and conditions: **2a**: +2 MesMgBr, toluene, 0 °C \rightarrow r.t., 12 h; **2b**: +2 (2-methylnaphthyl)MgBr, Et₂O–toluene, 0 °C \rightarrow r.t., 12 h; **2c**: +2 10-lithio-9-phenyl-2,7-di-*tert*-butylanthracene, Et₂O–toluene, -78 °C \rightarrow r.t., 12 h. **4a,c**: (1) Et₂O–THF, -78 °C \rightarrow r.t., 12 h; (2) +SnCl₂–HCl_{aq}, r.t., 12–24 h; **4b**: (1) Et₂O–THF, -78 °C \rightarrow r.t., 12 h; (2) +H₃PO₂– HI, CH₃COOH, 80 °C, 2 h.



Scheme 2 Synthesis of compounds $[Li(THF)_2]_2[\textbf{2a}]$ and $[Li(Et_2O)]_2[\textbf{2a}].$ Conditions: r.t., 12 h.

from solvents of significantly different polarity (*e.g.*, C_6H_6 *vs.* CHCl₃) we always obtained single crystals of *anti*-**2b** only; attempts at the isolation of *syn*-**2b** by column chromatography were also not successful. In the case of *syn/anti*-**4b**, the two stereoisomers could be separated by fractional crystallisation; a complete assignment of ¹H/¹³C{¹H} NMR resonances was possible after the X-ray diffraction data of *syn-* and *anti*-**4b** had been obtained (see below). Stereoisomerically pure *syn-* and *anti*-**4b** show no tendency to transform into each other in solution. In line with that, the ¹H NMR spectra of the related *syn-* and *anti*-9,10-di(1'-naphthyl)anthracene do not change up to 100 °C (toluene-d₈);⁴⁰ the naphthyl rotation barrier in

1',9-naphthylanthracene was computed to be as high as 38 kcal mol^{-1,41} Similar to their all-carbon congeners, solutions of *syn/anti-2b* show no signs of coalescence in their ¹H NMR spectra at temperatures up to 120 °C (toluene-d₈), which means that the barrier of rotation about the exocyclic B-C bond exceeds 21 kcal mol⁻¹.⁴² Very surprisingly, though, a single crystal of anti-2b, placed in a Shigemi-type NMR tube and dissolved in C₆D₆ at r.t., gave ¹H NMR signals of both the syn and the anti stereoisomer. The proton integral values of the CH₃ resonances again indicated a stereoisomer ratio of 1:1; moreover, these two signals are connected by clear-cut exchange peaks in the ROESY NMR spectrum of syn/anti-2b (cf. the ESI⁺ for more details). As an explanation we point out that, on the one hand, the exocyclic B-C bonds in anti-2b (1.581(2) Å) are longer by about 0.085 Å than the exocyclic C-C bonds in anti-4b (1.494(5) Å) and syn-4b (1.497(2) Å; cf. the ESI⁺ for more details), which reduces unfavourable steric interactions in the transition state of 2-methylnaphthyl rotation. Yet, this effect is probably small as can be deduced from the lack of coalescence phenomena in the high-temperature ¹H NMR spectrum of *syn/* anti-2b. An alternative explanation is offered by the DFT-calculated transition state for phenyl rotation in 9-phenylanthracene (TS(C); Fig. 2) in which the molecule adopts a highly strained non-planar conformation.^{41,43,44} A corresponding Lewis-acidic boron species can relieve angle strain in the transition state upon tetra-coordination with a σ donor Do (**TS(BDo**); Fig. 2). Even though the 2-methylnaphthyl substituent is bulky enough to protect syn/anti-2b from hydrolysis, a short-term adduct with $Do = OH^-$ or H_2O may nevertheless be sufficiently stable to catalyse naphthyl rotation. As a proof-of-principle, we treated yellow syn/anti-2b in CD₃CN with excess [Me₄N]F and observed discolouration of the sample together with an ¹¹B¹H NMR resonance of 7 ppm, which indicates the accessibility of the vacant boron p-orbital for small Lewis bases like F⁻ and OH^{-.45} Since the NMR investigation of the single crystal of anti-2b had been performed in dried C₆D₆, the rotation is obviously catalysed already by a very small amount of OH^{-/} H₂O.⁴⁵ A temperature rise will shift any B-Do association/dissociation equilibrium towards the side of the free components. It is therefore understandable that the proposed mechanism of catalytic isomerisation is no longer operative at elevated temperatures and that consequently no coalescence was observed in the VT-NMR spectra of syn/anti-2b. We further note that linking two aryl substituents in Ar₃B derivatives (as is

B derivatives (as is values in parentheses);

TS(C)	TS(BDo)				
Calculated transition state (TS(C)) of phenyl rotation in 9-phenylanthra- suggested structure of the corresponding dopor-stabilised transition state					

the case for DBA) obviously does not suffice to protect the boron atom efficiently from Lewis-base attack through structural constraints.

NMR spectroscopy is also a useful tool to map the π -charge density distribution in acenes. In the present context we are mainly interested in finding out (i) whether the different dangling substituents affect the π -electron cloud of the DBA or anthracene cores in **2a–c** or **4a–c** and (ii) to what extent the formally isoelectronic nature of $[2a]^{2-}$ and **4a** is reflected by a similar π -electron distribution. We will use the chemical shift values of the carbon nuclei C-a, C-b and C-c (*cf.* Scheme 1) as diagnostic tools, because the shielding of a specific arene carbon atom depends linearly on the corresponding π -electron density at this position and its ¹³C{¹H} shift remains largely unaffected by ring current anisotropies as well as the solvent employed (**2a** was measured in C₆D₆.⁴⁶

Neither in the DBA derivatives **2a–c** nor in the anthracene molecules **4a–c** do the chemical shift differences between resonances of like carbon atoms exceed a value of $\Delta \delta = 2.0$ (Table 1). We therefore conclude that the electronic influence of the 9,10-substituents on the DBA/anthracene cores is small in the ground state,¹⁷ which points towards a lack of conjugative interaction across the exocyclic B–C/C–C bonds as a result of large dihedral angles between adjacent aryl planes (*cf.* the X-ray crystal structure analyses discussed below).

