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# Synthesis and spectroscopic characterization of 3,5-diaryl-*cyclo*-1,2,4-trithia-3,5-diborolanes, $Ar_2B_2S_3$ ($Ar = Ph$, $2\text{-}MeC_6H_4$, $3\text{-}MeC_6H_4$, $4\text{-}MeC_6H_4$, $4\text{-}EtC_6H_4$, $3,5\text{-}Me_2C_6H_3$), and some related chemistry of boron-sulphur heterocyclic species

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## Abstract

The interaction of $S_8$ with $ArBBr_2$ ($Ar = Ph$, $4\text{-}MeC_6H_4$) at 140–160°C was reinvestigated and found to give poor yields of 3,5-diaryl-*cyclo*-1,2,4-trithia-3,5-diborolanes, $Ar_2B_2S_3$, and larger quantities of oligomeric/polymeric material containing $ArBS_n$ species. Reaction of $ArBBr_2$ ($Ar = Ph$, $2\text{-}C_6H_4$, $3\text{-}MeC_6H_4$, $4\text{-}MeC_6H_4$, $4\text{-}EtC_6H_4$, $3,5\text{-}Me_2C_6H_3$) with $^tBu_2S_2$ in refluxing toluene gave the thermally-stable, moisture-sensitive $Ar_2B_2S_3$ compounds in moderate yields. Previously reported ($Ar = Ph$, $4\text{-}MeC_6H_4$) and new ($Ar = 2\text{-}MeC_6H_4$, $3\text{-}MeC_6H_4$, $4\text{-}EtC_6H_4$, $3,5\text{-}Me_2C_6H_3$) compounds were characterized by NMR ($^{11}B$, $^1H$, $^{13}C$), IR and MS. The reaction of $ArBBr_2$ ($Ar = Ph$, $2\text{-}MeC_6H_4$, $3\text{-}MeC_6H_4$) with $(Me_3Si)_2S$ in toluene or benzene solution at room temperature rapidly (in minutes) afforded 2,4,6-triaryl-*cyclo*-1,3,5-trithia-2,4,6-triborinanes (borthiins, $Ar_3B_3S_3$) and not the expected 2,4-diaryl-cyclo-1,3-dithia-2,4-diboretanes ($Ar_2B_2S_2$). The BS heterocycles have been modelled by use of semi-empirical (AM1) methods. Lowest energy conformations, heats of formation, and barriers to rotation about the B–C bonds are discussed.

*Keywords:* Boron; Sulphur; Trithiadiborolanes; Borthiins; Dithiadiboretanes

## 1. Introduction

The first report of the five-membered heterocyclic $B_2S_3$ ring with substituents at boron and a S–S bond ($R_2B_2S_3$, *cyclo*-1,2,4-trithia-3,5-diborolanes, Fig. 1(a)) was made by Schmidt and Siebert in 1964 [1]. Since then diffraction studies have confirmed the heterocyclic structure of $Me_2B_2S_3$, $Cl_2B_2S_3$, and $Ph_2B_2S_3$ [2–4]. Preparative routes to trithiadiborolanes include the reactions of halogenoboranes $BX_3$ or $RBX_2$ with $H_2S_x$ ($x > 1$), [1,5], $Na_2S_2$ [6], $^tBu_2S_2$ [7], or $S_8$ [8–10]; substituted derivatives have been obtained from $X_2$-$B_2S_3$ [9–11]. In this paper we report on the synthesis and characterization of some new 3,5-diaryl-*cyclo*-1,2,4-trithia-3,5-diborolanes obtained from the reaction of $^tBu_2S_2$ with $ArBBr_2$. We also report on a reinvestigation of the reaction of $S_8$ with $PhBBr_2$ and on attempts to prepare 2,4-diaryl-*cyclo*-1,3-dithia-2,4-diboretanes ($Ar_2B_2S_2$, Fig. 1(b)) by reactions of $(Me_3Si)_2S$ with $ArBBr_2$. Molecular modelling studies involving semi-empirical (AM1) calculations on the conformations of these and related aryl-substituted BS heterocycles are also reported.

