Contributions to the Chemistry of Boron. Part 194.[1] Synthesis and Characterization of Mono, Bi-, and Tri-cyclic Boron–Nitrogen–Sulphur Ring Systems. Crystal Structure of 2,7,9,14-Tetrakis(diethylamino)-3,5,6,10,12,13-hexathia-1,8-diaza-2,4,7,9,11,14-hexaboratricyclo[9.3.0.0^{4,8}]tetradecane[†]

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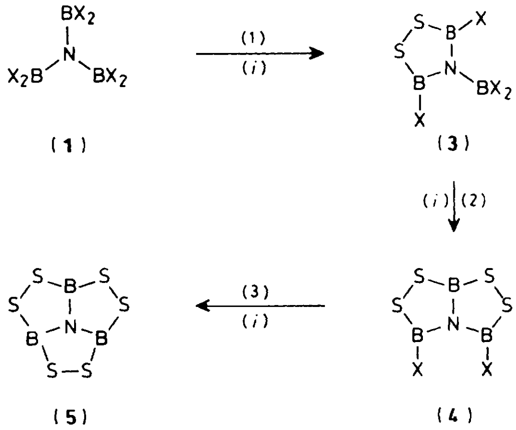
Reactions of the triborylamines N(BX$_2$)$_3$ (X = Cl or Br) with bis(dimethylboryl)disulphane (**2**) proceed *via* 4-dihalogenoboryl-3,5-dihalogeno-1,2,4,3,5-dithiazadiborolidines (**3**) to 2,8-dihalogeno-3,4,6,7-tetrathia-1-aza-2,5,8-triborabicyclo[3.3.0^{1,5}]octanes (**4a**) and (**4b**). The bromo derivative (**4b**) reacts with additional (**2**) (1 : 1 molar ratio) to produce impure NB$_3$S$_6$, but with an excess of (**2**) to yield a tricyclic system NB$_4$S$_6$(CH$_3$). The halogen atoms in (**4a**) and (**4b**) can be substituted by methyl groups from Sn(CH$_3$)$_4$ as the methylating agent. Amination of compound (**4a**) with Sn(CH$_3$)$_3$[N(C$_2$H$_5$)$_2$] seems to proceed *via* the bis(diethylamino) derivative, but a new tricyclic system (**8**) is the final product the structure of which has been determined by *X*-ray crystallography. U.v. and He I photoelectron spectra support n.m.r. evidence that the bicyclic rings (**4**) are planar 10π-electron systems. This conclusion is supported by MNDO and PPP calculations.

Amongst inorganic heterocyclic compounds of boron, the borazines form a particularly well characterized series.[2] Four- and five-membered BN heterocycles[3] containing additional heteroatoms including monocylic BS ring systems[4] are also well known. In contrast, only few bi- and tri-cyclic BN systems have so far been described.[5] Other polycycles of boron comprise the porphyrin-like B$_8$S$_{16}$,[6] a tricyclic BSNSi system[7], as well as a bicyclic BNS heterocycle.[5d]

The aim of this work was to develop a more systematic approach to bi- and tri-cycles of boron containing additional nitrogen and sulphur atoms. These are expected to reveal interesting molecular properties associated with a significant degree of π-electron delocalization. We report here the syntheses of such heterocycles and their characterization by various spectroscopic and theoretical techniques.



Scheme 1. X = Cl (*a*) or Br (*b*). (*i*) +(CH$_3$)$_2$BSSB(CH$_3$)$_2$, −2B(CH$_3$)$_2$X

Synthesis

To introduce the boron–nitrogen framework of the target heterocycles (**3**)—(**5**) perhalogenated triborylamines (**1**)[8] and bis(dimethylboryl)disulphane,[9] (**2**), which proved to be a particularly convenient source of the disulphur unit, were chosen as synthons. They react according to Scheme 1, equations (1)—(3).

