

How π Extension or Structural Bending Alters the Properties of **Boron-Doped Phenylene-Containing Oligoacenes**

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Supporting Information

ABSTRACT: Linear annulation of two 2,3-biphenylenediyl moieties to a 1,4-dibora-2,5-cyclohexadiene core via its carbon atoms leads to the boron-doped phenylenecontaining oligoacene (B-POA) DBI. The optoelectronic properties of DBI are unlike those of related boron-doped polycyclic aromatic hydrocarbons (B-PAHs), such as 6,13dihydro-6,13-diborapentacene (DBP). Herein we disclose two new B-POAs, which provide insight into fundamental structure-property relationships. The first is a π extended DBI congener (e-DBI), in which two 2,3-benzo[b]biphenylenediyl moieties



are linearly annulated to the central B_2C_4 ring and behaves partly similar to **DBI**: it is a strong electron acceptor and has a deep red color. In contrast to the nonluminescent DBI, it shows red fluorescence (quantum yield: 12%), which changes to blue-green upon addition of excess F-ions. In the presence of 0.4 equiv of F-, nearly white emission is observed (CIE1931: (0.3320) 0.4056). If biphenylenediyl moieties are angularly attached to the B_2C_4 ring via their 1,2-positions, the resulting mixture of "v"and "z"-shaped B-POA isomers (v/z-DBI) behaves distinctly different from linear DBI: the electrode potentials required for the reversible two-electron reductions of v/z-DBI are significantly more cathodic, and v/z-DBI is an orange rather than red solid and emits green light (quantum yields 65%) upon irradiation.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are an extensively investigated class of materials with widespread use.¹ Their properties can be enhanced further through the incorporation of main-group elements.² In particular, boron-doped PAHs (B-PAHs) have found numerous applications, ranging from metalfree catalysis³⁻⁷ to light-emitting devices^{5,8-11} and sensor technology.¹² Relatives of the PAHs are the phenylenecontaining oligoacenes (POAs), which contain an element of antiaromaticity due to their incorporated biphenylene moieties.^{13,14} Recently, we reported that the boron-doped POA (B-POA) DBI shows very different properties in comparison to its B-PAH analogues (Chart 1): in contrast to 9,10-dihydro-9,10-diboraanthracene (DBA) and 6,13-dihydro-6,13-diborapentacene (DBP), DBI is nonemissive and a stronger electron acceptor.^{15,16} The electron-withdrawing nature of a biphenylene backbone, combined with its unique peri distance, was also exploited by Gabbaï et al., who constructed a series of ditopic biphenylene-1,8-diyldiboranes, capable of trapping (ditopic) Lewis bases in a chelating manner (Chart 1). 17,18 Herein, we are exploring the field further to gain deeper insight into the fundamental characteristics of B-POAs. (1) The weakly luminescent DBA can be turned into an efficient blue emitter upon benzannulation to give DBP.^{15,19} We therefore also synthesized a π -extended congener of DBI, equipped with two peripheral 2,3naphthylene instead of 1,2-phenylene fragments and investigated its optoelectronic properties (e-DBI; Scheme 1). (2) We also assessed the consequences of an angular 1,2- instead of the linear 2,3-annulation of biphenylene subunits to the

 B_2C_4 core, which should afford bent isomers of DBI with "v"and "z"-shaped scaffolds (v/z-DBI; Scheme 1).

RESULTS AND DISCUSSION

Synthesis of e-DBI and v/z-DBI. The synthesis of e-DBI is based on the key intermediate 2,3-bis(trimethylsilyl)benzo-[b]biphenylene²⁰ (Scheme 2; see the Supporting Information for an optimized procedure). After cyclocondensation with BBr₃ (*n*-hexane, 120 $^{\circ}$ C, sealed ampule) and mesitylation with MesMgBr (toluene/THF, 0 °C), e-DBI was isolated in 27% yield over six steps starting from commercial 2,3-dihydroxynaphthalene.