The comparison of **2a** with **4a** reveals a predictable deshielding in **2a** of C-a ($\Delta \delta = +13$), C-b ($\Delta \delta = +8$) and C-c ($\Delta \delta = +15$), because **2a** is isoelectronic with [**4a**]²⁺ (Table 1). In turn, two-electron reduction of **2a** to Li₂[**2a**] leads to a better shielding in Li₂[**2a**] of the three carbon nuclei C-a ($\Delta \delta = -2$), C-b ($\Delta \delta = -15$) and C-c ($\Delta \delta = -11$; Table 1). Even though these qualitative trends are in line with *a priori* expectations, the quantitative data still show significant differences between Li₂[**2a**] and its isoelectronic all-carbon relative **4a** of $\Delta \delta$ (C-a) = +11, $\Delta \delta$ (C-b) = -7 and $\Delta \delta$ (C-c) = +5 (Table 1). The ⁷Li{¹H} NMR spectrum of Li₂[**2a**] indicated the presence of contact ion pairs similar to those established in the solid state (see the solid-state structure of [Li(THF)₂]₂[**2a**] below).⁴⁷ Exclusively on the basis of

Table 1 $^{13}C{^1H}$ chemical shift values of 2a–c, Li₂[2a] and 4a–c (calculated DFT values in parentheses); only computed data are available in the case of the hypothetical free dianion $[2a]^{2-}$

	$\begin{array}{c} \mathbf{2a} \\ (\mathrm{C}_6\mathrm{D}_6) \end{array}$	$\begin{array}{c} 2b\\ \left(\mathrm{C}_{6}\mathrm{D}_{6}\right)\end{array}$	$\begin{array}{c} 2c\\ \left(\mathrm{C}_{6}\mathrm{D}_{6}\right)\end{array}$	[2a] ^{2–} (gas phase)	Li ₂ [2a] (THF-d ₈)
C-a	139.4 (139.5)	140.2	141.1	(135.0)	137.5 (136.7)
C-b	134.0 (133.0)	134.3	134.6	(108.8)	118.8 (118.4)
C-c	145.8 (146.7)	146.0	146.8	(139.0)	134.9 (135.8)
	$4a\left(\mathrm{C_6D_6}\right)$		$4\mathbf{b}\left(\mathrm{C}_{6}\mathrm{D}_{6} ight)$		$4c (C_6 D_6)$
C-a	126.8	(126.2)	1	27.2	127.7
C-b	126.0	(124.8)	1	26.2	126.4
C-c	130.4	(130.9)	1	31.1	132.4
C-d	136.0	(141.1)	1	35.0	135.2

experimental data, it is therefore difficult to decide to what extent the differences in the $^{13}C\{^1H\}$ NMR spectra of Li₂[2a] and 4a are caused by an unequally distributed charge density or by the vicinity of the coordinating Li⁺ ion.

We have therefore performed a quantum-chemical analysis of the species 2a, $[\text{Li}(\text{THF})_2]_2[2a]$, $[2a]^{2-}$ and 4a with special emphasis on (i) the ¹³C chemical shift values (Table 1), (ii) the frontier orbital structures, and (iii) the atomic partial charges q according to natural population (q(NPA)) and atoms-in-molecules analyses of computed electron densities (q(AIM)). Density-functional theory calculations were performed at the B97D/TZVP level of theory^{48,49} using the Gaussian programme.⁵⁰ Atomic charges were computed using NBO software⁵¹ as implemented in Gaussian and within the atoms-inmolecules framework⁵² utilising a locally modified version of AIMPAC.⁵³ NMR shieldings were obtained within the GIAO formalism^{54,55} (*cf.* the ESI† for more details).

We first note pleasingly good agreement between the experimentally determined and the calculated ¹³C shift values of $[\text{Li}(\text{THF})_2]_2[2a]$; in contrast, significant deviations from the experimental data are obvious in the case of the free dianion $[2a]^{2^-,56}$ These findings lend further support to our previous conclusion that the Li⁺ ions stay coordinated to the anionic framework in THF solution. In the case of 4a, C-a and C-b possess essentially the same chemical shift values. In comparison, C-a of Li₂[2a] is deshielded by +11 ppm, whereas the signal of C-b experiences an upfield shift of -7 ppm. These effects are obviously not artefacts of Li⁺ coordination, because an even larger shielding of C-b is calculated for the free dianion $[2a]^{2^-}$ ($\Delta \delta = -16$ ppm; DFT results, Table 1).

Finally, calculations of nucleus-independent chemical shifts (NICS(0), NICS(1))⁵⁷ contribute a quantum-chemical criterion to compare the aromatic characters of the individual six-membered rings in $[\text{Li}(\text{THF})_2]_2[2a]$ and 4a. As can be expected, the NICS(0)/NICS(1) values of the mesityl substituents are the same for both compounds; larger differences are found for the NICS(0)/NICS(1) data of the peripheral C₆H₄ rings (*cf*. ESI[†]). The NICS(0)/NICS(1) values of the central B₂C₄ ring of $[\text{Li}(\text{THF})_2]_2[2a]$ also deviate somewhat from the corresponding parameters of the central C₆ ring of 4a (-9.0 ppm/-13.1 ppm *vs*. -9.9 ppm/-11.1 ppm, respectively). However, there remains no question that two-electron reduction transforms the anti-aromatic B₂C₄ ring of 2a (NICS(0)/NICS(1) = 10.5 ppm/4.4 ppm) into an aromatic π system (*cf*. the ESI[†] for more details).

Key structural features of the 9,10-dihydro-9,10diboraanthracenes and their all-carbon analogues

As alluded to above, the relative arrangement of the individual molecules in the solid state is of crucial importance for all organic electronic devices.^{13,58} A three-coordinate boron atom has a slightly larger atomic radius than a three-coordinate carbon atom.⁵⁹ Apart from that, **2a/4a**, **2b/4b** and **2c/4c** should possess very similar molecular structures and even adopt closely related conformations in the crystal lattice. Although

all six molecules are uncharged compounds, boron atoms are more electropositive than carbon atoms and the 2-type species have two π electrons less than the 4-type derivatives. The resulting delicate differences in the σ - and π -charge distributions along the DBA/anthracene scaffolds might well influence intermolecular interactions and, in turn, the solid-state structures of 2-type *vs.* 4-type compounds.

To test this hypothesis, we chose the crystal packing of *anti*-**2b** and *anti*-**4b** for a closer examination (note that 9,10-di(1'naphthyl)anthracenes are leading candidates as electroluminescence materials in OLEDs^{40,58}). Different packing motifs can, of course, be established by identical molecules as well. We have therefore also investigated two polymorphs of **2a** in order to carve out the effect of boron–carbon exchange and to distinguish it from other structure-determining factors. In addition, X-ray crystallography on Li₂[**2a**] as a benchmark system was used to validate the formal isoelectronic relationship between [**2a**]^{2–} and **4a**. Full details including ORTEP plots of the X-ray crystal structure analyses of **2a**, *anti*-**2b**, **4a**, *anti*-**4b**, *syn*-**4b**, [Li(THF)₂]₂[**2a**] and [Li(Et₂O)]₂[**2a**] are provided in the ESI.[†] In the following, we will only discuss selected aspects of the crystallographic work.