## 2. Results and discussion

### 2.1. Synthesis

The interaction of $PhBBr_2$ with $S_8$ has been reported to yield $BBr_3$ and $Br_2B_2S_3$ [10], $Ph_2B_2S_3$ [12], or $Ph_2B_2S_4$ (Fig. 1(c)) [13]. The reaction of $PhBBr_2$ with an excess of $S_8$ was reinvestigated by $^{11}B\text{-}\{^1H\}$-NMR spectroscopy and by mass spectrometry in order to clarify these contradictory reports and to determine

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whether this might be a general method for the preparation of $Ar_2B_2S_3$ compounds. A neat reaction mixure was heated at ca. 160°C for 16 h and a black viscous liquid/solid was obtained. The $^{11}B\text{-}\{^1H\}$ NMR spectrum ($C_6D_6$ solution) of this material revealed three clearly resolved peaks; the strongest signal was due to unchanged $PhBBr_2$ (55%), and $Ph_2B_2S_3$ [9] was identified as the minor product (5%). The major product ($\delta + 52.2$ ppm, 40%) was of interest, and attempts were made to isolate and identify it. Distillation of the black residue under reduced pressure removed starting materials and left a viscous black oil which would not distil further. Mass spectrometry (MS) on this material revealed ions with m/e values consistent with $[PhBS_n]^+$ ($n = 2$ to 8) fragments; no molecular ions arising from $Ph_2B_2S_4$ were evident. The $^{11}B$ chemical shift of the 'product' is consistent with strain-free cyclic $\{PhBS_n\}$ structures as detected by MS; species such as $PhBS_5$ have been postulated previously as reaction intermediates [14]. It is likely that the major 'product' is a complex mixture of both cyclic and polymeric species, and it is evident that this is a poor synthetic route to $Ph_2B_2S_3$. Analogous results were obtained for a $4\text{-}MeC_6H_4BBr_2/S_8$ reaction.

Thermal reactions of $PhBCl_2$ or $PhBI_2$ with $^tBu_2S_2$ have been reported to give $Ph_2B_2S_3$ [7]. We now report that $ArBBr_2$ compounds react with $^tBu_2S_2$ in toluene under thermal conditions to yield the diaryl-