The 1,2-bis(trimethylsilyl)biphenylene required for the synthesis of v/z-DBI was synthesized from the parent biphenylene,^{21–23} which was first brominated selectively at its 2-position.^{24,25} 2-Bromobiphenylene can subsequently be subjected to ortho-directed lithiation at its acidic 1-position using amide bases, such as lithium diisopropylamide (LDA)²⁶ and lithium 2,2,6,6-tetramethylpiperidide (LiTMP; cf. the Supporting Information) under cryogenic conditions. The fact that Me₃SiCl does not react with LiTMP in THF at -78 °C made an in situ quenching strategy possible, which furnished 2bromo-1-(trimethylsilyl)biphenylene in 88% yield. Li/Br exchange with n-BuLi and further reaction with Me₃SiCl furnished 1,2-bis(trimethylsilyl)biphenylene (90%). The cyclocondensation with BBr3 took place under the established conditions (n-hexane, 120 °C, sealed ampule), and after

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Chart 1. Structures of DBA, DBP, DBI, and Selected Biphenylene-Bridged Ditopic Boranes



Scheme 1. Structures of the B-POA DBI, Its π -Extended Derivative e-DBI, and the Bent Isomers v/z-DBI



protection of the boron atoms with mesityl substituents, a mixture of v/z-DBI was isolated by column chromatography (26%; Scheme 2). The stoichiometric ratio of v- vs z-DBI in this mixture amounted to 4:1. All attempts to separate the isomers (crystallization, normal-phase HPLC) were unsuccess-

Scheme 2. Syntheses of e-DBI (top) and v/z-DBI (bottom)^a



^{*a*}Reagents and conditions: (a) NfF (3.0 equiv), K_2CO_3 (5.0 equiv), MeCN, room temperature, 1 h; (b) Me₃SiC≡CZnCl·LiCl (2.5 equiv), Pd(PPh₃)₂Cl₂ (2 mol %), THF, Δ , 3.5 h; (c) TBAF (2.2 equiv), DCM, 0 °C, 30 min; (d) Me₃SiC≡CSiMe₃ (excess), CpCo(CO)₂ (10 mol %), neat, Δ , $h\nu$, 10 h; (e) BBr₃ (3.7 equiv), *n*-hexane, 120 °C, 3 days (sealed ampule); (f) MesMgBr (2.0 equiv), toluene/THF, 0 °C, 18 h; (g) LiTMP (1.1 equiv), Me₃SiCl (6.0 equiv), THF, -78 °C, 18 h; (h) *n*-BuLi (1.2 equiv), Me₃SiCl (2.0 equiv), THF, -78 °C, 18 h.

ful. However, reversed-phase HPLC (C18, MeOH) provided a sample of v/z-DBI that was further enriched in v-DBI (5:1).

NMR Spectroscopy. e-DBI and v/z-DBI were characterized by NMR spectroscopy in CDCl₃ solutions (cf. the Supporting Information for full details). The ¹H NMR spectrum of e-DBI contains only four biphenylene signals and one set of mesityl resonances, which fits to the proposed symmetric, linear structure (similar arguments hold for the $^{13}C{^{1}H}$ NMR spectrum of e-DBI). The v/z-DBI mixture gives rise to a major and a minor set of ¹H and ¹³C resonances. Considering the major isomer first, we note that its biphenylene halves are related by symmetry and give rise to six proton resonances. One of these signals appears upfieldshifted at 4.71 ppm, indicating that the corresponding proton experiences a shielding magnetic anisotropy effect from the nearby mesityl π system.²⁷ All of these features are in agreement with a kinked B-POA. The fact that its two mesityl substituents are magnetically inequivalent unequivocally identifies the dominant product as v-DBI. A full characterization of the minor product z-DBI was precluded by the small portion of this substance in the mixture and pronounced overlap of the v- and z-DBI proton resonances.

A comparison of the ¹³C{¹H} NMR spectra of e-**DBI** and v-**DBI** with those of their constituent hydrocarbons (e-**DBI**, benzo[*b*]biphenylene; v-**DBI**, biphenylene) revealed that only those ¹³C nuclei belonging to the rings directly attached to the B atoms are significantly deshielded, which is in accord with previous observations.^{15,28} As is typical for triarylboranes,²⁹ no resonances were detectable in the ¹¹B{¹H} NMR spectra of e-**DBI** and v/z-**DBI**.