We have determined the crystal structure of **2a** for comparison with the data of a polymorph (*i.e.* **2a**^{*}) obtained by Kawashima *et al.*³⁷ The respective single crystals (monoclinic, $P2_1/c)^{60}$ were grown by slow evaporation of saturated solutions of the compound in toluene (**2a**) and Et₂O (**2a**^{*}). A decisive difference between the two polymorphs lies in the fact that the molecules of **2a** (*Z* = 4) contain no symmetry element whereas



Fig. 3 Overlays of the two molecules of the polymorphic structures 2a (green) and 2a* (black). The position of the DBA centroids (COG) has been marked in red; for 2a* the COG is identical with the inversion centre.

those of $2a^*$ (Z = 2) possess an inversion centre. Fig. 3 shows an overlay of the molecular structures of 2a (green) and $2a^*$ (black) in two different orientations.

In Fig. 3 (top) the position of the DBA centroids (COG) has been marked in red; for $2a^*$ the COG is identical with the inversion centre. Both 2a and $2a^*$ reveal an orthogonal arrangement between the mesityl planes and the DBA core. In contrast to the planar DBA framework of compound $2a^*$, the B_2C_4 heterocycle in 2a adopts a shallow boat conformation (Fig. 3, bottom) resulting in an angle of 169.2° between the two Mes-*i* carbon atoms and the COG. All other key structural parameters of 2a and $2a^*$ are essentially the same. The mutual orientation of the molecules in the crystal lattices of the two polymorphs is strikingly dissimilar. Only in the case of 2a we observe an interpretable short contact, *i.e.* a parallel-displaced π -stacking interaction between two *o*-phenylene rings of adjacent DBA moieties (3.421 Å).

Crystals grown from a syn/anti-mixture of 2b in C₆H₆ exclusively contained the *anti* rotamer together with two equivalents of solvent molecules (monoclinic, $P2_1/c$; Z = 2). The all-carbon congener anti-4b also co-crystallises with two equivalents of C_6H_6 (triclinic, $P\bar{1}$; Z = 1) thereby allowing for a direct comparison of the two crystal structures. We first note that the density of anti-2b (1.169 g cm⁻³) is 3% lower than that of anti-4b (1.204 g cm⁻³). Both *anti-*2**b** and *anti-*4**b** are C_i-symmetric; the dihedral angles between the 2-methylnaphthyl substituents and the DBA or 9,10-anthrylene cores amount to 85.5(1)° and 82.8(3)°, respectively. As can be expected, all three B-C bonds in anti-2b are longer than the corresponding C-C bonds in anti-4b. Moreover, the difference between the lengths of the B-Cexo single bond (1.581(2) Å) and the average B-Cendo bond (1.561(2) Å) is considerably smaller ($\Delta = 0.020(2)$ Å) than the difference between C-C_{exo} (1.494(5) Å) and C-C_{endo} (1.408(5) Å) in *anti*-4b ($\Delta = 0.086(5)$ Å). This feature reflects a low degree of B=C_{endo} π bonding in the ground state of *anti*-2b as opposed to significant C=C_{endo} double-bond character in anti-4b. Apart from these subtle variations, the general molecular frameworks of anti-2b and anti-4b are very much alike as illustrated by the overlay of both structures in Fig. 4 (anti-2b: green; anti-4b: black).

Fig. 4 also shows the short contacts between adjacent molecules, which are basically the same in both species (anti-2b/ anti-4b: H(33)-C(21) = 2.81/2.87 Å; C(33)-H(33)-C(21) = 135/2 131° ; Ar(C(21))//Ar(C(33)) = 84.8(1)/81.3(1)^{\circ}. A most interesting difference between anti-2b and anti-4b is visible in their interaction with the C_6H_6 solvate molecules (Fig. 5): in the case of the organoborane, C₆H₆ acts as a hydrogen donor in a T-shaped arrangement and the C-H vector points to a boronbonded carbon atom (H(45)-C(31) = 2.90 Å; C(45)-H(45)-C(31) = 170° ; $C_6H_6//B_2C_4$ = $76.1(1)^{\circ}$). In the all-carbon species, however, the π -electron system of C₆H₆ acts as a hydrogen acceptor and the 2-methylnaphthyl substituent as the donor $(H(4)-COG(C_6H_6) = 2.69 \text{ Å}; C(4)-H(4)-COG(C_6H_6) = 148^\circ;$ $C_6H_6/(Ar(C(4))) = 64.6(2)^\circ)$. We wish to emphasise in this context that syn-4b, which also crystallises as solvate with two equivalents of C₆H₆, establishes the same short contacts



Fig. 4 Overlay of *anti*-2b (green) and *anti*-4b (black) with the shortest contacts between neighbouring molecules indicated.



Fig. 5 Different interactions between the C_6H_6 solvate molecules and the main molecules in the crystal lattices of *anti-***2b** (green) and *anti-***4b** (black).

between the main molecule and the benzene centroids as *anti-***4b**.

Since the steric boundary conditions are the same in *anti-***2b** and *anti-***4b**, the different modes of C_6H_6 interaction are probably of electronic origin. A comparison of the relevant ${}^{13}C{}^{1}H$ chemical shift values of *anti-***2b** and *anti-***4b** gives no

indication of an accumulation of π -charge density at the endocyclic boron-bonded carbon atoms in *anti*-2b (δ (C-c) = 146.0 (*anti*-2b), 131.1 (*anti*-4b)). We therefore assume that it is the +I effect of the electropositive boron atom that leads to a negative partial charge at the neighbouring carbon atoms and, in turn, to an attraction of the C-H dipole of C₆H₆. This interpretation is fully supported by the calculated atomic charges on C-c (equiv. to C(31) in the X-ray structures shown in Fig. 5) of *anti*-2b and 4b, which amount to q(NPA) = -0.38 or q(AIM) = -0.63 in the organoborane, but only to q(NPA) = -0.05 or q(AIM) = -0.01 in the all-carbon compound.

