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Supramolecular behaviour of bulky arylboranes in the crystalline state

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The aromatic monoboranes **1**, **2** and bisboranes **3**, **4** of which **4** is a newly synthesised compound have been studied with reference to their supramolecular behaviour in the crystalline state. While the monoboranes crystallise purely, the bisboranes form channel-type solvent inclusions with *m*-xylene (**3a**) and nitrobenzene (**4a**) in the crystals, showing their potential as clathrate hosts in the realm of optically and electronically interesting compounds.

Keywords: aromatic boranes; solvent inclusion; X-ray crystal structures; non-covalent interactions

Introduction

Organoboranes in general and triarylboranes in particular are important types of compounds due to their interesting conformational (*1*) and Lewis acid (*2*) behaviour. For example, the chemistry of the so-called 'frustrated Lewis pairs' (*3*) has recently been extended to generate H_2 splitting systems (*4*) in which a combination of (t-Bu$_3$P and B(C_6F_5)$_3$ can activate molecular hydrogen by forming a sterically demanding adduct (*5*). Three-coordinate aromatic organoboron compounds possessing an empty p_π orbital on the boron centre have also a tendency to display intense intramolecular charge-transfer transition when an appropriate electron donor is present (*6*, *7*). This property has enabled a number of promising applications in materials chemistry such as nonlinear optical materials (*8*) and charge transport materials in organic light emitting devices (*9*). Moreover, it has been demonstrated that the corresponding boron compounds can be applied as effective colorimetric fluorescent sensors for the detection of fluoride by utilising the empty p_π orbital on the boron centre (*10*).

Current efforts are centred on using the outstanding properties of triarylboranes in specific crystalline systems (*11*). Hence, to study the modes of supramolecular contacts and packing structures of analogous boron compounds is a challenging task, which has been performed only in first steps (*12*), whereas basic crystal engineering concepts applicable to this particular class of triarylboron compounds are rather undeveloped (*13*). In this paper, we report preparation of two three-coordinate aromatic monoboranes (**1**, **2**) and two related bisboranes (**3**, **4**), including the bisboranes as the solvated complexes **3a** and **4a** (Scheme 1). Crystal structures of **1**, **2**, **3a** and **4a** are described and discussed in view of the raised question.

Results and discussion

Criteria of selection and synthesis of compounds

It is a well-known fact that the three-coordinate boron tends to be susceptible to hydrolysis by moisture, including that present in the air (*14*). For this reason, protecting bulky groups with shielding *ortho*-substituents, such as the 2,4,6-trimethylphenyl (mesityl) group, are commonly used (*6*, *7*, *13*). Experience has shown that two mesityl groups are usually sufficient to confer air stability (*8*). Bulky dimesitylboron groups should also produce this effect on a molecule rendering close packing difficult in the lattice and thus promote the formation of solvent inclusions (*15*). Moreover, anthracene and ethynylene subunits (*16*) as well as bromo substituents (*17*, *18*) occurring in a molecule may cause particular modes of supramolecular interactions in a crystal lattice, such as π-stacking (*19*), C—H···π (*20*) or Br···Br (*21*) contacts. Hence, the selected boranes **1–4**, having these structural features not only qualify stability in air but also meet the structural requirements as model compounds suitable for the intended study.

Three of the boranes studied here (**1–3**) are known from the literature (*1*, *12*, *22*), whereas **4** is a new compound, but was prepared by the procedure similar to that of **1–3**. This involves treatment of bis(4-bromophenyl)ethyne with *n*-BuLi to give the corresponding dilithiated intermediate, followed by reaction with dimesitylboron fluoride.

X-ray structural study

Although boranes **1** and **2** are described in the literature (*1*, *22*), to our knowledge, single-crystal X-ray structures of these compounds have not been reported. However,

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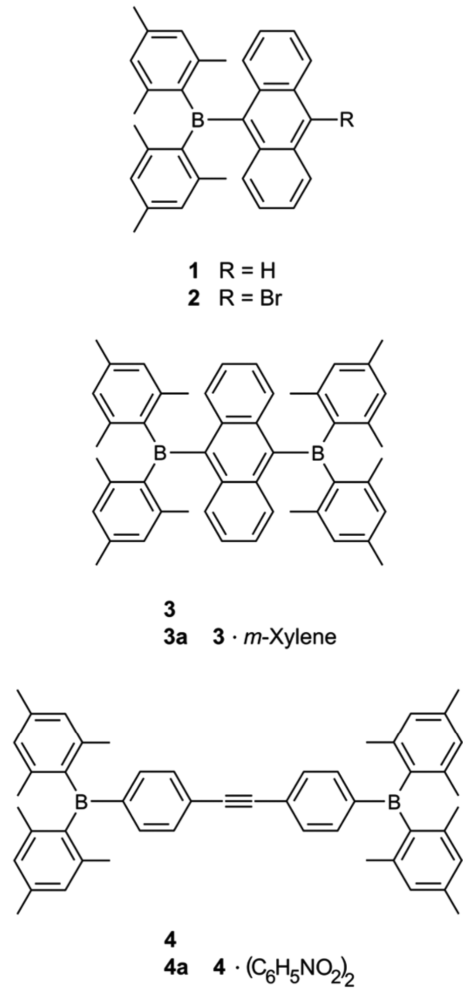

1 R = H
2 R = Br

3
3a **3** · *m*-Xylene

4
4a **4** · $(C_6H_5NO_2)_2$

Scheme 1. Compounds studied in this paper.

crystal structures of similar compounds have previously been published (*23*). They involve different p-phenyl substituted dimesitylboranes, including a 4-bromophenyl derivative. On the other hand, not only the crystal structure of a compound analogue of **3**, being a corresponding phenylene derivative of **3**, but also a crystal structure of a solvate of **3** [**3**·mesitylene (1:1)] has been described (*12*). In comparison with these known structures, the presently obtained X-ray crystal structures of **1**, **2**, **3a** [**3**·*m*-xylene (1:1)] and **4a** [**4**·nitrobenzene (1:2)] provide a good basis for demonstrating relationships between molecular structures, supramolecular contacts and packing modes typical of this particular compound class of arylboranes.