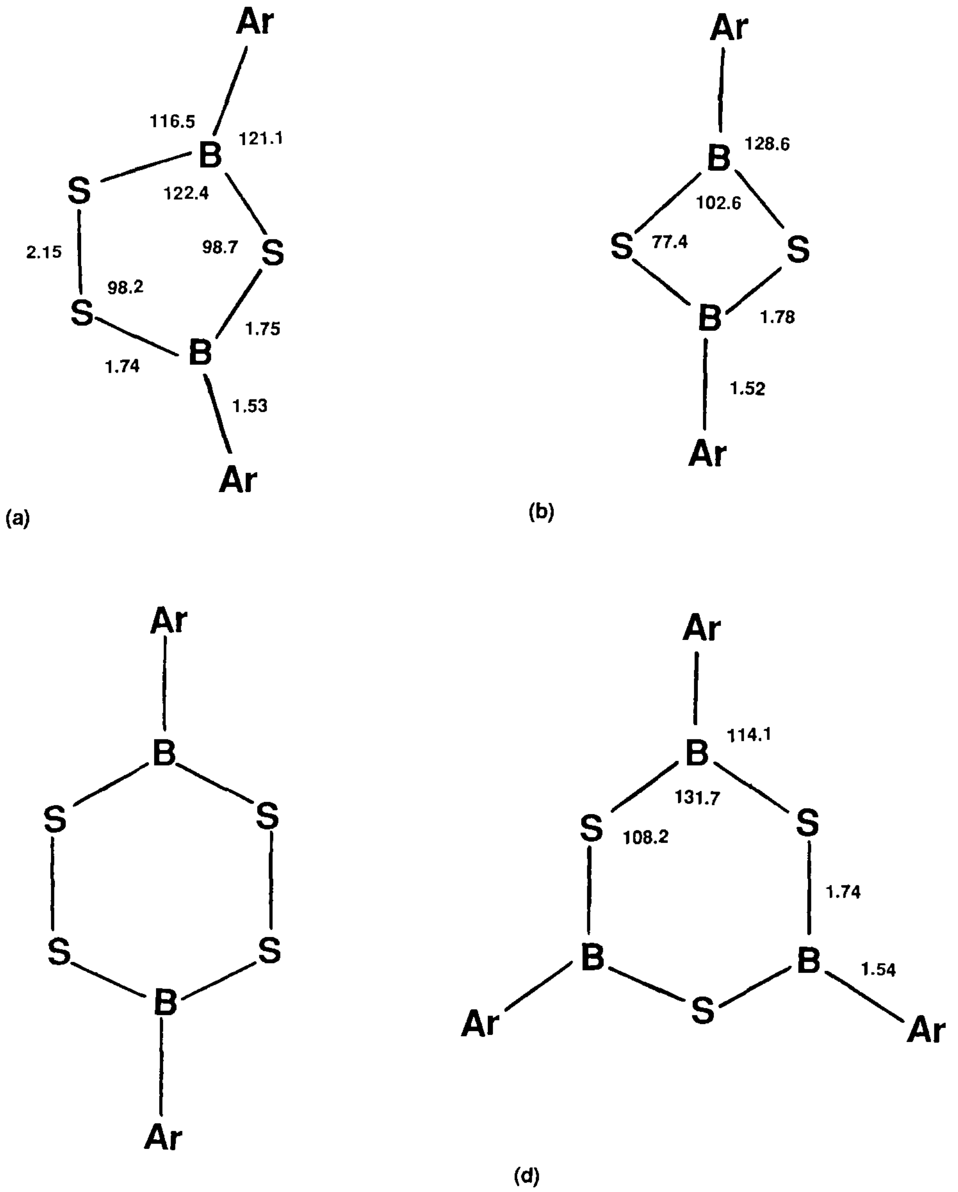

Fig. 1. Structures of the aryl BS heterocyclic ring systems. (a) 3,5-diaryl-1,2,4,3,5-trithiadiborolane; (b) 2,4-diaryl-1,3,2,4-dithiadiboretane; (c) 3,6-diaryl-1,2,4,5,3,6-tetrathiadiborinane; (d) 2,4,6-triaryl-1,3,5,2,4,6-trithiatriborinane. Numbers represent the calculated (AM1) bond lengths (Å) and bond angles (°) for the optimized structures of the $Ar = 4\text{-}MeC_6H_4$ derivatives.

*cyclo*-trithiadiborolane derivatives (Eq. (1): Ar = Ph, 2-$MeC_6H_4$, 3-$MeC_6H_4$, 4-$MeC_6H_4$, 4-$EtC_6H_4$, 3,5-$Me_2C_6H_3$). Typically, reaction mixtures were heated under reflux for 120 h and the product was obtained as the residue after removal of all volatile material by vacuum distillation in ca. 50% yield. The compounds $Ph_2B_2S_3$ and $(4\text{-}MeC_6H_4)_2B_2S_3$ have been previously reported but the other derivatives are new. The trithiadiborolanes are thermally robust and moisture-sensitive, and were characterized by NMR ($^{11}B$, $^1H$, $^{13}C$) and by IR spectroscopy and MS (Table 1, and see below for discussion).

$$2ArBBr_2 + 2{}^tBu_2S_2 \rightarrow Ar_2B_2S_3 + 4{}^tBuBr + 1/8S_8 \qquad (1)$$