In order to gain deeper insight into the electron-accepting properties of 9,10-diaryl-DBAs and to explore the scope and limitations of the isoelectronic principle in this particular case, we compared the solid-state structures of 2a, $Li_2[2a]$ and 4a. Crystals of the lithium compound were obtained as ether adducts $[Li(THF)_2]_2[2a]$ and $[Li(Et_2O)]_2[2a]$. Fig. 6 shows a plot of the molecular structure of $[Li(THF)_2]_2[2a]$; details of the crystal structure analysis of $[Li(Et_2O)]_2[2a]$ are provided in the ESI,[†]

The molecules of $[\text{Li}(\text{THF})_2]_2[2a]$ exist as discrete centrosymmetric entities in the crystal lattice. In each of these molecules, two $[\text{Li}(\text{THF})_2]^+$ ions are η^6 -coordinated to both sides of the B₂C₄ ring to form an inverse sandwich complex. The distance Li(1)····COG(B₂C₄) is 1.937 Å. The general structural motif of the $[\text{Li}(\text{Et}_2O)]_2[2a]$ complex is largely identical, apart from the fact that the distance Li(1)···COG(B₂C₄) = 1.740 Å is shorter by 0.197 Å, obviously as a result of the reduced steric demand of the complex cation. Remarkably, the Li···COG (B₂C₄) distance in the lithium salt $[\text{Li}(\text{THF})_2]_2[\text{HB}(C_6H_4)_2\text{BH}]$ of pristine DBA (1.960 Å)⁶¹ is longer than that in [Li-



Fig. 6 Molecular structure of $[\text{Li}(\text{THF})_2]_2[2a]$ in the solid state; displacement ellipsoids are drawn at the 50% probability level; H atoms have been omitted for clarity. Selected bond lengths (Å), bond angles (°), and dihedral angle (°): B(1)–C(1) 1.624(3), B(1)–C(31) 1.509(2), B(1)–C(36A) 1.545(3), C(31)–C(36) 1.480 (3), C(31)–C(32) 1.449(3), C(32)–C(33) 1.347(2), C(33)–C(34) 1.425(3), C(34)–C(35) 1.366(3), C(35)–C(36) 1.420(2), Li(1)···COG(B₂C₄) 1.937; C(1)–B(1)–C(31) 123.6(2), C(1)–B(1)–C(36A) 119.5(1), C(31)–B(1)–C(36A) 116.9(2); Ar(C1)//C(31) B(1)C(36A) 65.8(1); Ar = phenyl. The symmetry transformation used to generate equivalent atoms: A: -x, -y + 1, -z + 1.

 $(THF)_2]_2[2a]$, thereby suggesting that the bulky mesityl substituents have no negative impact on the ${\rm Li}^+\cdots(B_2C_4)$ coordination. We further note that X-ray crystallography on $[{\rm Li}-(THF)_2]_2[2a]$ leads to results that are fully consistent with the conclusions drawn from our $^7{\rm Li}\{^1{\rm H}\}$ NMR spectroscopic investigation of ${\rm Li}_2[2a]$ in THF-d_8 (see above).

A comparison of the DBA bond lengths of 2a with those of $[Li(OR_2)_n]_2[2a]$ revealed a major perturbation of the DBA scaffold upon reduction:⁶² the endocyclic B-C distances become shorter (-0.032 Å), thereby testifying to an increased B=C double bond character in $[Li(OR_2)_n]_2[2a]$. All C-C bond lengths change within the range -0.035 Å to +0.052 Å. We interpret these changes in the light of a frontier orbital analysis, which reveals essentially identical isosurfaces of the LUMO of 2a and the HOMO of the reduced species [Li- $(THF)_2_2[2a]$ (Fig. 7 and ESI[†]). The individual bond-length variations quantified in Fig. 7 appear as a direct consequence of the occupation of the LUMO of 2a with its specific nodal structure.⁶³ The C–C bond lengths of **4a**, the isoelectronic congener of $[Li(OR_2)_n]_2$ [2a], deviate in the same qualitative fashion from those of 2a; the quantitative differences, however, are smaller (Fig. 7). Also this finding is reflected in the particular structure of the HOMO of 4a, to which the C-c atoms do not contribute to a significant extent (Fig. 7).

A further interesting analogy to the couple **2a** (Hückel 4π -antiaromatic central ring)/[**2a**]²⁻ (Hückel 6π -aromatic central ring) is provided by cyclobutadiene and its lithium dianions, which also crystallise as contact ion pairs with two Li⁺ ions located above and below the plane of the four-membered ring.⁶⁴

Electrochemical properties of the 9,10-dihydro-9,10diboraanthracenes and their all-carbon analogues

Cyclic voltammograms of **2a–c** and **4a–c** were recorded on THF solutions using $[nBu_4N][PF_6]$ (0.1 M) as the supporting electrolyte; all potential values (Table 2) are referenced against the ferrocene/ferrocenium couple (FcH/FcH⁺ = 0 V).

The assignment of redox waves was achieved by means of spectroelectrochemistry using the UV/vis spectra of the monoand dianion of pristine 9,10-dihydro-9,10-diboraanthracene, $[HB(C_6H_4)_2BH]^-$ and $[HB(C_6H_4)_2BH]^{2-}$, as references.^{32,61} In situ UV/vis monitoring of the reduction of 2a (with Li) and 2b (with K, which gave better results than Li) in THF first showed the signature of the DBA monoanion develop in the spectrum. After some time, the corresponding bands vanished and absorptions characteristic of the DBA dianion appeared instead (cf. the ESI⁺ for plots of the spectra and ref. 32 for a more detailed discussion of the NIR absorptions that occur upon reduction). We therefore assign the redox events at -1.84/-2.73 V (2a) and -1.72/-2.58 V (2b) to DBA-centred electron transitions. Similar spectroelectrochemical experiments have in previous studies led to the conclusion that also the redox transitions of 2c with $E_{1/2} = -1.68$ and -2.46 V occur at the DBA π -system whereas the irreversible electron transition at $E_{\rm pc}$ = -3.32 V is likely associated with the pendant anthryl substituents.32 In line with these experimental observations we



Fig. 7 Differences between average endocyclic bond lengths (10^{-3} Å) of [Li- $(OR_2)_n]_2$ [**2a**] vs. **2a** (top; OR₂ = THF, n = 2; Et₂O, n = 1) and of **4a** vs. **2a** (bottom), which are in agreement with the nodal structures of the calculated HOMOs of [Li(THF)₂]₂[**2a**] and **4a** (surfaces drawn at an isovalue of 0.05 $a_0^{-3/2}$; the Li⁺ ions are marked in magenta; the THF ligands have been omitted for clarity).