The reaction of tris(dichloroboryl)amine (**1a**) with compound (**2**) in a molar ratio of 1 : 1 proceeds in pentane below 0 °C with the predominant formation of the *N*-borylated dithiazadiborolidine (**3a**); X = Cl. Boron-11 n.m.r. spectra of the reaction mixture reveal the presence of *ca.* 10% of unreacted (**1a**) and of the bicyclic compound (**4a**; X = Cl). Heating under reflux for several hours leads to no significant change in the product distribution, indicating that there is no interaction between (**1a**) and (**4a**). Addition of compound (**2**) to the reaction mixture resulted in a loss of intensity of the signals due to the triborylamine (**1a**) and the monocycle (**3a**) and in a corresponding increase of those of (**4a**) and (**3a**) with respect to the diboryldisulphane. Owing to the similar boiling points of (**1a**) and (**3a**), analytically pure (**3a**) was not accessible *via* this route.[‡]

Compound (**1b**; X = Br) reacts smoothly with (**2**) at −50 °C, and the monocyclic compound (**3b**; X = Br) formed is less contaminated by both (**1b**) and (**4b**; X = Br) (approximately 2 mol % each). Again, (**3b**) could not be separated from (**1b**) by fractional distillation. On the other hand, the higher reactivity of (**1b**) as compared to (**1a**) enables reactions (1) and (2) to proceed to the corresponding bicyclic compound (**4b**) under milder conditions (16 h, 40 °C) than for (**1a**) to (**4a**) (16 h, 65 °C). Both (**4a**) and (**4b**) exhibit remarkable thermal stability. They survive heating in boiling xylene for 20 h without significant decomposition.

Since the radical cation of (**5**) has been observed in high abundance during the mass spectrometric fragmentation of tris(1,3,2-dithiaborolanyl)amine, N(BS$_2$C$_2$H$_4$)$_3$,[10] it was

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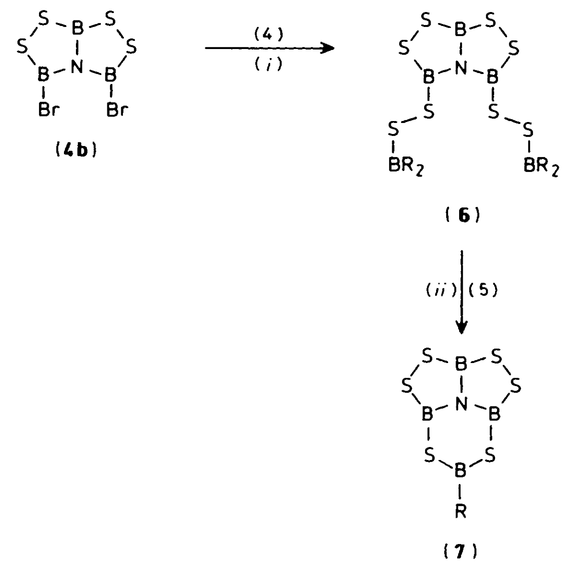
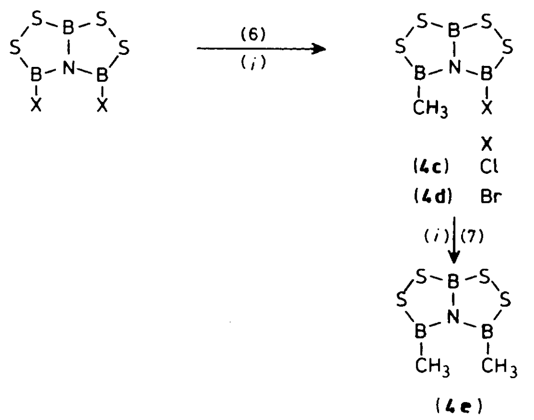
[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: eV ≈ 1.60 × 10^{-19} J.

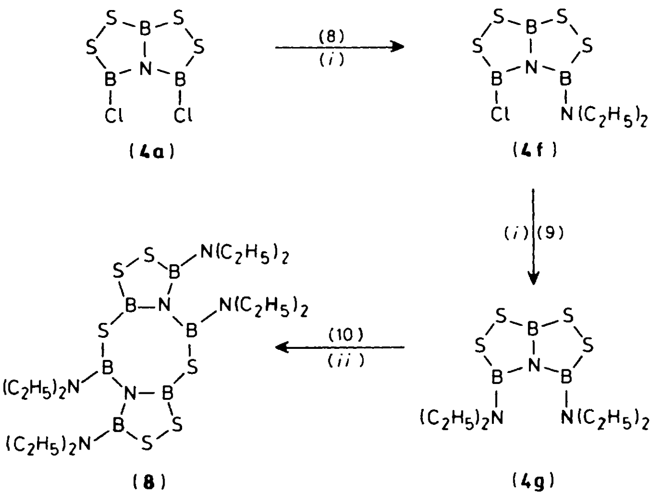
[‡] This refers to the small samples so far prepared. In large-scale preparations separation of (**1a**) from (**2a**) should be possible.



