Substituent effects on the structure and supramolecular assembly of bis(dioxaborole)s†

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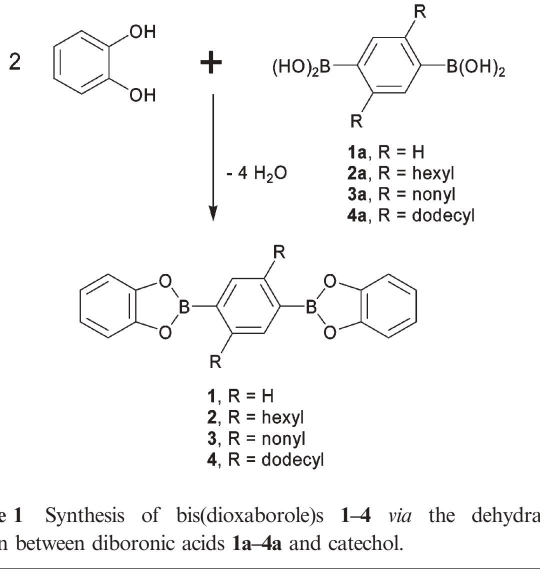
Solid-state and solution analysis shows that dialkyl substituents on the central phenyl ring of bis(dioxaborole)s, such as 2–4, do not have an appreciable effect on the planarity but do significantly alter the supramolecular assembly of these compounds.

Bis(dioxaborole)s result from the condensation reaction connecting a diboronic acid with an aromatic 1,2-diol such as catechol (Scheme 1). In these materials the empty p-orbitals on the boron atoms and the lone pairs of electrons on the oxygen atoms are in conjugation with the phenyl rings generating an extended π-conjugated system.[1] The planarity between linked aromatic rings plays a great role in defining the optical and electronic properties of this type of material.[2] Furthermore, investigations of the supramolecular structure within this class of compounds are also of interest since conjugated organic oligomers exhibiting π–π interactions in the solid-state have potential application as organic thin film transistors (OTFTs), sensors, switches, wires, *etc.*[3] Due to the low solubility and difficulties processing large extended aromatics, alkyl substituents are frequently introduced into these materials to improve processability. However, this substitution can often result in deplanarization of the conjugated system diminishing the π-stacking ability of the materials in the solid-state. Given the reduced steric demands of the borole linkage we hypothesized that substitution on the central phenyl ring would not cause such adverse outcomes. In order to evaluate the degree of planarity and investigate the supramolecular assembly of bis(dioxaborole)s a series of four bis(dioxaborole)s were synthesized (**1–4**) and studied using single-crystal X-ray diffraction and absorbance spectroscopy.



Scheme 1 Synthesis of bis(dioxaborole)s **1–4** *via* the dehydration reaction between diboronic acids **1a–4a** and catechol.

The synthesis of diboronic acids **2a–4a**, was achieved from the dihalo-analogs *via* metal–halogen exchange with *n*-BuLi followed by quenching the resulting dianion with trimethylborate and an acidic work-up (ESI-1,2†). Bis(dioxaborole)s **1–4** were readily synthesized from a mixture of the respective diboronic acid and excess catechol through the azeotropic removal of water with toluene (Scheme 1). Formation of the bis(dioxaborole)s was confirmed from mass spectral data as well as by the disappearance of the hydroxyl protons from both catechol and the diboronic acid in the ^{1}H NMR spectra. Sublimation of unreacted catechol under reduced pressure afforded pure product as determined by ^{1}H NMR.

To investigate the degree of planarity for this series in the solid state, the X-ray structures of **1** and **2** were solved.‡ To the best of our knowledge these represent the first X-ray structures of aromatic bis(dioxaborole)s. Borole **1** is centrosymmetric and only slightly deviates from planarity with a small dihedral angle of 2.2° between the central phenyl ring and the borole (Fig. 1). The summary of the three bond angles around the boron atoms (359.9°) is consistent with the expected 360° around trigonal-planar boron.