 Table 2
 Electrochemical data of 2a-c and 4a-c^a

	$E_{1/2}$ in [V] vs. FcH/FcH ⁺
2a	$-1.84, -2.73^{b}$
2b	-1.72, -2.58
2c	$-1.68, -2.46, -3.32^{c,d}$
4a	$-2.59, -3.40^{\circ}$
4b	$-2.50, -3.30^{\circ}$
4c	$-2.50, -2.81, -2.96, -3.54^{\circ}$

^{*a*} THF, supporting electrolyte: $[nBu_4N]$ [PF₆] (0.1 M), scan rate: 200 mV s⁻¹. ^{*b*} Literature values: -1.82, -2.78 V, *cf*. ref. 37. ^{*c*} E_{pc} value. ^{*d*} Ref. 32. note that the calculated LUMOs of **2a–c** are exclusively located on the respective DBA fragments (*cf.* the ESI^{\dagger} for corresponding orbital plots).⁶⁵

Comparing the DBA derivatives, we find a small but significant anodic shift along the sequence $2a \rightarrow 2b \rightarrow 2c$ for both redox waves. More importantly, the potential values required for the one-electron reduction of 2a-c are lower by 0.75, 0.78 and 0.82 V, respectively, than those necessary for the reversible mono-reduction of 4a-c; all these potential differences are larger than in the case of 1,2,3,4,5,6,7,8-octafluoro-9,10-diphenylanthracene vs. 9,10-diphenylanthracene ($\Delta(E_{1/2}) = 0.52$ V;²² recorded in CH₃CN). Both one-electron reductions of 2a-c are fully reversible and can even be achieved on a preparative scale as evidenced by the successful synthesis of Li₂[2a]. In contrast, the more cathodically shifted second redox waves of 4a-c show features of chemical irreversibility. As has already been documented in the literature for other anthracene derivatives, the highly basic dianions tend to undergo protonation through Hofmann elimination of the supporting tetraalkylammonium electrolyte.66,67 In summary, the comparatively anodic reduction potentials and the stability of the mono- and dianions obtained lead to the conclusion that boron doping renders 2a-c excellent candidates for n-type organic materials.

We recorded cyclic voltammograms of **4a–c** also in the positive potential regime but found no electron transitions up to the limit of the solvent window (THF). According to the literature, 9,10-di(1'-naphthyl)anthracene undergoes electrochemical oxidation in CH_2Cl_2 to a cation radical, which, however, slowly decomposes to another electroactive species.⁶⁸ It can therefore be concluded that DBA derivatives are potentially useful substitutes for the isoelectronic, yet elusive, stable anthracene dications.

Optical spectra of the 9,10-dihydro-9,10-diboraanthracenes and their all-carbon analogues

Unless noted otherwise, all absorption/emission wavelengths refer to solutions in C_6H_6 (Table 3). The all-carbon species **4a** and *anti*-**4b** give rise to essentially identical UV/vis absorption and emission spectra (Fig. 8). All bands show the vibrational fine structure usually observed for anthracene derivatives and the Stokes shifts are very small.⁶⁹ The trianthrylene **4c** possesses an only marginally red-shifted absorption maximum; the emission, however, appears at lower energy than in the

Table 3 Photophysical data of 2a-c and 4a-c in C₆H₆

	$\lambda_{\max}(abs) [nm]$ ($\varepsilon [mol^{-1} dm^3 cm^{-1}]$)	$\lambda_{\max}(em) [nm]$ $(\lambda_{m}[nm])$	Stokes shift [cm ⁻¹]	$\phi_{\rm E}{}^a$
		(ex [])	[****]	ΎΓ
2a	349 (10 400)	460 (350)	6900	0.03
2b	357 (8600), 422 (1300)	513 (420)	4200	0.07
2c	374 (28 200), 531 (1500)	635 (530)	3100	0.05
4a	399 (22 300)	403 (358)	250	0.80
4b	399 (17 900)	404 (358)	300	0.77
4c	406 (47 700)	442 (380)	2000	0.71
		<pre></pre>		

 a Quantum yields were determined using a calibrated integrating sphere.



Fig. 8 UV/vis absorption (left) and emission (right) spectra of 2a-c and 4a-c in C₆H₆; 2a (blue), syn/anti-2b (green), 2c (red), 4a (black), anti-4b (orange) and 4c (purple).

cases of **4a** and *anti*-**4b** ($\Delta(\lambda_{max}(em)) \sim 40 \text{ nm}$) and the corresponding band is devoid of any fine structure.⁷⁰

The absorption spectra of **2a** and **2b** contain intense bands at $\lambda_{max}(abs) = 349$ and 357 nm, respectively, which are tentatively assigned to π - π^* excitations of the DBA core (Fig. 8; Table 3).³² In the spectrum of **2c**, this band is likely hidden underneath the broad, structured absorption of the 9-anthryl substituents. As additional features, we observe a shoulder at ~400 nm in the spectrum of **2a** and well-resolved bands at 422 nm (ε = 1300 mol⁻¹ dm³ cm⁻¹) and 531 nm (ε = 1500 mol⁻¹ dm³ cm⁻¹) for **2b** and **2c**, respectively, which are responsible for the yellow (**2a**, **2b**) and deep red (**2c**) colours of the compounds. Especially the extremely broad line width of the 531 nm-band of **2c** suggests that these features originate from a charge-transfer interaction between the respective electron-rich 9,10-aryl donors and the electron-poor DBA acceptors.³²

In contrast to the anthracene compounds 4a-c, which are all blue-light emitters, the emission wavelengths of 2a (460 nm), **2b** (513 nm) and **2c** (635 nm) cover the full range from blue to green to red. Pronounced differences are also obvious in the solvatochromic behaviour of 4a-c, on the one hand, and 2a-c, on the other. Spectra have been recorded in C_6H_{12} , C_6H_6 , THF and CH_2Cl_2 (cf. the ESI⁺ for more details). 4a and anti-4b reveal no noteworthy solvatochromism at all; the emission band of 4c shifts continuously to the red by an overall $\Delta(\lambda_{max}(em))$ of 62 nm. The DBA derivatives, in contrast, show marked positive solvatochromism, *i.e.*, **2a** $(\Delta(\lambda_{max}(em)) =$ 74 nm), 2b ($\Delta(\lambda_{max}(em)) = 97$ nm) and 2c ($\Delta(\lambda_{max}(em)) =$ 165 nm). These data provide further evidence for the assumption that charge-transfer transitions play a major role in the optical properties of 2a-c, whereas the low-energy regime of the electronic spectra of 4a and *anti*-4b is largely governed by

 π - π * interactions within the individual anthracene fragments.¹⁷

Correspondingly, the calculated HOMOs of 2a-c are located on the aryl substituents but the LUMOs are all DBA-centred, whereas in the cases of 4a-c both the HOMOs and the LUMOs are 9,10-anthrylene-centred. We further find a satisfactory correlation between the calculated HOMO-LUMO gaps of 2a-cand the corresponding values derived from the UV-vis spectra^{71,72} (*cf.* the ESI[†] for more details).