Scheme 2. R = CH_3. (*i*) $+2(CH_3)_2BSSB(CH_3)_2$, $-2B(CH_3)_2Br$; (*ii*) $-B(CH_3)_3$, $-\frac{1}{4}S_8$



Scheme 3. (*i*) $+Sn(CH_3)_4$, $-Sn(CH_3)_3X$



Scheme 4. (*i*) $+Sn(CH_3)_3[N(C_2H_5)_2]$, $-Sn(CH_3)_3Cl$; (*ii*) $-\frac{1}{4}S_8$

expected that the neutral B_3NS_6 tricycle (**5**) would also be stable. Attempts to achieve the synthesis of (**5**) either by reaction (3) or from $N(BBr_2)_3$ with H_2S_x or Li_2S_2,[11] however, led only to the formation of intractable products containing four-co-ordinate boron.[12] A more attractive route is offered by (**4a**), (**4b**) since much of the required framework is already in place. Indeed, both these derivatives react with bis(dimethylboryl)-disulphane in a 1:1 molar ratio to yield very pale yellow powders, insoluble in hydrocarbon solvents at ambient temperature and slightly soluble in boiling toluene. The mass spectra of both these products contained the radical cation of (**5**) as the parent peak. However, it was found to be impossible to separate analytically pure (**5**) from accompanying impurities, primarily elemental sulphur, despite repeated attempts of solvent extraction (including CS_2) and sublimation. In the case of the reaction between compounds (**4a**) and (**2**) the dominant impurity was S_8, whereas in the reaction with (**4b**) much less sulphur was found but some bromine-containing material believed to be (**4b**) was always present. In addition, the crude product from (**4b**) before solvent extraction exhibited ^{11}B n.m.r. signals at δ 50.4, 55.3, and 69.6 p.p.m. The latter would correspond to a $(CH_3)(Br)BS$ grouping which can be readily explained by a Br/CH_3 exchange process involving (**4b**) and (**2**).

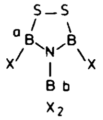
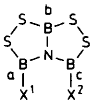
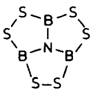
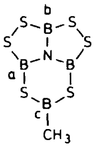
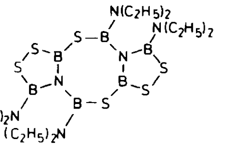
The insolubility of the product believed to be (**5**) combined with its very low volatility suggest it not to be tricyclic but rather polymeric in the solid state, probably with extensive intermolecular S • • • S interactions. The extrusion of elemental sulphur on heating the product at attempted sublimation could be explained on these grounds. Thus, a neutral tricyclic species (**5**), although highly favoured as a gaseous radical cationic species, is elusive.

When compound (**4b**) was treated with an excess of (**2**) a species containing four boron atoms was detected mass spectroscopically (Scheme 2). This species proved to be the new BNS tricycle (**7**) with (**6**) as a likely intermediate. The elimination products $B(CH_3)_3$ and S_8 were determined independently by ^{11}B n.m.r. and mass spectrometry. In order to maximize the yields of (**7**) the vacuum applied for the sublimation process should be less than 1.33 Pa. Compound (**7**) is a pale yellow, microcrystalline solid, the suggested structure being in accord with spectroscopic data.

Although compounds (**4a**) and (**4b**) are crystalline, attempts to obtain single crystals suitable for an *X*-ray determination of their structure failed owing to their tendency to form fibrous bundles of extremely fine needles. Therefore, we looked for derivatives better suited for this purpose. Alkylations of (**4a**), (**4b**) by organolithium reagents resulted in ring cleavage. Nucleophilic methylation by $Sn(CH_3)_4$ proceeds within 2 h at 40 °C. By employing a 1:1 molar ratio for (**4a**) a partial formation of the monomethylated product (**4c**) was achieved (Scheme 3). Further reaction to the dimethyl derivative (**4e**) requires an excess of $Sn(CH_3)_4$ in refluxing toluene. It was also formed from (**4b**) and $Sn(CH_3)_4$, and no monomethylated intermediate (**4d**) could be detected by ^{11}B n.m.r. spectroscopy in this case. Further, a large excess of $SnMe_4$ is indispensable in order to prevent formation of $Sn(CH_3)_2X_2$, separation of which from (**4e**) can be achieved only with great difficulty.