Nöth and Rattay have reported the preparation 2,4-diphenyl-*cyclo*-1,3-dithia-2,4-diboretane ($Ph_2B_2S_2$) from $PhBCl_2$ and $(Me_3Si)_2S$ in refluxing benzene [15] and we attempted to prepare a series 2,4-diaryl derivatives of this $B_2S_2$ ring system from $ArBBr_2$. We were unsuccessful in this respect but within minutes at room temperature in toluene or benzene the reactions gave the 2,4,6-triaryl-1,3,5-trithia-2,4,6-triborinane (triarylborthiin, Fig. 1(d)) in high yields (Eq. (2): Ar = Ph, 2-$MeC_6H_4$, 3-$MeC_6H_4$). We were unable to detect by $^{11}B$ NMR spectroscopy any signal attributable to $Ph_2B_2S_2$ (+45 ppm, thf) [15] in the $PhBX_2/(Me_3Si)_2S$ (X = Cl, Br) reaction mixtures, which, like the substituted aryl derivatives, cleanly gave $Ph_3B_3S_3$. Products were identified by comparison of their spectroscopic properties with those of authentic samples [16]. This is a very convenient procedure for the preparation of triarylborthiins.

$$3ArBBr_2 + 3(Me_3Si)_2S \rightarrow Ar_3B_3S_3 + 6Me_3SiBr \qquad (2)$$

We recently reported that the reaction of HgS with 2-$MeC_6H_4BBr_2$ in refluxing benzene gave an unidentified product in addition to the expected triaryborthiin [16]; NMR data reported herein supports the formulation of this product as $(2\text{-}MeC_6H_4)_2B_2S_3$. We have also found that other, less sterically demanding, triarylborthiins (eg. Ar = Ph, 4-$MeC_6H_4$), slowly thermally decompose over a period of several months to give the related diaryltrithiadiborolanes even when stored under nitrogen at −20°C in the dark.

Table 1
Spectroscopic data for 3,5-diaryl-*cyclo*-1,2,4-trithia-3,5-diborolanes [a]

| | |
|---|---|
| $Ph_2B_2S_3$ | NMR: $\delta(^{11}B)$: +66.4 (+65.9, ref. 9); $\delta(^1H)$: 7.2m; $\delta(^{13}C)$: 128.2, 128.4, 132.8, 134.8, Ar.<br>IR: 1594m, 1432s, 1332m, 1308m, 1220s, 1163w, 1072w, 1024w, 991m, 966s (B–S?), 928m, 885s (B–S?), 747s, 691s, 628w.<br>MS: 272, $M^+$(67%); 152, $PhBS_2^+$ (100%); 119, $C_6H_4BS$ (10%); 77, $Ph^+$ (89%). |
| $(2\text{-}MeC_6H_4)_2B_2S_3$ | NMR: $\delta(^{11}B)$: +64.8; $\delta(^1H)$: 2.50s (3H) Me; 7.0–7.25m (3H), 7.85d (1H), Ar.<br>$\delta(^{13}C)$: 21.6, Me; 122.9, 128.0, 128.7, 133.1, 133.2, 139.0, Ar.<br>IR: 3058w, 1596m, 1565w, 1457s, 1374s, 1290s, 1206s, 1032w, 1069w, 964m (B–S?), 887m (B–S?), 747s, 631s.<br>MS: 300, $M^+$ (44%); 166, $ArBS_2^+$ (100%); 133, $C_7H_6BS^+$ (47%); 91, $Ar^+$ (50%); accurate mass: found 300.0444 ± 0.004 amu, calculated 300.0444. |
| $(3\text{-}MeC_6H_4)_2B_2S_3$ | NMR: $\delta(^{11}B)$: +65.1; $\delta(^1H)$: 2.05s (3H) Me; 6.9–7.10m (3H), 7.75m (1H), Ar;<br>$\delta(^{13}C)$: 20.8, Me; 128.2, 131.6, 132.8, 135.0, 137.6, 156.2(?), Ar.<br>IR: 1597w, 1576w, 1400w, 1253s, 1181m, 1167m, 969m (B–S?), 947m, 924w, 890w, (B–S?), 780s, 693m, 638w.<br>MS: 300, $M^+$ (68%); 166, $ArBS_2^+$ (100%); 133, $C_7H_6BS^+$ (53%); 91, $Ar^+$ (29%); accurate mass: found 300.0444 ± 0.004 amu, calculated 300.0444. |
| $(4\text{-}MeC_6H_4)_2B_2S_3$ | NMR: $\delta(^{11}B)$: +65.7; $\delta(^1H)$: 2.60s (3H) Me; 7.40d (2H), 8.05d (2H), Ar.<br>$\delta(^{13}C)$: 22.5, Me; 129.7, 136.7, 136.8, 143.6, Ar.<br>IR: 1602m, 1376s, 1222w, 1208w, 1183m, 962m (B–S?), 885m (B–S?), 803m, 775w, 732s.<br>MS: 300, $M^+$ (39%); 166, $ArBS_2^+$ (100%); 133, $C_7H_6BS^+$ (37%); 91, $Ar^+$ (47%). |
| $(3,5\text{-}Me_2C_6H_3)_2B_2S_3$ | NMR: $\delta(^{11}B)$: +65.4; $\delta(^1H)$: 2.20s (6H) Me; 6.95 (1H), 7.70 (2H), Ar.<br>$\delta(^{13}C)$: 21.7, Me; 137.7 (x2?), 140.5, 148.7, Ar.<br>IR: 1601m, 1330m, 1290m, 1185m, 1038m, 989w, 959m (B–S?), 926m, 895m (B–S?), 850m, 816m, 726s, 694w.<br>MS: 328, $M^+$ (64%); 180, $ArBS_2^+$ (100%); 147, $C_8H_8BS^+$ (49%); 105, $Ar^+$ (25%); accurate mass: found 328.0757 ± 0.004 amu, calculated 328.0757. |
| $(4\text{-}EtC_6H_4)_2B_2S_3$ | NMR: $\delta(^{11}B)$: +66.1; $\delta(^1H)$: 1.15t (3H), 2.50q (2H), 7.05d (2H), 7.90d (2H);<br>$\delta(^{13}C)$: 14.6, Me; 28.6, $CH_2$; 127.3, 134.3, 134.6, 148.3, Ar.<br>IR: 1605s, 1510w, 1403m, 1224s, 1187m, 1140w, 1057w, 990m, 968s (B–S?), 924m, 889s (B–S?), 852w, 824s, 761m.<br>MS: 328, $M^+$ (60%); 180, $ArBS_2^+$ (100%); 165 (50%); 147, $C_8H_8BS^+$ (15%); 105, Ar (37%); accurate mass: found 328.0757 ± 0.004 amu, calculated 328.0757. |