Crystallographic data and selected refinement parameters of the new structures are summarised in Table 1. Perspective views of the molecular structures and illustrations of the crystal packings are shown in Figures 1–8, respectively. The conformation of the triaryl boranes can be described by three interplanar angles, which define the inclination of the aromatic rings with respect to the plane given by the BC_3 fragment. These data together with relevant bond angles are summarised in Table 2. Information regarding intermolecular interactions is listed in Table 3.

Monoboranes 1 and 2

Crystallisation of the 9-(dimesitylboryl)anthracene (**1**) from ethylacetate yields yellow prisms of the monoclinic space group $P2_1/n$ with two independent molecules within the asymmetric unit of the cell (Figure 1). In each of the molecules, the sum of the C_{aryl}—B—C_{aryl} angles is exactly 360°, indicating ideal planar geometry of the BC_3 fragment. Taking into consideration experimental error, the B—C bond distances are nearly identical [1.569(2)-1.584(3)Å]. In order to reduce intramolecular steric interactions, the aromatic building blocks adopt a propeller-like conformation with the planes of mesityl groups inclined at dihedral angles of 69.3(1)/88.1(1)° (molecule 1) and 68.5(1)/86.5(1)° (molecule 2) with respect to the plane of their neighbouring anthracene moieties.

According to the hydrophobic nature of **1**, the molecular arrangement of the crystal is controlled by close packing rather than directed non-covalent bonding, which is restricted to only one C—H···π arene contact per molecule (*20*) [C—H···*centroid* 2.82, 2.95 Å] with one of the outer rings of the anthryl moiety acting as an acceptor (Figure 2). This part of the molecule, but involving the opposite lateral ring of the anthryl unit, also participates in an offset face-to-face interaction (*24*) with a symmetry-related anthryl moiety of a neighbouring molecule (*centroid*···*centroid* distance of 4.03 Å). Thus, strands of molecules interacting via the anthryl units characterise the packing mode of the crystal, while the mesityl groups fill lattice space.

Crystals of 9-(dimesitylboryl)-10-bromoanthracene (**2**) grown from ethylacetate were found to have the same space group as **1**. And, as before, the asymmetric cell unit comprises two crystallographically independent molecules (Figure 3). However, the parameters of the unit cell indicate that the presence of the bromo substituent induces a crystal structure which is different from **1**. This relates to both the molecular and packing structure. Although the two molecules of the asymmetric cell unit reveal similar propeller-like conformations, the anthryl part of one of them is considerably bent with a maximum atomic distance of −0.12 [C(14)] and 0.13 [C(11)]Å from the least-squares plane of this unit. These two molecules show also different contact modes to form a dimer unit, which is stabilised by a *side-on* (type II geometry) C—Br···Br—C contact (*18*) [C(7A)—Br(1A)···Br(1) 161.0°, C(7)—Br(1)···Br(1A) 69.2°], a C—H···π hydrogen bond (*20*) [C(5A)—H(5A)···*centroid*(ringB) 2.75 Å,

Table 1. Crystallographic and structure refinement data of the compounds studied.

Compound	**1**	**2**	**3a**	**4a**
Empirical formula	$C_{32}H_{31}B$	$C_{32}H_{30}BBr$	$C_{50}H_{52}B_2 \cdot C_8H_{10}$	$C_{50}H_{52}B_2 \cdot 2\ C_6H_5NO_2$
Formula weight	426.38	505.27	780.70	920.76
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	P-1	P-1
a (Å)	8.4220(3)	13.3195(11)	8.2913(3)	8.2306(3)
b (Å)	46.4359(19)	22.4175(18)	10.8109(3)	11.1645(4)
c (Å)	12.3895(5)	17.4298(15)	14.2956(5)	14.3775(6)
α (°)	90.0	90.0	110.826(1)	88.664(2)
β (°)	93.158(2)	104.234(5)	101.890(2)	85.731(2)
γ (°)	90.0	90.0	96.442(1)	76.815(2)
V (Å^3)	4838.0(3)	5044.6(7)	1147.56(7)	1282.73(8)
Z	8	8	1	1
$F(000)$	1824	2096	420	490
D_c (Mg m^{-3})	1.171	1.331	1.130	1.192
μ (mm^{-1})	0.065	1.648	0.063	0.073
Data collection				
Temperature (K)	173(2)	93(2)	153(2)	153(2)
No. of collected reflections	66230	136375	27594	30068
within the $\theta -$ limit (°)	1.9–30.3	1.5–30.7	1.6–29.3	2.3–30.1
Index ranges $\pm h$, $\pm k$, $\pm l$	$-11/11$, $-65/65$, $-17/15$	$-19/19$, $-32/31$, $-24/24$	$-11/11$, $-14/14$, $-19/19$	$-11/11$, $-15/15$, $-20/20$
No. of unique reflections	14379	15483	6207	7495
R_{int}	0.0989	0.1318	0.0751	0.0431
Refinement calculations: full-matrix least- squares on all F^2 values				
Weighting expression w [a]	$[\sigma^2(F_0^2)+(0.0526P)^2+(0.0000P)]^{-1}$	$[\sigma^2(F_0^2)+(0.0534P)^2+(0.0000P)]^{-1}$	$[\sigma^2(F_0^2)+(0.0981P)^2+(0.6016P)]^{-1}$	$[\sigma^2(F_0^2)+(0.0000P)^2+(0.9098P)]^{-1}$
No. of refined parameters	607	625	302	322
No. of F values used $[I > 2\sigma(I)]$	6265	6663	3422	4767
Final R-Indices				
$R(=_3\|\Delta F\|/_3\|F_0\|)$	0.0537	0.0468	0.0587	0.0471
wR on F^2	0.1287	0.1209	0.1832	0.0914
S (= Goodness of fit on F^2)	0.832	0.986	0.832	0.951
Final $\Delta\rho_{max}/\Delta\rho_{min}$(eÅ^{-3})	0.39/−0.22	0.76/−0.67	0.45/−0.35	0.29/−0.23