Crystal Structure of e-DBI. Crystals of e-**DBI** suitable for X-ray analysis were obtained by recrystallization from toluene. The molecule possesses C_i symmetry in the solid state (Figure 1). In contrast to the planar **DBI**,¹⁵ but similar to the higher all-carbon [N]phenylenes,³⁰ e-**DBI** shows a sigmoidal curvature when it is viewed along the imaginary B···B axis. This distortion is mainly due to the fact that the planar 2,3-naphthylene moieties include dihedral angles of $13.5(1)^{\circ}$ with



Figure 1. Structure of e-**DBI** in the solid state (C atoms, black; B atoms, green; H atoms omitted for clarity, only Mes- C_{ipso} is shown). Selected bond lengths (Å) and angles (deg): $B-C_{endo} = 1.564(3)/1.570(3)$, $B-C_{exo} = 1.583(3)$, C1-C6 = 1.373(3), C5-C6 = 1.418(3), C4-C5 = 1.376(3), C5-C9 = 1.504(3), C6-C8 = 1.509(3), C7-C8 = 1.357(3), C8-C9 = 1.451(3), C9-C10 = 1.347(3); $C_{endo}-B-C_{endo} = 119.79(17)$, $C_{endo}-B-C_{exo} = 120.27(17)/119.91(17)$. Symmetry operator for generating equivalent atoms: (i) 2 - x, 1 - y, 1 - z.

the essentially planar DBA core. The π -electron distribution within each naphthylene fragment can be approximated by drawing a Clar's sextet in either the inner or the outer benzenoid ring. An inspection of the C–C bond length distribution agrees better with the latter description: with an average value of 1.352 Å, C7–C8 and C9–C10 are the shortest C–C bonds in the entire molecule while the connecting C8–C9 bond is rather long (1.451(3) Å). The C7=C8–C9=C10 fragment thus possesses characteristic features of a butadiene moiety (cf., *s-trans*-1,3-butadiene: C=C, 1.348(1) Å (exp),³¹ 1.338 Å (calcd);³² C–C, 1.468(2) Å (exp), 1.454 Å (calcd)). In contrast, the C–C bond lengths in the outer benzenoid ring are more evenly distributed (range: 1.372(3)–1.427(3) Å) and thus more typical of delocalized π bonds (cf. C₆H₆: average 1.378 Å).³³

The pronounced tilt at the four-membered rings of the benzo[b]biphenylene substructures has no significant influence on the C5-C9/C6-C8 bond lengths (average 1.507 Å), as they are still similar to the corresponding values in pristine biphenylene $(1.511 \text{ Å})^{34}$ and DBI (1.516 Å);¹⁵ a comparison with pristine benzo[b] biphenylene is not possible due to disorder problems.³⁵ C5-C9/C6-C8 are best regarded as elongated σ bonds with only minimal delocalization of π electrons across them (length of a typical $C(sp^2)-C(sp^2)$) single bond: 1.47 $Å^{36}$). When all relevant structural parameters are taken together, the four-membered-ring fragments of e-DBI are more reminiscent of [4]radialenes than cyclobutadienes. Significantly longer exocyclic (1.583(3) Å) than endocyclic (average 1.567 Å) B-C distances reflect the steric repulsion of the bulky mesityl substituents as well as a partial B=C double-bond character within the DBA substructure.

Electrochemistry. Both e-DBI and v/z-DBI show two redox waves with features of electrochemical reversibility in the cathodic regions of their cyclic voltammograms (THF, 0.1 M $[n-Bu_4N][PF_6]$; vs FcH/FcH⁺). According to the first reduction event, e-DBI ($E_{1/2} = -1.51$ V) possesses the same electron affinity as DBI (-1.52 V) but a higher affinity than v/z-DBI (-1.82 V). This trend persists for the second reduction event, which again proves e-DBI (-2.27 V) to be more readily reducible than v/z-DBI (-2.51 V). Two further redox transitions of e-DBI are irreversible ($E_{pc} = -2.70$, -3.41 V) and likely originate from one-electron uptake at each of the 2,3-naphthylene moieties. Neither e-DBI nor v/z-DBI showed redox events in the anodic regions of their cyclic voltammograms. Electrochemical and spectroscopic data for DBI, e-DBI, and v/z-DBI are given in Table 1.