[a] NMR data in $C_6D_6$, IR in nujol mull (s, strong; m, medium; w, weak).

### 2.2. *Spectroscopic studies on 3,5-diaryl-cyclo-1,2,4-trithia-3,5-diborolanes*

The trithiadiborolanes have been characterized by NMR ($^{11}$B, $^{1}$H, $^{13}$C) and by IR spectroscopy and MS (Table 1). The compounds $Ph_2B_2S_3$ and $(4\text{-}MeC_6H_4)_2B_2S_3$ have been previously prepared but, with the exception of $^{11}$B data for the former, no spectroscopic data were reported [7,9]. The $^{11}$B NMR shifts for the diaryltrithiadiborolanes are within a narrow range centred at +65.5 ppm, and lie downfield (ca. 5 ppm) from those for the related 6-membered borthiin ring systems [14]. Any upfield shift that could be expected as a result of increased $\pi$-shielding, associated with an increased S/B ratio, is outweighed by the effects of changing the bond angles at boron as a consequence of incorporating the sp$^2$ hybridized boron atoms into a 5-membered ring [17]. The chemical shift for $(2\text{-}MeC_6H_4)_2B_2S_3$ is consistent with those for the other trithiadiborolanes, indicating that steric congestion between the ortho-methyl groups and the heterocyclic ring system is not as pronounced (see below for results of molecular modelling) as in the case of $(2\text{-}MeC_6H_4)_3B_3S_3$, for which an anomolously lowfield shift was observed [16,18]. The IR spectra show two bands in the region 965 cm$^{-1}$ and 890 cm$^{-1}$ that are attributable either to B–S stretches [19] or to ring breathing modes. These stretches are at lower energy than those for the related triarylborthiins [16]. Mass spectra (El, 70 eV) were generally characterized by a relatively strong molecular ion peak, with $[ArBS_2]^+$ as the parent ion and $[ArBS]^+$ notably absent. This breakdown pattern contrasts with that for related triarylborthiin systems for which $[ArBS]^+$ were the parent ions and $[ArBS_2]^+$ ions were not observed [16]. An ion consistently found in all spectra of the tolyl derivatives was at *m/e* 133, and this we assign, by analogy with an ion reported [20] for the breakdown of $Ph_3B_3S_3$, to $C_7H_6BS^+$ (with 4-membered $BSC_2$ ring). The corresponding ions at *m/e* 147 and 119 were also observed in the mass spectrum of $(3,5\text{-}Me_2C_6H_3)_2B_2S_3$, $(4\text{-}EtC_6H_4)_2B_2S_3$, and $Ph_2B_2S_3$, respectively. High resolution mass spectra confirmed the molecular ions for the new diarytrithiadiborolanes.