[a] $P = (F_0^2 + 2F_c^2)/3$

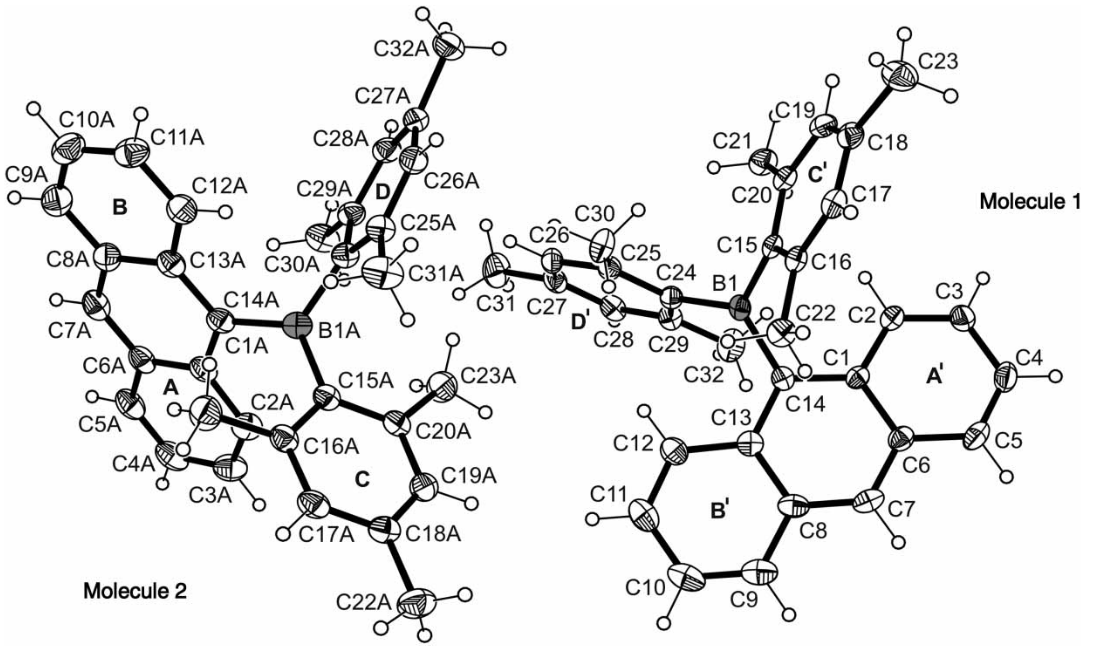

Figure 1. Perspective view of the asymmetric unit of **1**, including numbering scheme of atoms and ring specification. The thermal displacement ellipsoids of the non-hydrogen atoms are drawn at the 40% probability level.

141.4°] and a *face-to-face* anthryl···mesityl interaction (*19*, *24*). The dimeric unit represents the basic supramolecular element of the crystal structure. In the crystal packing (Figure 4), these molecular dimers are associated between each other by relatively strong C—H···π contacts [C(11A)—H(11A)···*centroid*(ringB) 2.59 Å, 160.7°]. A comparative inspection of the crystal structure of **2** with that of an analogous 4-bromophenyl modified derivative (space group *P*-1, $Z = 2$) (*23*) reveals markedly different packing modes. In the bromophenyl compound, a weak C—H···Br contact (*25*) represents the only supramolecular interaction of certain relevance, resulting in the formation of linear molecular strands which are packed in a parallel manner.

Bisboranes 3 (3a) and 4 (4a)

Recrystallisation of 9,10-bis(dimesitylboryl)anthracene (**3**) from *m*-xylene yields yellow columns of the space group *P*-1, which turned out to be a solvent inclusion compound **3a** with *m*-xylene of host:guest stoichiometric ratio of 1:1. The unit cell contains one bisborane host and

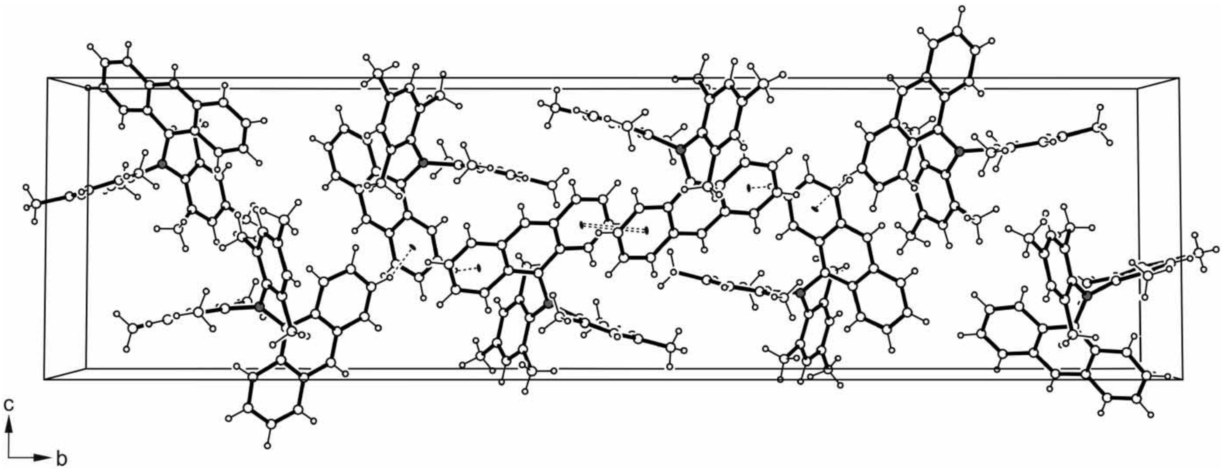

Figure 2. Packing excerpt of **1** viewed along the crystallographic *a*-axis. C—H···π interactions are marked as broken lines, aromatic face-to-face interactions as broken double lines.