Amination of compound (**4a**) with $Sn(CH_3)_3[N(C_2H_5)_2]$ in a molar ratio of 1:2 in toluene proceeds below −20 °C with stepwise substitution. Signals in the ^{11}B n.m.r. spectrum at δ 52, 38, and 36 p.p.m. (ratio approximately 1:1:1) could be attributed to (**4f**) (Scheme 4). However, since the signals of compound (**4a**) and the disubstituted (**4g**) were also present, no attempt was made to isolate (**4f**). Complete substitution of the chlorine atoms of (**4a**) by $(C_2H_5)_2N$ groups according to equations (8) and (9) to produce (**4g**) required 80 °C for 72 h, the sluggishness of reaction (9) being presumably of steric origin. However, (**4g**) could not be purified since during work-up a new compound (**8**) formed, the structure of which was acertained by a single-crystal *X*-ray analysis.

Table 1. N.m.r. spectroscopic data for the heterocycles (3), (4), (5), and (8). Chemical shifts refer to the standards $Si(CH_3)_4$ (^1H), external $BF_3{\cdot}O(C_2H_5)_2$ (^{11}B), and external 1 mol dm^{-3} aqueous $NaNO_3$ (^{14}N). The solution investigated contained, except for (5), *ca.* 20% by weight of the compound. In the case of (5) a saturated toluene solution was studied at 80 °C

Compound		$\delta(^{11}B)$	$\delta(^{14}N)$	$\delta^1H)$	Solvent
	(3a)	46.0 (a) 45.0 (b)	−200		Pentane–C_6D_6
	(3b)	41.5 (a) 46.4 (b)	−191		Pentane–$CDCl_3$
	(4a)	45.6 (a,c) 55.9 (b)	−204		
	(4b)	43.3 (a,c) 56.5 (b)	−196		
	(4c)	56.0 (a,b) 50.2 (c)			
	(4e)	57.3 (a,c) 56.1 (b)	−189	1.02	Toluene–$CDCl_3$
	(5)	56	−193		Toluene, 80 °C
	(7)	49.8 (a) 56.1 (b) 66.7 (c)	−198	1.12	Toluene–C_6D_6
	(8)	36.5 48.8	−238	1.03 (t)* 3.0 (q)	C_6D_6

* See Experimental section.

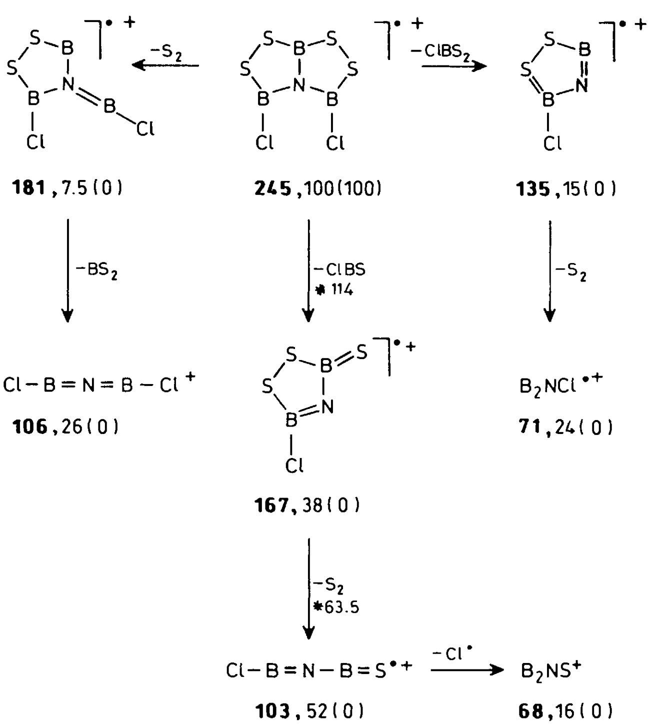
Spectroscopic Investigations

N.m.r. data for the new heterocyclic compounds are summarized in Table 1. All ^{11}B and ^{14}N chemical shifts demonstrate the presence of three-co-ordinate nuclei. The boron atom of the exocyclic dihalogenoboryl group in the dithiazadiborolidines (**3a**), (**3b**) exhibits an unusually pronounced deshielding comparable to *N*-borylated borazines[13] where this group is strongly twisted out of the borazine plane. The Cl_2B group in (**3a**) is slightly less deshielded as compared with that in $(ClBNBCl_2)_3$ (Δ 2.8 p.p.m.), and this may be indicative of a somewhat less twisted Cl_2B group in the five-membered ring as expected for geometrical reasons. Consequently, the nitrogen nucleus in compound (**3b**) is somewhat more deshielded than the chlorine derivative (**3a**), reflecting the influence of the stronger Lewis acid group Br_2B in comparison with Cl_2B.