### 2.3. *Molecular Modelling studies on BS heterocyclic rings*

Semi-empirical calculations were performed using a commercially available AM1 program. To assess the accuracy of the method on molecules containing B and S atoms in heterocyclic rings the calculated structures of $Me_2B_2S_3$ and $Ph_2B_2S_3$ were compared with their experimentally determined structures [2,3]. Similarly, the heterocyclic ring structure of $Br_3B_3S_3$ [21] was compared with calculated parameters of $Ph_3B_3S_3$. The calculated parameters of all three compounds are generally within a few per cent of the experimental values, with the AM1 method tending slightly to systematically shorten the B–S bond distances, decrease internal ring angles at sulphur, increase internal ring angles at boron, and elongate the S–S bond distance in the trithiadiborolanes. However, for the purposes of this study it was concluded that the AM1 method models these BS heterocycles satisfactorily.

Geometry minimizations were performed on the 4-$MeC_6H_4$ and 2-$MeC_6H_4$ derivatives of $Ar_2B_2S_2$, $Ar_2B_2S_3$, and $Ar_3B_3S_3$ to assess steric effects in these compounds. Calculated optimized structure for 4-$MeC_6H_4$ derivatives are given in Fig. 1(a), 1(b), and 1(d) other selected data are given in the Experimental section. The BS heterocycles are, with the exception of $(2\text{-}MeC_6H_4)_3B_3S_3$, approximately co-planar at minimum energy (CCBS torsion angles $< 3.0°$). This preferred co-planar geometry is indicative of a B–C ($\pi$) interaction. Rotational barriers about the B–C bonds in these compounds are calculated at 0.3–1.8 kcal mol$^{-1}$ with the aryl ring in the destabilized conformation perpendicular to the heterocyclic ring. The rotational barrier about the B–N bond in $(Me_2N)_2B_2S_2$, for which $^{11}$B NMR chemical shift data support a strong $\pi$ interaction [13], is calculated to be 16.3 kcal mol$^{-1}$. The approximately co-planar (CCBS torsion angles of ca. 2.8°) calculated optimized geometry of $Ph_2B_2S_3$ differs significantly from the experimentally determined solid state structure which shows the Ph rings to be tilted 18.8° to the $B_2S_3$ ring. This discrepancy could, in the light of the low calculated B–C rotational barrier, be attributable to the effects of crystal packing forces on the solid state conformation. In $(2\text{-}MeC_6H_4)_3B_3S_3$ the aryl rings are substantially tilted (av. 67°) with respect to the planar heterocyclic ring in its lowest energy conformation. The B–C rotational barrier is higher (3.9 kcal mol$^{-1}$) than in the other BS heterocycles and the co-planar structure is destabilized by steric (*ortho*-$CH_3 \cdots S$) interactions. This interaction is not so marked in $(2\text{-}MeC_6H_4)_2B_2S_3$ and $(2\text{-}MeC_6H_4)_2B_2S_2$ owing to the larger *exo*-CBS angles. Calculated $\Delta H_f$ values show that the 4-$MeC_6H_4$ isomers are all thermodynamically more stable than the corresponding 2-$MeC_6H_4$ isomers, indicating that such steric interactions still persist in a weak form even for $(2\text{-}MeC_6H_4)_2B_2S_2$. Calculated $\Delta H_f$ values for compounds of stoichiometry 'ArBS' clearly show the thermodynamic stability of the trimer (borthiin) over the dimer (dithiadiboretane).