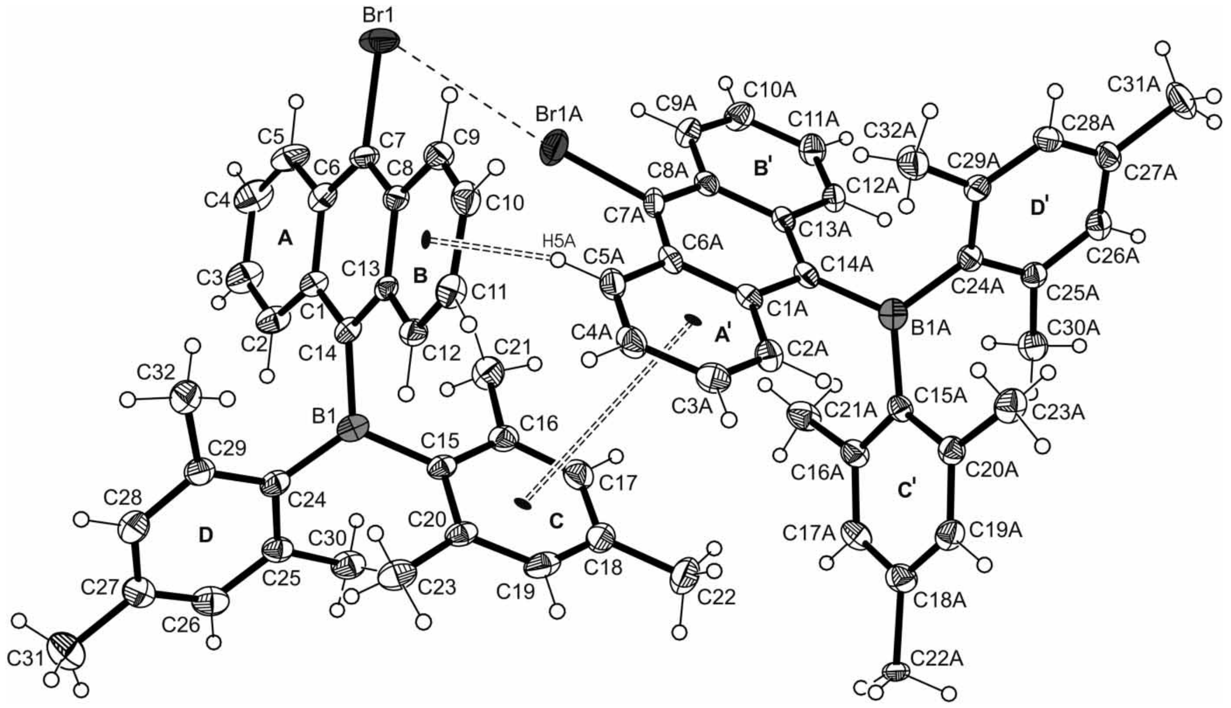

Figure 3. Perspective view of the asymmetric unit of **2**, including numbering scheme of atoms and ring specification. The thermal displacement ellipsoids of the non-hydrogen atoms are drawn at the 40% probability level. Broken line represents Br···Br, broken double lines C—H···π and aromatic face-to-face interactions, respectively.

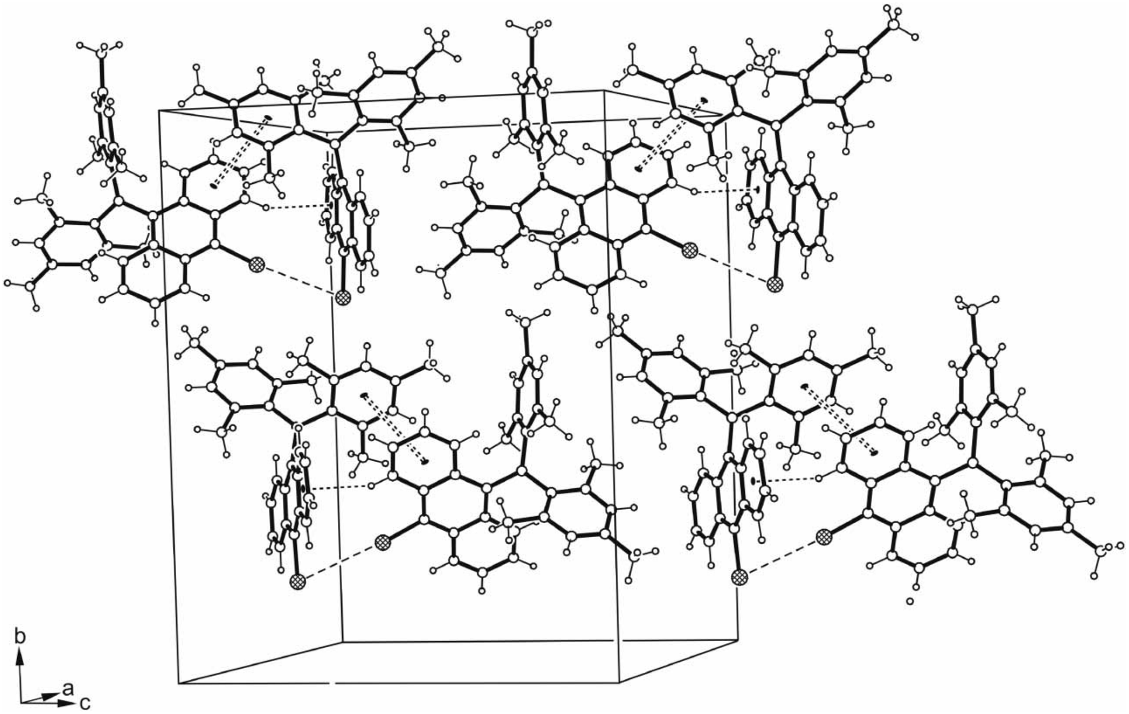

Figure 4. Packing structure of **2**. Br atoms are indicated as cross-hatched circles. Broken lines represent Br···Br, dotted lines C—H···π and broken double lines aromatic face-to-face interactions.