Introduction of the solubilizing hexyl side-chains in **2** did not significantly alter the planarity of the bis(dioxaborole) backbone (Fig. 2). In the solid state the dihedral angle between the borole and phenyl rings only deviates from planarity by 9.9°. While the

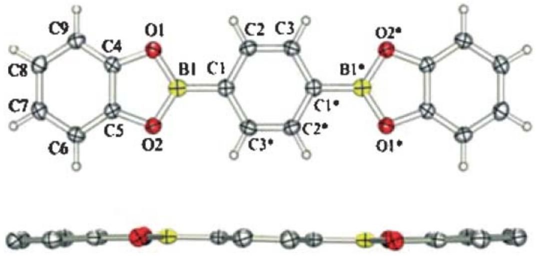


Fig. 1 Front and side views of the structure of **1**. Selected bond lengths (Å) and angles (°): B1–C1 1.541(2), B1–O1 1.389(2), B1–O2 1.390(2), O1–C4 1.384(2), O2–C5 1.384(2); O1–B1–C1 124.1(1), O2–B1–C1 124.5(1), O1–B1–O2 111.4(1), B1–O1–C4 105.1(1), B1–O2–C5 105.1(1), O1–C4–C5 109.2(1), O2–C5–C4 109.2(1).

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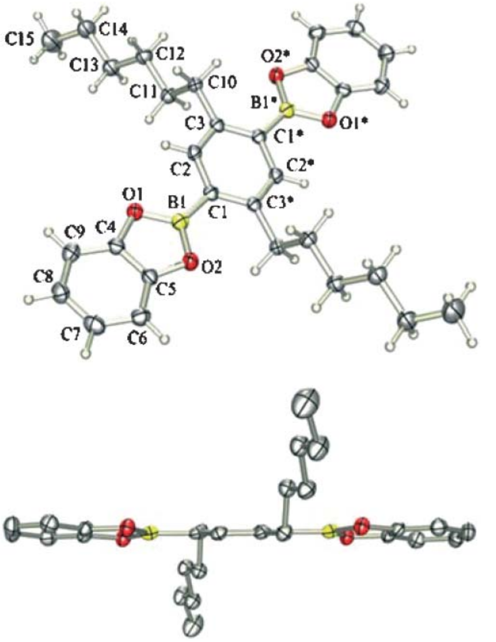

Fig. 2 Front and side views of the structure of **2**. Selected bond lengths (Å) and angles (°): B1–C1 1.543(3), B1–O1 1.395(2), B1–O2 1.390(2), O1–C4, 1.384(2), O2–C5 1.387(2); O1–B1–C1 121.6(2), O2–B1–C1 127.9(2), O1–B1–O2 110.5(2), B1–O1–C4 105.5(1), B1–O2–C5 105.4(1), O1–C4–C5 109.3(1), O2–C5–C4 109.3(1).

weak steric effect of the 2,4-dihexyl substituents does slightly alter the bond angles around boron (∠O2–B1–C1 in **2** is 127.9(2)° *vs.* **1** at 124.1(1)°) the boron atoms of **2** still meet the expected bond angle summation (360.0°) to qualify as trigonal planar.

Compared to traditionally defined conjugated oligo-aryl compounds, boroles display reduced steric interactions between the borole and the substituents on the central phenyl ring (as found in **2**). For example, even in unsubstituted *p*-terphenylene the dihedral angle between phenyl rings in the solid state is approximately 16–25°.[4] In dimethoxy substituted terphenylenes this dihedral angle can grow to 45°,[2b] and tetramethyl versions are nearly orthogonal with a dihedral angle around 82°.[5] While the systems discussed in this manuscript are only disubstituted, the alkyl substituents are large (hexyl in this case) compared to methoxy and are therefore more sterically demanding, yet the degree of twisting is diminished and subsequently the conjugation between phenyl rings is greatly enhanced.