In the cases of **4a–c**, the quantum yields $\phi_{\rm F}$ are high and vary in the range between 0.71 and 0.80 (C₆H₆; Table 3). In contrast to that, **2a–c** show lower quantum yields of 0.03–0.07 (C₆H₆; Table 3), likely because intramolecular charge transfer acts as an efficient non-radiative decay channel.

Conclusions

9,10-Dihydro-9,10-diboraanthracene (DBA) derivatives carrying mesityl (2a), 2-methylnaphthyl- (2b) and 9-phenyl-2,7-di-*tert*butylanthryl (2c) substituents at the boron atoms are stable towards air and moisture even in solution over several hours (2c) or even days (2a, 2b). According to NICS(0)/NICS(1) calculations, the compounds contain Hückel-anti-aromatic central B_2C_4 rings; upon two-electron reduction, they are transformed into the Hückel-aromatic dianions $[2a-c]^{2-}$.

As exemplified by the crystal structure analyses of *anti*-**2b** and *anti*-**9**,10-bis(2'-methylnaphthyl)anthracene (*anti*-**4b**), the DBA derivative and its all-carbon analogue possess very similar molecular structures and also show similar crystal packing motifs. Subtle differences between the crystal lattices of *anti*-**2b** and *anti*-**4b** are, however, evident in the kinds of intermolecular C-H··· π (arene) interactions (T-stacking).

2a–c behave as blue-, green- and red-emitting materials, respectively, and consequently provide the three primary colours required for full-colour displays. In marked contrast, each of the three corresponding all-carbon systems **4a–c** is a blue-light emitter. According to the frontier orbital structures, the underlying transitions are (i) a charge transfer from the electron-rich aryl substituents to the electron-poor DBA cores in the cases of **2a–c** and (ii) a local π – π * excitation of the central 9,10-anthrylene fragments in the cases of **4a–c**.

The boron species **2a–c** undergo sequential and reversible two-electron reductions at their DBA cores. The most cathodic reduction potentials of **2a–c** are lower by 0.75–0.82 V than those necessary for the reversible mono-reductions of **4a–c**, which leads to the conclusion that boron doping increases the electron affinity of anthracene derivatives to a higher degree than 1,2,3,4,5,6,7,8-octafluorination.

In summary, our results demonstrate that the performance of organic materials can indeed be significantly modified if selected carbon atoms are replaced by boron atoms.

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References

- 1 S. W. Thomas III, G. D. Joly and T. M. Swager, *Chem. Rev.*, 2007, **107**, 1339–1386.
- 2 J. Zaumseil and H. Sirringhaus, Chem. Rev., 2007, 107, 1296-1323.
- 3 S. Günes, H. Neugebauer and N. S. Sariciftci, *Chem. Rev.*, 2007, **107**, 1324–1338.
- 4 B. C. Thompson and J. M. J. Fréchet, *Angew. Chem., Int. Ed.*, 2008, 47, 58–77.
- 5 D. Pisignano, M. Anni, G. Gigli, R. Cingolani, M. Zavelani-Rossi, G. Lanzani, G. Barbarella and L. Favaretto, *Appl. Phys. Lett.*, 2002, **81**, 3534–3536.
- 6 A. P. Kulkarni, C. J. Tonzola, A. Babel and S. A. Jenekhe, *Chem. Mater.*, 2004, **16**, 4556–4573.
- 7 S. Chen, L. Deng, J. Xie, L. Peng, L. Xie, Q. Fan and W. Huang, *Adv. Mater.*, 2010, **22**, 5227–5239.
- 8 F. Jäkle, Chem. Rev., 2010, 110, 3985-4022.
- 9 G. Yu, S. Yin, Y. Liu, J. Chen, X. Xu, X. Sun, D. Ma, X. Zhan, Q. Peng, Z. Shuai, B. Tang, D. Zhu, W. Fang and Y. Luo, *J. Am. Chem. Soc.*, 2005, **127**, 6335–6346 and references cited herein.
- 10 Y. Shirota and H. Kageyama, Chem. Rev., 2007, 107, 953– 1010.
- 11 T. Baumgartner and R. Réau, *Chem. Rev.*, 2006, **106**, 4681–4727.
- 12 Handbook of Oligo- and Polythiophenes, ed. D. Fichou, Weinheim, Germany, 1999.

- 13 J. E. Anthony, Chem. Rev., 2006, 106, 5028-5048.
- 14 W. R. Dawson and M. W. Windsor, *J. Phys. Chem.*, 1968, 72, 3251–3260.
- 15 J. V. Morris, M. A. Mahaney and J. R. Huber, *J. Phys. Chem.*, 1976, **80**, 969–974.
- 16 K. Danel, T.-H. Huang, J. T. Lin, Y.-T. Tao and C.-H. Chuen, *Chem. Mater.*, 2002, **14**, 3860–3865.
- 17 H. Park, J. Lee, I. Kang, H. Y. Chu, J.-I. Lee, S.-K. Kwon and Y.-H. Kim, *J. Mater. Chem.*, 2012, **22**, 2695–2700.
- 18 V. Langer and H.-D. Becker, Z. Kristallogr., 1992, 199, 313– 315.
- 19 N. I. Nijegorodov and W. S. Downey, J. Phys. Chem., 1994, 98, 5639–5643.
- 20 H. Usta, A. Facchetti and T. J. Marks, Acc. Chem. Res., 2011, 44, 501–510.
- 21 M.-H. Yoon, A. Facchetti, C. E. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 2006, **128**, 5792–5801.
- 22 J. F. Tannaci, M. Noji, J. McBee and T. D. Tilley, J. Org. Chem., 2007, 72, 5567–5573.
- 23 J. F. Tannaci, M. Noji, J. L. McBee and T. D. Tilley, J. Org. Chem., 2008, 73, 7895–7900.
- 24 H. E. Katz, J. Johnson, A. J. Lovinger and W. Li, J. Am. Chem. Soc., 2000, 122, 7787–7792.
- 25 The following reviews provide more detailed insight into optical, electronic andsensory applications of organoboranes. (a) C. D. Entwistle and T. B. Marder, Angew. Chem., Int. Ed., 2002, 41, 2927–2931; (b) C. D. Entwistle and T. B. Marder, Chem. Mater., 2004, 16, 4574–4585; (c) S. Yamaguchi and A. Wakamiya, Pure Appl. Chem., 2006, 78, 1413–1424; (d) F. Jäkle, Coord. Chem. Rev., 2006, 250, 1107–1121; (e) M. Elbing and G. C. Bazan, Angew. Chem., Int. Ed., 2008, 47, 834–838; (f) Ref. 8 (g) A. Lorbach, A. Hübner and M. Wagner, Dalton Trans., 2012, 41, 6048–6063.
- 26 A. Lorbach, C. Reus, M. Bolte, H.-W. Lerner and M. Wagner, *Adv. Synth. Catal.*, 2010, 352, 3443–3449.
- 27 A. Lorbach, M. Bolte, H.-W. Lerner and M. Wagner, *Chem. Commun.*, 2010, **46**, 3592–3594.
- 28 E. Januszewski, A. Lorbach, R. Grewal, M. Bolte, J. W. Bats, H.-W. Lerner and M. Wagner, *Chem.–Eur. J.*, 2011, 17, 12696–12705.
- 29 C. Reus, N.-W. Liu, M. Bolte, H.-W. Lerner and M. Wagner, J. Org. Chem., 2012, 77, 3518–3523.
- 30 Ö. Seven, Z.-W. Qu, H. Zhu, M. Bolte, H.-W. Lerner, M. C. Holthausen and M. Wagner, *Chem.-Eur. J.*, 2012, 18, 11284-11295.
- 31 A. Lorbach, M. Bolte, H. Li, H.-W. Lerner, M. C. Holthausen, F. Jäkle and M. Wagner, *Angew. Chem.*, *Int. Ed.*, 2009, **48**, 4584–4588.
- 32 C. Hoffend, F. Schödel, M. Bolte, H.-W. Lerner and M. Wagner, *Chem.-Eur. J.*, 2012, 18, 15394–15405.
- 33 E. Januszewski, M. Bolte, H.-W. Lerner and M. Wagner, *Organometallics*, 2012, **31**, 8420–8425.
- 34 Selected references that have not been covered by the earlier reviews cited above: (*a*) A. Wakamiya, T. Taniguchi and S. Yamaguchi, *Angew. Chem., Int. Ed.*, 2006, **45**, 3170–