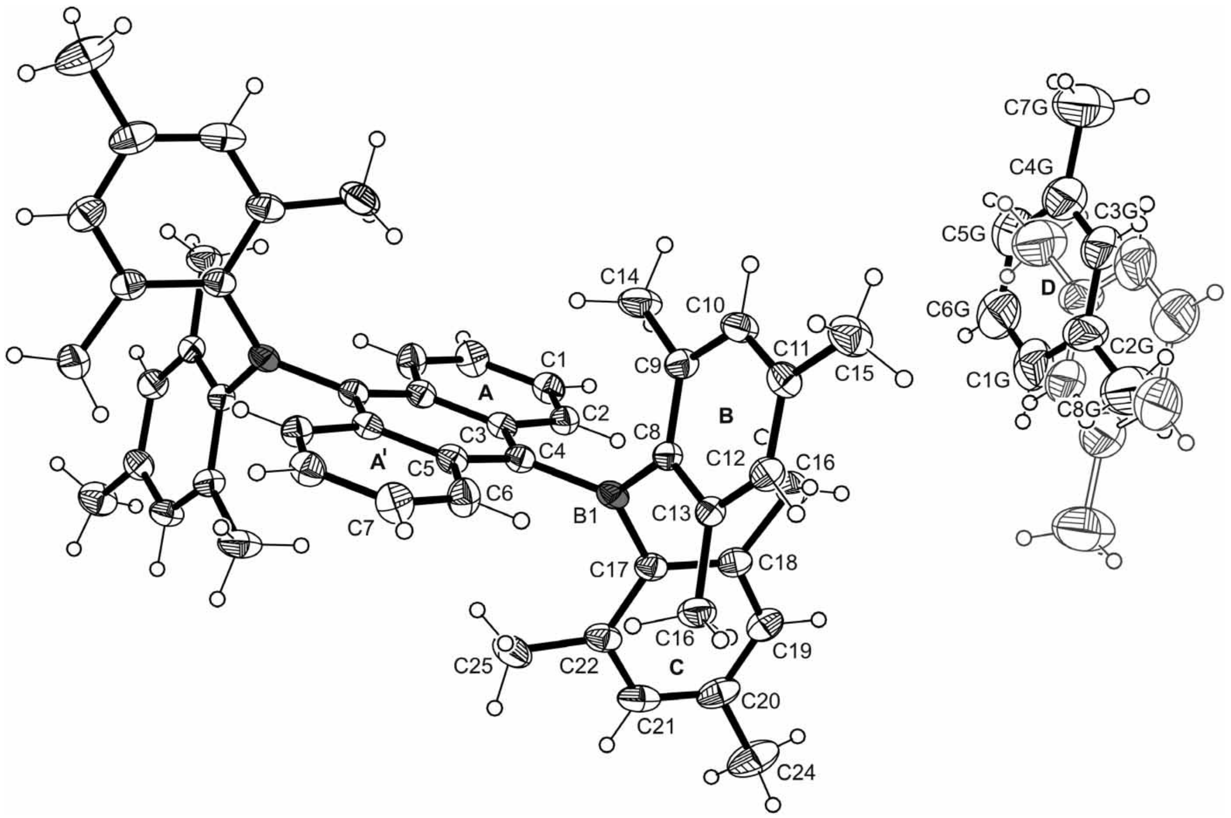

Figure 5. Perspective view of the asymmetric unit of **3a**, including numbering scheme of atoms and ring specification. The thermal displacement ellipsoids of the non-hydrogen atoms are drawn at the 40% probability level. Both disorder sites of the *m*-xylene guest molecule are shown.

one molecule of *m*-xylene, i.e. the host molecule exhibits inversion symmetry (Figure 5). Moreover, the solvent molecule is disordered around a centre of inversion. The mean planes of the mesityl residues are inclined at angles of 86.1(1) and 86.4(1)° with respect to the central anthracene unit.

It should be noted at this point that the present crystal structure significantly differs from the known inclusion structure of **3** with mesitylene (*12*). The asymmetric cell unit of the latter structure contains two halves of the host molecule and one molecule of solvent which is located on a general position. Hence, a rather insignificant appearing modification of the guest component exerts an influence on molecular composition of the unit cell and induces conformational changes of the host which is evident from dihedral angles of 87.9(1)/89.0(1) and 80.5(1)/80.4(1)° between mesityl residues and the anthracene part of the molecules. Nevertheless, in both inclusion structures, the solvent molecules are accommodated in channels running along the crystallographic *a*-axis. As depicted in Figure 6(a), the channels of the **3**·*m*-xylene inclusion structure show a nearly rectangular cross-section with dimensions of approximately 5.5 × 6.5 Å. More extended channels with an elongated profile (6.5 × 11.5 Å) are found in the corresponding structure of **3**·mesitylene (Figure 6(b)). A view of the packing structures reveals the predominance of stacking interactions between the aromatic units of the crystal components. However, remarkable deviations exist with regard to the molecular order along the stacking direction of molecules.

4,4′-Bis(dimesitylboryl)tolane (**4**) crystallised from nitrobenzene yielded a solvent inclusion compound **4a** with nitrobenzene of host:guest stoichiometric ratio 1:2 (space group *P*-1). The unit cell contains one host and two molecules of nitrobenzene (Figure 7), i.e. the bisborane is located on a special position and the aromatic rings of the diphenylethyne fragment display coplanarity. The aromatic rings of the molecular unit are slightly irregular hexagons with C—C bond lengths ranging between 1.382(2) and 1.406(2) Å. The B—C distances are 1.569(2), 1.573(2) and 1.577(2) Å, which exclude a partial quinoid character of the phenylene rings compared to a related compound (*12*). Similar to the aforementioned case, the cavity structure of the host lattice is of the channel-type. Each channel (7.0 × 9.2 Å) is filled with a pair of infinite C—H···O bonded strands of nitrobenzene