In a heteroatom based analog similar to the borole linkage described above, unfunctionalized 1,4-bis(2-benzimidazolyl) benzene diverges from planarity in the solid state with a dihedral angle of 31° between the benzimidazole and phenyl rings.[6] The dihedral angle found between rings in 1,4-bis(2-benzobisoxazole)benzene is similar to that found for compound **1** (0.3°). However substituted versions have not been crystallized likely due to a highly disordered solid state caused by twisting of the conjugated backbone resulting from substitution on the central ring.[7] As a result of the enhanced planarity found in **2** over various structurally similar analogs this class of materials are expected to have superior packing in the solid state.

The intermolecular packing of **1** in the solid state forms a classical herringbone geometry (Fig. 3). The mean perpendicular distance between adjacent parallel molecules is 3.4 Å, consistent with typical π-stacking interactions.[3b,8] The electron deficient boron of the borole ring is sandwiched between the π-clouds of the central and terminal phenyl rings of adjacent layers. This offset π-stacking interaction is the dominate assembly force leading to a columnar structure. Adjacent columns are connected through CH–π interactions[9] into two-dimensional sheets with a CH–centroid distance of 3.618(2) Å. The columns are stacked together with alternately changing tilt angles of approximately ±75°.

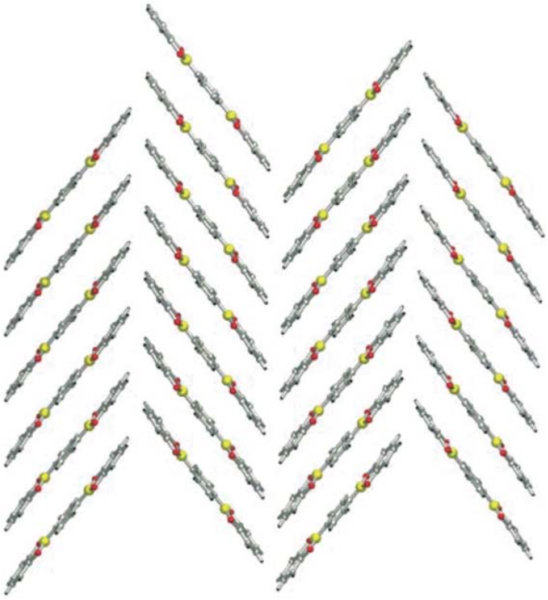

Fig. 3 Herringbone crystal packing of **1**. CH–π interactions (not indicated) occur at the "elbow" of each stack in a herringbone layer.

The solid-state structure of **2** also features offset π-stacking interactions between adjacent molecules with a mean perpendicular intermolecular stacking distance of 3.5 Å. Again the boron atom of the borole is sandwiched between the electron rich phenyl rings of neighboring molecules. It has been shown that substitution on planar aromatics can change the intermolecular packing in the solid state.[10] The supramolecular assembly of **2** however, does not display the herringbone packing geometry found in **1**, rather, the molecules assemble into two-dimensional sheets through CH···O hydrogen bonding (Fig. 4). These weak bonding interactions[11] between C9(H9)–O1′ are 3.475(2) Å long (∠C9(H9)···O1 179.0°). The resulting eight-membered rings tie molecules together into infinite chains along the [110] direction. The chains are linked together through the same hydrogen bonding motif and van der Waals interactions between the hexyl chains to create the two-dimensional sheets. The presence of the alkyl substituents on the central phenyl ring play an important role in defining the structure of the supramolecular assembly. This unique assembly pattern could provide enhanced stability of the material in electronic or photonic applications.

Solution based analysis supports similar structural preferences as indicated in the solid state. The ^{11}B NMR spectra of **1–4** in $CDCl_3$ show resonances between 30 and 32 ppm ($BF_3{\cdot}OEt_2$ external reference at 0 ppm) indicating the presence of only sp^2 boron,[12] thus supporting the argument for planar boron in solution. Additionally, the absorbance spectrum for **1** exhibits a