Table 1. Electrochemical and Spectroscopic Data for DBI, e-DBI, and v/z-DBI

	$E_{1/2}/V^{a}$	$\lambda_{\rm abs}/{\rm nm}^{b,c}$	$\lambda_{\rm ex}/{\rm nm}$	$\lambda_{\rm em}/{\rm nm}^{b,c}$	$\Phi_{ ext{PL}}/\%^{m{b},m{d}}$
DBI ^e	-1.52	570 ^f			
	-2.30	399			
		330			
		317			
e-DBI	-1.51	570 ^f	364	646	12
	-2.27	364		672	
	-2.70^{g}	346			
	-3.41^{g}	331			
		315			
		250			
v/z-DBI	-1.82	495	256	506	65
	-2.51	464		540	
		425		585	
		400			
		288			
		256			

^{*a*}Conditions: THF, 0.1 M $[n-Bu_4N][PF_6]$, vs FcH/FcH⁺. ^{*b*}In cyclohexane solution. ^{*c*}Values assignable to vibrational bands are italicized. ^{*d*}Quantum yields were determined from degassed samples using a calibrated integrating sphere. ^{*c*}Values taken from ref 15. ^{*f*}Onset value of a flat plateau. ^{*g*}Irreversible redox event.

UV/Vis Spectroscopy. All electronic spectra were recorded on cyclohexane solutions (Figure 2a). e-DBI is a deep red compound, whereas v/z-DBI possesses an orange color. As in the case of DBL¹⁵ the red color of e-DBI originates from a very broad absorption plateau with an onset wavelength of approximately 570 nm (Figure S29 in the Supporting Information). The UV/vis spectrum of the 5:1 mixture of bent isomers v/z-DBI shows a nicely resolved longest-wavelength absorption band at λ_{max} = 495 nm and a distinct vibrational fine structure. In this respect, v/z-DBI resemble a known derivative of DBA carrying the 1,2biphenylenediyl fragment at only one side.²⁷ The linear DBI is nonemissive, likely due to a low-lying doubly excited state.¹⁵ Twofold benzannulation in e-DBI turns on a red fluorescence, associated with a very broad, poorly resolved emission band at $\lambda_{\rm em}$ = 646 nm (Figure 2b, right; $\Phi_{\rm PL}$ = 12%). In addition to π extension, also the simple change in the annulation mode from 2,3 (DBI)- to 1,2-annulation (v/z-DBI) leads to appreciable fluorescence ($\lambda_{em} = 506 \text{ nm}, \Phi_{PL} = 65\%$).

In the case of e-DBI, we also observed two very small emission bands at wavelengths of λ = 438 and 465 nm (cf. the Supporting Information), which became more pronounced with increasing water content of the solvent and are thus likely attributable to adducts with H₂O or OH⁻. For a further investigation of the phenomenon, we resorted to a titration of e-DBI in CHCl₃ using [*n*-Bu₄N]F·3H₂O (TBAF) as a more quantifiable ligand source (Figure 2b).

As the amount of added TBAF was increased, the original main absorption band of e-**DBI** at 364 nm gradually vanished and two new bands emerged instead ($\lambda_{abs} = 328$ and 465 nm). Only after 2 equiv of TBAF had been added did the absorption spectrum of the mixture not change further with increasing F⁻ concentration. Accordingly, the emission spectrum of e-**DBI** in the presence of 1 equiv of TBAF still showed the emission band of native e-**DBI** at 646 nm, together with a second, hypsochromically shifted band at 477 nm. After the addition of 2 equiv of F⁻ ions, the band at 646 nm was completely

norm. absorbance / a.u. 🛈

0.8

0.6 0.4

0.2

0.0

300

..... DBI 1.0 e-DBI norm. intensity / a.u. v/z-DBI 0.8 0.6 0.4 0.2 0.0 600 600 700 400 500 500 400 wavelength / nm wavelength / nm Addition of TBAF: 0 eq 1.0 1 ea 2 eq 0.8



Figure 2. (a) UV/vis absorption (left) and emission spectra (right) of DBI, e-DBI, and v/z-DBI in cyclohexane. DBI is nonfluorescent. (b) UV/vis absorption and emission spectra of e-DBI in the presence of varying amounts of $[n-Bu_4N]F\cdot 3H_2O$ (TBAF) in dry and alcohol-free CHCl₃.