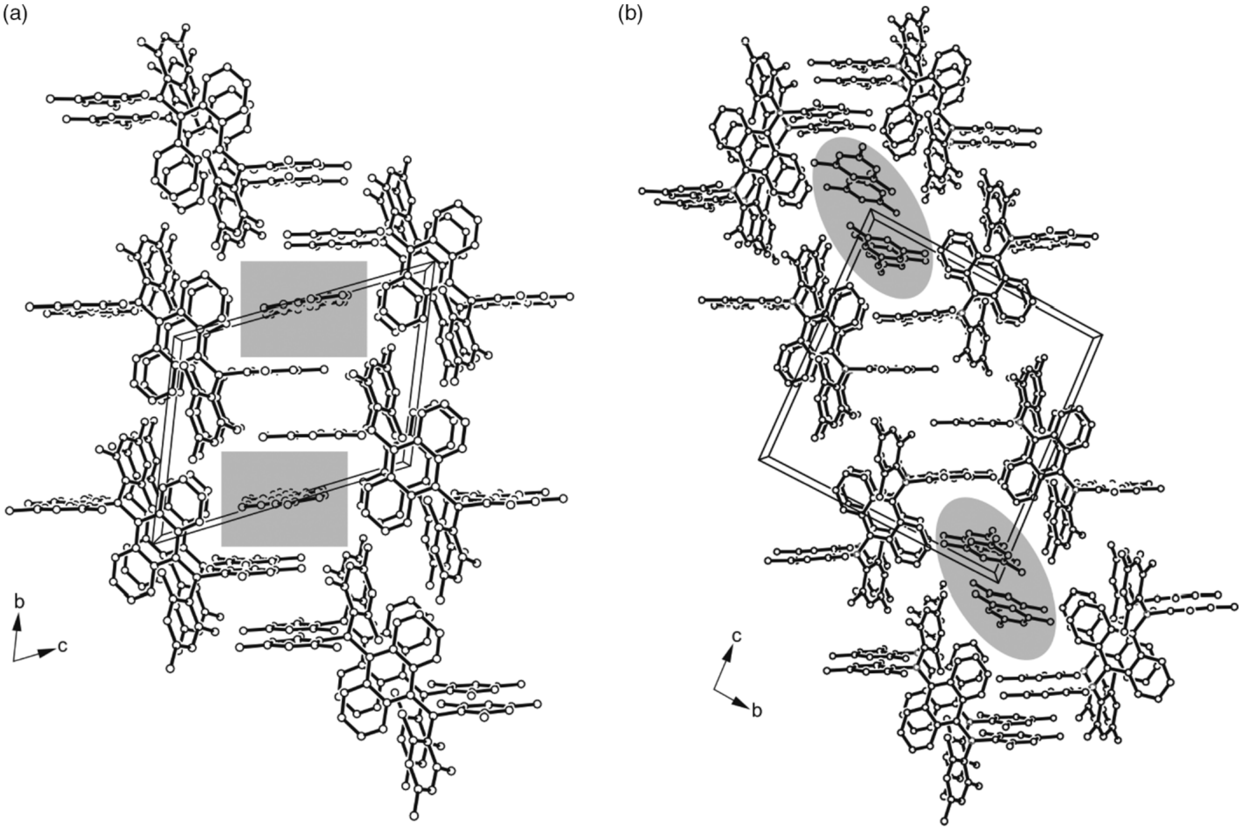

Figure 6. Packing structures of (a) **3**·*m*-xylene (1:1) (**3a**) and (b) **3**·mesitylene (1:1) (*12*) viewed along the crystallographic *a*-axis, showing the host channels filled with guest molecules.

molecules (*25*) extending along the *a*-axis and with opposite running directions (Figure 8). Association between the strands occur via offset face-to-face arene interactions (*24*) with a distance of 3.8 Å between the ring centroids. As controlling interactions between host molecules do not exist, the crystal lattice of **4a** is mainly stabilised by the incorporation of the solvent molecules which optimises the packing density.

Conclusions

Corresponding with previous findings, the X-ray crystal structures of both the aromatic mono- (**1**, **2**) and diboryl compounds (**3**, **4**) show planar geometry of the BC_3 fragment and a propeller-like conformation of the aromatic units. In case of diborane **3** and particularly in **4**, this gives rise to a molecular structure being suggestive of the so-called wheel-and-axle (*26*, *27*) or dumb-bell-shaped compounds (*28*, *29*). The latter compounds are typical of their distinct behaviour to be effective clathrate hosts (*15*, *30*). In conformity with this structural resemblance, diboranes **3** and **4** were found to crystallise as solvent inclusions with *m*-xylene (**3a**) and nitrobenzene (**4a**), unlike monoboranes **1** and **2** although featuring a bulky structure. The tendency of **3** to act as crystalline host has also been proven by a previously formed clathrate with mesitylene (*12*). Nevertheless, while the host:solvent stoichiometry in the inclusion compounds of **3** has been determined as 1:1, the stoichiometry in the clathrate **4a** shows 1:2 host:guest stoichiometry, indicating the consequence of the differently shaped spacer units in the two bisboranes. But a channel-type structure is revealed in each of the clathrates. The packing is mostly stabilised by apolar weak interactions including π-stacking contacts (*19*, *20*), which does also apply for the crystal structure of **1**. Only in the case of **2**, owing to the bromine substituent, specific Br···Br contacts (*18*) are there in addition exerting an influencing control on the packing behaviour which gives rise to the formation of molecular dimers.

In summary, it is to be expected from this study that bisboranes of similar structure may initiate a new promising class of clathrate compounds, combining channel structure, potential Lewis acid behaviour (*2*) as well as the optical and electronic material properties (*6–9*) known for the triarylboranes in general.