## 3. Experimental

### 3.1. *General*

Reactions were carried out under standard Schlenk conditions under dry $N_2$ and all solvents were dried before use. The reagents $^{t}Bu_2S_2$, $(Me_3Si)_2S$ and $BBr_3$ were obtained commercially, and $ArBBr_2$ species were prepared by standard methods [16,22,23]. The IR spectra were recorded on a Perkin-Elmer FT-IR 1600 spectrometer as Nujol mulls in standard cells with NaCl windows. Mass spectra were recorded on a Finnigan 1020GC/mass spectrometer. The NMR spectra were recorded on a Bruker AC 250 CP/MAS NMR spectrometer operating at 250 MHz for $^{1}H$, 62.9 MHz for $^{13}C$-$\{^{1}H\}$ and 80.25 MHz for $^{11}B$-$\{^{1}H\}$ with samples dissolved in $C_6D_6$. Chemical shifts ($\delta$) are given in ppm, with positive values towards high frequency (downfield) from $SiMe_4$ for $^{1}H$ and $^{13}C$-$\{^{1}H\}$ and from $BF_3.OEt_2$ for $^{11}B$-$\{^{1}H\}$. Molecular modelling calculations involved use of programs from the HyperChem [24] package.

### 3.2. Reaction of $PhBBr_2$ with $S_8$

The bromide $PhBBr_2$ (1.80g, 4.0 mmol) was added to powdered $S_8$ (0.77g, 24.1 mmol) and the mixture was heated (16 h at 140–160°C) with stirring in a Schlenk tube. Cooling to room temperature gave a black solid, $^{11}B$-$\{^{1}H\}$ NMR [$\delta$ (relative intensity, identity)] + 65.6 (5%, $Ph_2B_2S_3$), +57.1 (55%, $PhBBr_2$), +52.2 (40%, 'product'). Fractional distillation (0.1 mmHg) of this solid resulted in removal of $PhBBr_2$ and $S_8$ and left a black residue, $m/e$: 344 (2%, $PhBS_8$), 312 (5, $PhBS_7$), 280 (20, $PhBS_6$), 256 (7, $S_8$), 248 (17, $PhBS_5$), 236 (11), 224 (3, $S_7$), 216 (10, $PhBS_4$), 206 (20), 192 (7, $S_6$), 184 (15, $PhBS_3$), 172 (45), 160 (12, $S_5$), 152 (1, $PhBS_2$), 142 (60), 128 (20, $S_4$), 96 (40, $S_3$) 80 (82), 69 (70), 64 (100, $S_2$).

### 3.3. Synthesis of $(3\text{-}MeC_6H_4)_2B_2S_3$

A mixture of $^{t}Bu_2S_2$ (3.22g, 18.1 mmol) and 3-$MeC_6H_4BBr_2$ (4.71 g, 19.0 mmol) in dry toluene (20 $cm^3$) was heated under reflux (120 h), to give a dark solution along with small amounts of a black solid adhering to the walls of the vessel. The solution was transferred to a distillation flask and the product, $(3\text{-}MeC_6H_4)_2B_2S_3$, was obtained from it as a dark solid (1.34 g, 47%) after removing all volatile materials by vacuum distillation (0.1 mmHg/ up to 180°C). Yields of the other $Ar_2B_2S_3$ compounds were similar. Spectroscopic data ($^{1}H$, $^{11}B$, $^{13}C$ NMR; IR, MS) are given in Table 1.