3173; (b) H. Li and F. Jäkle, Macromol. Rapid Commun., 2010, 31, 915-920; (c) H. Li, A. Sundararaman, T. Pakkirisamy, K. Venkatasubbaiah, F. Schödel and F. Jäkle, Macromolecules, 2011, 44, 95-103; (d) Z. M. Hudson, X.-Y. Liu and S. Wang, Org. Lett., 2011, 13, 300-303; (e) Z. M. Hudson, M. G. Helander, Z.-H. Lu and S. Wang, Chem. Commun., 2011, 47, 755-757; (f) C. Sun, J. Lu and S. Wang, Org. Lett., 2011, 13, 1226-1229; (g) E. Sakuda, Y. Ando, A. Ito and N. Kitamura, Inorg. Chem., 2011, 50, 1603-1613; (h) Y. Kim, H.-S. Huh, M. H. Lee, I. L. Lenov, H. Zhao and F. P. Gabbaï, Chem.-Eur. J., 2011, 17, 2057-2062; (i) C. Bresner, C. J. E. Haynes, D. A. Addy, A. E. J. Broomsgrove, P. Fitzpatrick, D. Vidovic, A. L. Thompson, I. A. Fallis and S. Aldridge, New I. Chem., 2010, 34, 1652-1659.

- 35 (a) Z. Zhou, A. Wakamiya, T. Kushida and S. Yamaguchi, J. Am. Chem. Soc., 2012, 134, 4529–4532; (b) T. Kushida,
 Z. Zhou, A. Wakamiya and S. Yamaguchi, Chem. Commun., 2012, 48, 10715–10717; (c) S. Saito, K. Matsuo and
 S. Yamaguchi, J. Am. Chem. Soc., 2012, 134, 9130–9133; (d) C. Dou, S. Saito, K. Matsuo, I. Hisaki and S. Yamaguchi, Angew. Chem., Int. Ed., 2012, 51, 12206–12210.
- 36 We have prepared the unsubstituted species 9,10-diphenyl-DBA, 9,10-bis(1'-naphthyl)-DBA and 9,10-bis(9'-anthryl)-DBA and found only negligible differences in their optoelectronic properties compared to **2a–c**. However, because of higher sensitivity to air and moisture or pure solubility in all common solvents, analytically pure samples could not be obtained. We therefore restrict our discussion to **2a–c**.
- 37 A six-step synthesis protocol together with an X-ray crystal structure analysis of 2a has already been described (*i.e.* 2a*): T. Agou, M. Sekine and T. Kawashima, *Tetrahedron Lett.*, 2010, 51, 5013–5015. Herein, we report an alternative synthesis route to 2a, its NMR data in C₆D₆ and THF-d₈, which we require for comparison, and the X-ray crystal structure analysis of a polymorph.
- 38 J. E. Anthony, D. L. Eaton and S. R. Parkin, Org. Lett., 2002, 4, 15–18.
- 39 U. Müller, M. Adam and K. Müllen, *Chem. Ber.*, 1994, **127**, 437–444.
- 40 C. H. Lee, M. J. Kim, S.-P. Han, Y.-S. Lee, S. K. Kang, J. H. Song, J. T. Je, H.-Y. Oh and Y.-J. Kim, *Tetrahedron*, 2010, 66, 3360–3364.
- 41 D. Nori-shargh, S. Asadzadeh, F.-R. Ghanizadeh,
 F. Deyhimi, M. M. Amini and S. Jameh-Bozorghi, *J. Mol. Struct. (THEOCHEM)*, 2005, 717, 41–51.
- 42 A. R. Katritzky, C. H. Marson, G. Palenik, A. E. Koziol, H. Luce, M. Karelson, B.-C. Chen and W. Brey, *Tetrahedron*, 1988, 44, 3209–3214.
- 43 W. Nowak and M. Wierzbowska, J. Mol. Struct. (THEO-CHEM), 1996, 368, 223-234.
- 44 K. Nikitin, H. Müller-Bunz, Y. Ortin, J. Muldoon and M. J. McGlinchey, *Org. Lett.*, 2011, **13**, 256–259.
- 45 (*a*) This interpretation is in line with preliminary computational results, clearly indicating a substantial barrier for 2-methylnaphthyl rotation in **2b**, which drops significantly

in the corresponding B–F adduct: E. M. L. Fink, *Bachelor thesis*, Goethe Universität Frankfurt, Frankfurt (Main), Germany, 2010; (*b*) The *syn/anti*-re-equilibration of single-crystalline *anti*-2**b** in dried C_6D_6 is fast and already complete immediately after preparation of the NMR sample. We therefore found it impossible to deliberately dope the sample with varying amounts of H₂O at various pH and to systematically examine the resulting effect on the equilibration rate.