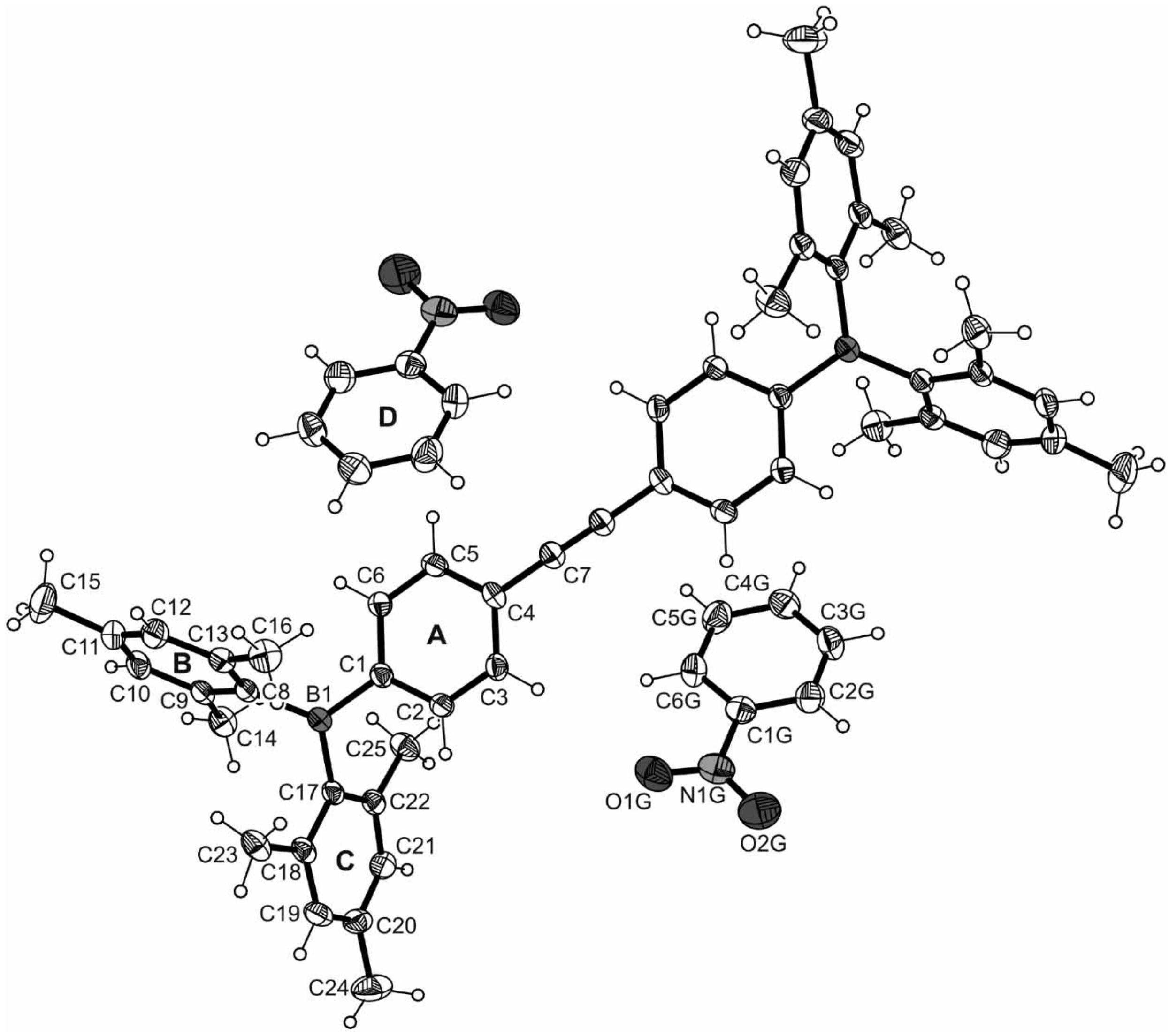

Figure 7. Perspective view of the 1:2 host–guest unit of **4a**, including numbering scheme of atoms and ring specification. The thermal displacement ellipsoids of the non-hydrogen atoms are drawn at the 40% probability level.

Experimental

General

The melting point (uncorrected) was determined by using a microscope heating stage PHMK Rapido (Wägetechnik Dresden). The IR spectrum was recorded on a Nicolet FT-IR 510 using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 400 at 400 and 100 MHz, respectively, using TMS as reference. The MS was determined on a SCIEX API 365 instrument. The TLC analysis was performed with aluminium sheets precoated with silica gel 60 F_{254} (Merck). Solvents were purified by standard procedures. Bibenzyl and dimesitylboron fluoride were purchased (Sigma-Aldrich) and used without further purification.

Synthesis of compounds

9-(Dimesitylboryl)anthracene (**1**) (*1*), 9-(dimesitylboryl)-10-bromoanthracene (**2**) (*22*) and 9,10-bis(dimesitylboryl)-anthracene (**3**) (*12*) were prepared as described in the literature. Bis(4-bromophenyl)ethyne was synthesised from bibenzyl via bromination and dehydrobromination according to the known procedure (*16*).

*4,4′-Bis(dimesitylboryl)tolane (**4**)*

A solution of *n*-BuLi in *n*-hexane (1.6 M, 5.25 ml, 8.50 mmol) was added to a stirred suspension of bis(4-bromophenyl)ethyne (1.41 g, 4.20 mmol) in dry diethylether (45 ml) and *n*-hexane (20 ml) at −78°C under argon. The mixture was warmed up to 0°C and stirred for 30 min.

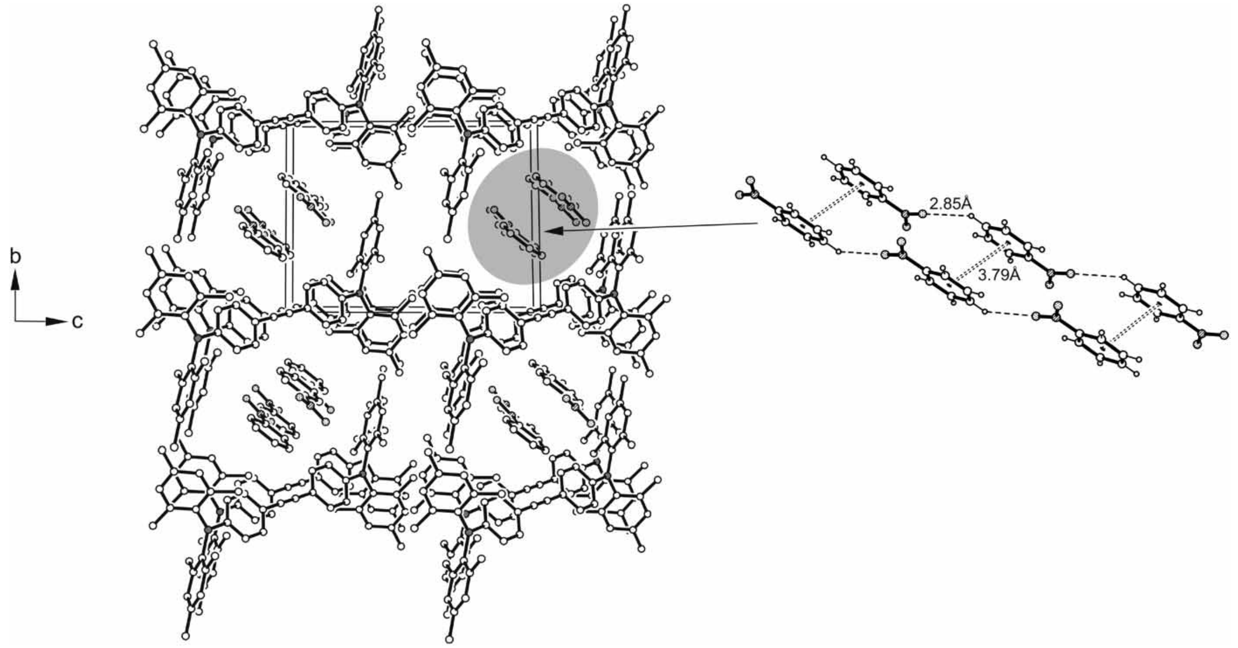

Figure 8. Packing structure of **4a** viewed along the crystallographic *a*-axis, showing the host channels filled with guest molecules and the mode of guest···guest interactions. Broken lines represent C—H···O and double broken lines aromatic face-to-face contacts.