Figure 3. Emission spectra of e-DBI, [e-DBI·F]⁻, 2-BMes₂-benzo[b]biphenylene, and benzo[b]biphenylene in DCM.

suppressed and exclusively the band at 477 nm remained. This latter emission appears at wavelengths similar to those of the previously mentioned small features, which supports our assumption that they originate from $e\text{-}\text{DBI}\cdot(\text{H}_2\text{O}/\text{OH}^-)$ complexes.

The following facts strongly suggest that the association/ dissociation equilibrium between e-**DBI** and F⁻ ions does not go beyond the stage of the monoadduct [e-**DBI**·F]⁻. (1) A Job plot of the e-**DBI**/TBAF system using the most intense of the emerging bands (λ = 453 nm) has its maximum at χ_{TBAF} = 0.5 (CHCl₃, Figure S31 in the Supporting Information). (2) Even the stronger Lewis acid **DBI** forms only monoadducts [**DBI**· F]⁻.¹⁵ (3) Two nearly isosbestic points are conserved during the TBAF titration (Figure 2b, left). (4) The green fluorescence of the monoadduct [e-**DBI**·F]⁻ is very similar to the emission color of the tricoordinate monoborane 2-BMes₂-benzo[b]biphenylene. In the putative diadduct [e-**DBI**· (F)₂]²⁻, neither of the two boron atoms would be capable of mediating a π interaction between the two 2,3-benzo[b]biphenylenediyl units, which should therefore be largely isolated from each other. As a result, we would expect a blue emission, reminiscent of that of pristine benzo[b]biphenylene (Figure 3; cf. the Supporting Information for the syntheses of the two model compounds). In summary, the 2 equiv of TBAF necessary for the complete quenching of the e-**DBI** emission is just required to push the association/dissociation equilibrium toward the formation of [e-**DBI**·F]⁻.

The $[e-DBI\cdotF]^-$ emission band ($\Phi_{PL} = 42\%$) and e-DBI absorption band do not overlap significantly, and the photoluminescence colors of both compounds are complementary to each other. This offers a possibility to create white light through proper adjustment of the amount of added F⁻ ions. Indeed, irradiation of a mixture of e-DBI and 0.4 equiv of TBAF in DCM at 325 nm produced nearly white light, thereby rendering e-DBI a boron-based stimuli-responsive material (CIE1931: (0.3320l0.4056); Figure 4).^{37,38}

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Figure 4. CIE1931 plot calculated from the emission spectra of e-**DBI** in the presence of varying amounts of TBAF in DCM. CIE coordinates (*X*|*Y*): 0 equiv, (0.5428|0.3778); 0.4 equiv (0.3320| 0.4056); 1 equiv, (0.2145|0.4640). $\lambda_{ex} = 325$ nm.

CONCLUSION

The compound DBI, which consists of two 2,3-biphenylenediyl moieties linked through two B-Mes bridges, represents an archetypal boron-doped phenylene-containing oligoacene (B-POA). DBI is distinguished from related boron-doped polycyclic aromatic hydrocarbons (B-PAHs) by its higher electron affinity and lack of photoluminescence. A change in the connection mode from 2,3- to 1,2-biphenylenediyl shifts the first reduction potential of the kinked v/z-DBI isomers by 0.31 V to more cathodic values and turns on an appreciable turquoise fluorescence (λ_{em} = 506 nm, Φ_{PL} = 65%). Benzannulation on both sides of DBI leads to the extended congener e-DBI, which is a comparably strong electron acceptor and a red emitter ($\lambda_{em} = 646$ nm, $\Phi_{PL} = 12\%$). Our results thus demonstrate that seemingly subtle structural modifications can have a dramatic effect on the optoelectronic properties of B-POAs. Moreover, e-DBI forms the greenemitting monoadduct $[e-\mathbf{DBI}\cdot\mathbf{F}]^-$ and thus behaves as a stimuli-responsive material, capable of producing white light upon addition of 0.4 equiv of $[n-Bu_4N]F$.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.9b00330.

Experimental details and characterization data (PDF)

Accession Codes

CCDC 1915623 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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