- 46 (a) M. Karplus and J. A. Pople, J. Chem. Phys., 1963, 38, 2803–2807; (b) H. Günther, H. Schmickler, H. Königshofen, K. Recker and E. Vogel, Angew. Chem., Int. Ed., 1973, 12, 243–245; (c) R. H. Levin and J. D. Roberts, Tetrahedron Lett., 1973, 14, 135–138; (d) D. G. Farnum, Adv. Phys. Org. Chem., 1975, 11, 123–175.
- 47 The ⁷Li{¹H} NMR spectrum of Li₂[**2a**] in THF-d₈ gave one signal at 0.4 ppm and a second signal at -7.2 ppm with an integral ratio of approximately 1:8. The smaller, low-field resonance falls in the range of solvent-separated ion pairs, whereas the larger, high-field signal is indicative of contact ion pairs in which the Li⁺ ion resides above the plane of an aromatic π system and thus in the shielding region of the ring current. For comparison, we note that the ⁷Li resonance of the contact ion pair η^5 -LiCp is detected at -8.37 ppm (THF). (*a*) R. H. Cox and H. W. Terry Jr., *J. Magn. Reson.*, 1974, 14, 317–322; (*b*) L. A. Paquette, W. Bauer, M. R. Sivik, M. Bühl, M. Feigel and P. v. Ragué Schleyer, *J. Am. Chem. Soc.*, 1990, 112, 8776–8789.
- 48 S. Grimme, J. Comput. Chem., 2006, 27, 1787-1799.
- 49 A. Schäfer, C. Huber and R. Ahlrichs, J. Chem. Phys., 1994, 100, 5829–5835.
- 50 M. J. Frisch, et al., Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford, CT, USA, 2010.
- 51 For an overview, see: E. D. Glendening, C. R. Landis and F. Weinhold, *WIREs Comput. Mol. Sci.*, 2012, **2**, 1–42.
- 52 *The Quantum Theory of Atoms in Molecules*, ed. C. F. Matta and R. J. Boyd, Weinheim, Germany, 2007.
- 53 R. F. W. Bader, Atoms in Molecules: A Quantum Theory, Clarendon Press, Oxford, UK, 1994; see http://www.chemistry. mcmaster.ca/aimpac/
- 54 R. Ditchfield, Mol. Phys., 1974, 27, 789-807.
- 55 K. Wolinski, J. F. Hinton and P. Pulay, J. Am. Chem. Soc., 1990, 112, 8251–8260.
- 56 The gas-phase calculations for the dianionic species are of approximate value only: due to the lack of diffuse functions (and the lack of solvation) the electrons in the free dianionic species are formally unbound (the orbital energies are positive).
- 57 P. v. Ragué Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. v. Eikema Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317–6318.
- 58 T. Hinoue, Y. Shigenoi, M. Sugino, Y. Mizobe, I. Hisaki, M. Miyata and N. Tohnai, *Chem.-Eur. J.*, 2012, **18**, 4634– 4643.
- 59 P. Pyykkö and M. Atsumi, *Chem.-Eur. J.*, 2009, **15**, 12770–12779.

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- 60 T. Kawashima *et al.* have used the equivalent setting $P2_1/a$ for $2a^*$.
- 61 A. Lorbach, M. Bolte, H.-W. Lerner and M. Wagner, *Organometallics*, 2010, **29**, 5762–5765.
- 62 For this comparison we used averaged bond lengths of (i) our structure 2a and Kawashima's structure 2a*, (ii) [Li-(THF)₂]₂[2a] and [Li(Et₂O)]₂[2a].
- 63 Related arguments have been used by Bogdanović *et al.* and Bock *et al.* to explain C–C bond length changes occurring upon the one-electron reduction of anthracene to [anthracene]⁻⁻. (*a*) B. Bogdanović, N. Janke, C. Krüger, R. Mynott, K. Schlichte and U. Westeppe, *Angew. Chem., Int. Ed. Engl.*, 1985, 24, 960–961; (*b*) H. Bock, C. Arad, C. Näther and Z. Havlas, *J. Chem. Soc., Chem. Commun.*, 1995, 2393–2394.
- 64 (a) G. Boche, H. Etzrodt, W. Massa and G. Baum, Angew. Chem., Int. Ed. Engl., 1985, 24, 863–864; (b) A. Sekiguchi, T. Matsuo and H. Watanabe, J. Am. Chem. Soc., 2000, 122, 5652–5653; (c) A. Sekiguchi, T. Matsuo and M. Tanaka, Organometallics, 2002, 21, 1072–1076. See also the pioneering work of Katz on the cyclooctatetraenyl dianion: T. J. Katz, J. Am. Chem. Soc., 1960, 82, 3784–3785.
- 65 In the case of **2c** we have not included the *tert*-butyl groups and the phenyl rings on the anthryl substituents in our

calculations in order to save computer time (*cf.* $[2c]_{model}$ in the ESI[†]).

- 66 B. S. Jensen and V. D. Parker, J. Am. Chem. Soc., 1975, 97, 5211–5217.
- 67 K. Meerholz and J. Heinze, J. Am. Chem. Soc., 1989, 111, 2325–2326.
- 68 L. S. Marcoux, A. Lomax and A. J. Bard, *J. Am. Chem. Soc.*, 1970, **92**, 243–250.
- 69 At higher optical densities, the shortest-wavelength emission of anthracene is selectively attenuated by self-absorption as a result of the small Stokes shift (in our case, the bands at $\lambda_{\max}(em) = 403 \text{ nm } (4a) \text{ or } 404 \text{ nm } (anti-4b)$ are affected). S. Kao, A. N. Asanov and P. B. Oldham, *Instrum. Sci. Techol.*, 1998, **26**, 375–387.
- 70 For a detailed study of the optical properties of a series of oligomeric 9,10-anthrylenes see: R. Fritz, W. Rettig, K. Nishiyama, T. Okada, U. Müller and K. Müllen, *J. Phys. Chem. A*, 1997, **101**, 2796–2802.
- 71 D. A. M. Egbe, C. Bader, J. Nowotny, W. Günther and E. Klemm, *Macromolecules*, 2003, 36, 5459–5469.
- 72 D. A. M. Egbe, T. Kietzke, B. Carbonnier, D. Mühlbacher, H.-H. Hörhold, D. Neher and T. Pakula, *Macromolecules*, 2004, 37, 8863–8873.