Dimesitylboron fluoride (2.50 g, 8.40 mmol) in dry diethylether (20 ml) was added dropwise. The mixture was stirred at room temperature for 10 h. The solid was collected and repeatedly washed with *n*-hexane to yield 1.80 g (64%) of a colourless powder; m.p. 245–247°C. IR (KBr) $\tilde{\nu}$ 3063, 3022 (C—H, arom.), 2955, 2918, 2856, 2732 (CH_3), 1604, 1595, 1546 (C═C), 1443, 1374 (CH_3), 1290, 1239, 1218, 1174, 1154 (C═C—B), 1028, 976, 873, 848, 830, 664, 545 (C—C≡C), 514 (C—B); ^1H NMR (400 MHz, $CDCl_3$) δ 2.00 (s, 24 H, *o*—CH_3), 2.31 (s, 12 H,

Table 2. Selected conformational parameters of the compounds studied.

Compound	**1**	**2**	**3a**	**4a**
Interplanar angles (°)				
mpln[a]/anthryl	54.2(1)	58.4(2)	58.5(1)	
mpln/anthryl	51.1(1)	56.2(2)		
mpln/mesityl(B)	50.4(1)	52.7(2)	52.1(1)	52.4(1)
mpln/mesityl(B′)	52.5(1)	50.6(1)		
mpln/mesityl(C)	48.3(1)	41.2(2)	45.6(1)	58.1(1)
mpln/mesityl(C′)	47.2(1)	42.9(2)		
mpln/phenyl				27.5(1)
Bond angles				
C(14)—B(1)—C(15)	115.1(1)	116.5(2)		
C(14)—B(1)—C(24)	122.6(1)	123.0(2)		
C(15)—B(1)—C(24)	122.3(1)	120.5(2)		
C(14A)—B(1A)—C(15A)	122.2(2)	118.9(2)		
C(14A)—B(1A)—C(24A)	117.6(1)	119.3(2)		
C(15A)—B(1A)—C(24A)	120.2(1)	121.8(2)		
C(4)—B(1)—C(8)			119.6(2)	
C(4)—B(1)—C(17)			120.3(2)	
C(8)—B(1)—C(17)			120.1(2)	
C(1)—B(1)—C(8)				119.4(1)
C(1)—B(1)—C(17)				118.2(1)
C(8)—B(1)—C(17)				122.3(1)

[a] **1**, **2**: mpln means least-squares plane through the BC_3 fragment [B(1),C(14),C(15),C(24)]; least-squares plane through the BC_3 fragment [B(1A),C(14A),C(15A),C(24A)]; **3a**: least-squares plane through the BC_3 fragment [B(1),C(1),C(10),C(22)]; **4a**: least-squares plane through the BC_3 fragment [B(1),C(1),C(8),C(17)].

Table 3. Distances and angles of possible hydrogen-bond-type interactions of the compounds studied.

Atoms involved	Symmetry	Distances (Å)		Angle (°)
		D···A	H···A	D—H···A
1				
C(17A)—H(17A)···*centroid* (A′)[a]	$1+x, y, z$	3.765(3)	2.82	172.4
C(28)—H(28)···*centroid* (B)[a]	$-1+x, y, z$	3.885(3)	2.95	169.9
2				
C(26A)—H(26A)···*centroid* (A)[a]	$x, y, -1+z$	3.933(3)	2.99	172.8
C(5A)—H(5A)···*centroid* (B)[a]	x, y, z	3.547(3)	2.75	141.4
C(11A)—H(11A)···*centroid* (B)[a]	$0.5+x, 0.5-y, -0.5+z$	3.501(3)	2.59	160.7
C(30A)—H(30A)···Br(1)	$0.5-x, 0.5+y, 1.5-z$	3.979(2)	2.94	149.1
3a				
C(24)—H(24C)···*centroid* (C)[a]	$2-x, 1-y, -z$	3.767(3)	2.99	136.7
C(15)—H(15C)···*centroid* (D)[a]	$1-x, 1-y, 1-z$	3.722(3)	2.82	152.7
4a				
C(3)—H(3)···O(1G)	$2-x, 1-y, -z$	3.771(2)	2.83	169.6
C(4G)—H(4G)···O(1G)	$-1+x, y, z$	3.532(2)	2.85	129.3
C(2G)—H(2G)···*centroid* (C)[a]	$-1+x, y, z$	3.740(3)	2.94	143.2

[a] Centroid means centre of gravity of the respective aromatic ring. **1**, **2**: ring A: C(1)···C(6); ring B: C(8)···C(13); ring C: C(15)···C(20); ring D: C(24)···C(29); ring A′: C(1A)···C(6A); ring B′: C(8A)···C(13A); ring C′: C(15A)···C(20A); ring D′: C(24A)···C(29A); **3a**, **4a**: ring C: C(17)···C(22); ring D: C(1G)···C(6G).

p—CH_3), 6.82 (s, 8 H, mesityl-*H*), 7.46–7.49 (m, 8 H, phenylene-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 23.4 (*C*H_3, 91.8 (*C*≡*C*), 126.3 (*C*—C≡C), 128.3 (*C*—H, mesitylene), 131.1 (*C*—H, phenylene), 136.1 (*C*—CH_3, *para*), 138.9 (*C*—CH_3, *ortho*), 140.7 (*C*—B, mesitylene), 141.6 (*C*—H, phenylene, 146.2 (*C*—B, phenylene); MS (EI) *m*/*z* Calcd for $C_{50}H_{52}B_2$: 674.57. Found: 674.43 [M^+].

X-ray crystallography

Crystals of **1**, **2**, **3a** and **4a** were grown by slow evaporation of solutions of **1–4** in ethyl acetate (**1** and **2**), *m*-xylene (**3**) and nitrobenzene (**4**), respectively, under ambient conditions. The intensity data were collected on a Bruker APEX II diffractometer with Mo K_α radiation ($\lambda = 0.71073$ Å) using ω- and *N*-scans. Reflections were corrected for background, Lorentz and polarisation effects. Preliminary structure models were derived by application of direct methods (*31*) and were refined by full-matrix least-squares calculation based on F^2 for all reflections (*31*). All hydrogen atoms were included in the models in calculated positions and were refined as constrained to bonding atoms. The crystal data and experimental parameters are summarised in Table 1. Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 771643 (**1**), CCDC 771642 (**2**), CCDC 771641 (**3a**) and CCDC 771640 (**4a**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Read, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033, Email: deposit@ccdc.cam.ac.uk).

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