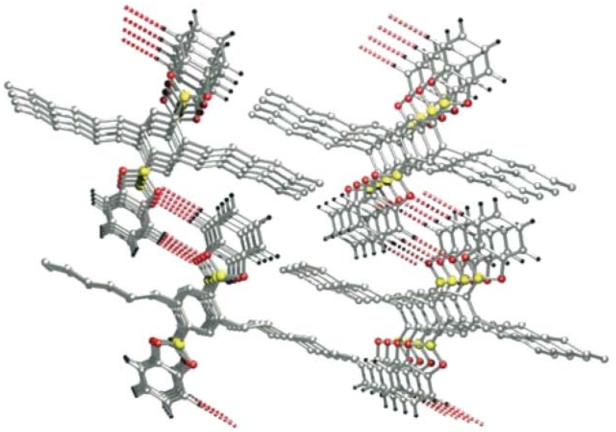

Fig. 4 Crystal packing of **2**. Intermolecular CH···O hydrogen bonding indicated by dashed red lines. Some hydrogen atoms omitted for clarity.

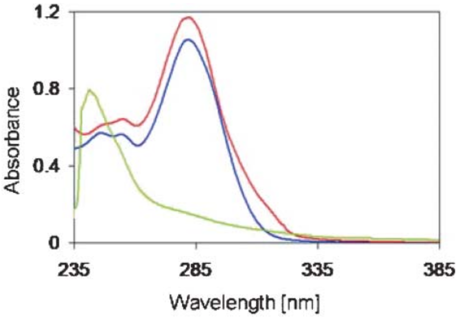

Fig. 5 Absorbance spectra of the starting diboronic acid **1a** (green), and bis(dioxaborole)s **1** (blue) and **2** (red) in CH_2Cl_2, all at 3.0×10^{-5} M.

40 nm red-shift as compared to the starting diboronic acid **1a** indicating that the borole linkage provides a π-conjugated bridge between the phenyl rings (Fig. 5).[1a] Introduction of alkyl substituents (**2–4**) onto the central phenyl ring enhances solubility by ~10-fold compared to **1**. However, the absorbance spectra for all of the substituted bis(dioxaborole)s are virtually identical to the unsubstituted version, **1** (Fig. 5, the spectrum for compound **2** is characteristic of compounds **2–4**), strongly suggesting that the alkyl groups on the central phenyl ring do not disturb the electronic interactions in these bis(dioxaborole)s.

In summary, bis(dioxaborole)s **1–4** were readily assembled through a facile condensation reaction in high yields. To the best of our knowledge, the solid-state structures of **1** and **2** are the first X-ray data obtained for aromatic bis(dioxaborole)s and represent the first structural examples of π-stacking interactions involving the borole ring in any dioxaboroles. From these studies, it has been determined that alkyl substituents on the central phenyl ring do not significantly influence the planarity and subsequently the degree of conjugation in these compounds. This substitution pattern however, greatly affects the supramolecular assemblies generated in the solid state such that **2** deviates from the herringbone geometry adopted by **1** to form planar infinite two-dimensional sheets assembled *via* CH–O hydrogen bonds and van der Waals interactions. Future studies will investigate the electronic and photonic properties of these materials in thin films.

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Notes and references

‡ *Crystal data* for **1**: $C_{18}H_{12}B_2O_4$, M = 313.90, monoclinic, space group $C2/c$, a = 11.2841(9), b = 5.5991(4), c = 22.864(2) Å, β = 95.695(1)°, V = 1437.5(2) Å^3, T = 150 K, Z = 4, 1464 independent reflections measured, final $R1$ = 0.0414 and $wR2$ = 0.0933. *Crystal data* for **2**: $C_{30}H_{36}B_2O_4$, M = 482.21, triclinic, space group $P\bar{1}$, a = 4.8191(5), b = 9.7761(10), c = 14.2815(14) Å, α = 77.386(2), β = 82.507(2), γ = 84.416(2)°, V = 649.33(11) Å^3, T = 150 K, Z = 1, 2304 independent reflections measured, final $R1$ = 0.0451 and $wR2$ = 0.0890. CCDC 261873 and 261874. See http://dx.doi.org/10.1039/b507475d for crystallographic data in CIF or other electronic format.

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