### 3.4. Synthesis of $(3\text{-}MeC_6H_4)_3B_3S_3$

A mixture of $(Me_3Si)_2S$ (1.28g, 7.2 mmol) and 3-$MeC_6H_4BBr_2$ (1.78 g, 6.7 mmol) in dry toluene (20 $cm^3$) was stirred at room temperature, and samples were periodically removed for $^{11}B$ NMR spectroscopy. After 2 h the mixure was cooled to −20°C and then left overnight at this temperature, to give a white precipitate of $(3\text{-}MeC_6H_4)_3B_3S_3$. This was isolated by removing the solvent with a syringe and pumping the residue to dryness (0.60 g, 66%). A similar reaction in toluene solution under reflux was complete within minutes. Monitoring ($^{11}B$ NMR) of the reactions for Ar = Ph, 2-$MeC_6H_4$ showed clean conversion to $Ar_3B_3S_3$.

### 3.5. Molecular Modelling

$(Me_2N)_2B_2S_2$, $Me_2B_2S_3$, $Ar_2B_2S_3$ (Ar = Ph, 4-$MeC_6H_4$, 2-$MeC_6H_4$), $Ar_2B_2S_2$ (Ar = 4-$MeC_6H_4$, 2-$MeC_6H_4$), and $Ar_3B_3S_3$ (Ar = 4-$MeC_6H_4$, 2-$MeC_6H_4$) were initially geometry-optimized by a molecular mechanics program ($MM^+$) to obtain global minima. Structures were then further refined by semi-empirical methods (AM1) using the Polak-Ribiere algorithm with termination conditions of RMS $< 0.1$ kcal $Å^{-1}$ $mol^{-1}$. Calculated data include optimized molecular geometry, total energy ($E$), and heats of formation ($\Delta H_f^0$). Calculated geometry parameters for $Me_2B_2S_3$ and $Ph_2B_2S_3$ follow. $Me_2B_2S_3$: distances (Å): B–S(B) 1.746, B–S(S) 1.733, S–S 2.154, B–C 1.532; angles (°): SBS 121.9, BSS 98.4, BSB 99.3. $Ph_2B_2S_3$: distances (Å): B–S(B) 1.744, B–S(S) 1.736, S–S 2.153, B–C 1.53; angles (°): SBS 122.5, BSS 98.2, BSB 98.7. Calculated geometry parameters for $(4\text{-}MeC_6H_4)_2B_2S_2$, $(4\text{-}MeC_6H_4)_2B_2S_3$, $(4\text{-}MeC_6H_4)_3B_3S_3$ are given in Fig. 1. Calculated $E$ (kcal $mol^{-1}$) and $\Delta H_f^0$ (kcal $mol^{-1}$): $Me_2B_2S_3$: −24543, −65.71; $Ph_2B_2S_3$: −55299, +8.16; $(2\text{-}MeC_6H_4)_2B_2S_2$: −57982, +11.01; $(4\text{-}MeC_6H_4)_2B_2S_2$: −57985, +7.73; $(2\text{-}MeC_6H_4)_2B_2S_3$: −62487, −6.91; $(4\text{-}MeC_6H_4)_2B_2S_3$: −62488, −7.46; $(2\text{-}MeC_6H_4)_3B_3S_3$: −86998, −8.57; $(4\text{-}MeC_6H_4)_3B_3S_3$: −87003, −14.25; $(Me_2N)_2B_2S_2$: −37442, −87.72. Single point AM1 calculations on these optimized geometries with constrained rotations about the B–X bonds gave energies from which barriers to rotation (kcal/mol) were calculated: $Ph_2B_2S_3$: 0.3; $(2\text{-}MeC_6H_4)_2B_2S_2$: 1.5; $(4\text{-}MeC_6H_4)_2B_2S_2$: 1.7; $(2\text{-}MeC_6H_4)_2B_2S_3$: 1.8; $(4\text{-}MeC_6H_4)_2B_2S_3$: 0.4; $(2\text{-}MeC_6H_4)_3B_3S_3$: 3.9; $(4\text{-}MeC_6H_4)_3B_3S_3$: 0.4; $(Me_2N)_2B_2S_2$: 16.3.

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