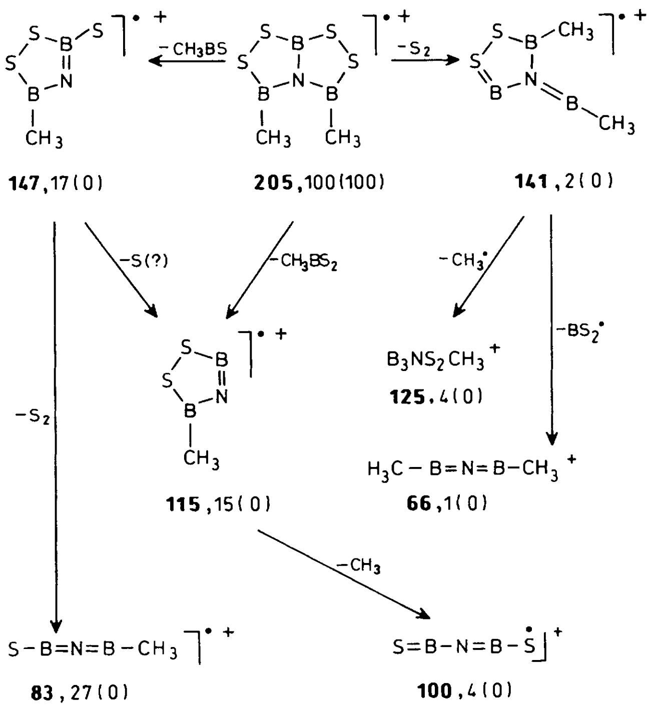
Two ^{11}B n.m.r. signals are observed for the bicyclic compounds (**4a**), (**4b**) in a 1:2 ratio. From this, the bridgehead boron is found at lower field, its shielding being comparable to that in tris(1.3,2-dithiaborolanyl)amine[10] [$\delta(^{11}B)$ 56.3 p.p.m.] while those of the XB groups resemble those in (**3a**), (**3b**). However, the ^{14}N chemical shifts for (**4a**), (**4b**) occur at distinctly lower field than for triborylamines $N[B(SR)_2]_3$ (δ −256 to −240 p.p.m.)[10] and compare well with those of the perhalogenotriborylamines $N(BX_2)_3$ [$\delta(^{14}N)$ −218 and −196 p.p.m. for X = Cl and Br].[8] This suggests strong delocalization of the nitrogen lone pair of electrons over the ring boron atoms, and this is also evidence for a planar bicyclic ring system. This hypothesis fits well with u.v. and photoelectron (p.e.) spectra as well as with molecular-orbital (m.o.) calculations. Methylation to give (**4e**) leaves the shielding of the bridgehead boron atom almost untouched while the resonance for the $(CH_3)B$ groups moves downfield to 57 p.p.m. which is close to $\delta(^{11}B)$ 54.2 p.p.m. as found for trimethyl-1,2,4,3,5-dithiazadiborolidine.[5b] Since neither the sulphur atoms nor the CH_3 groups possess significant donor properties, the nucleus ^{14}N of (**4e**) is strongly deshielded and corresponds to that in $N[B(CH_3)_2]_3$.[14] No ^{13}C n.m.r. resonances for compound (**4d**) were observed.

A hot toluene solution of the presumed compound (**5**) exhibited a single and sharp signal at 56 p.p.m. in the ^{11}B n.m.r. spectrum in accord with expectations based on compounds (**4**). The same chemical shift is also found for the tricyclic system (**7**). Since $\delta(^{11}B)$ 66.7 p.p.m. is typical for a BCS_2 substructural unit, *e.g.* 67.8 p.p.m. for $B(CH_3)(SCH_3)_2$,[15] the remaining signal at 49.8 p.p.m., which has the highest intensity, must be assigned to the ring boron atoms *a* having a NS_2 environment. $\delta(^{14}N)$ −198 p.p.m. fits well with the proposed structure.

Vibrational spectra of BNS heterocycles have not yet been systematically studied in any detail except for a series of the related trithiadiborolanes.[16] However, bands assignable to symmetrical and antisymmetrical B_3N stretching vibrations are recognizable in the i.r. spectra of compounds (**4a**), (**4b**), (**4e**), and (**8**). Frequencies for ν_{asym} are 1 287, 1 278 (broad), 1 318, and 1 230 cm^{-1}, respectively, and these are comparable with bands

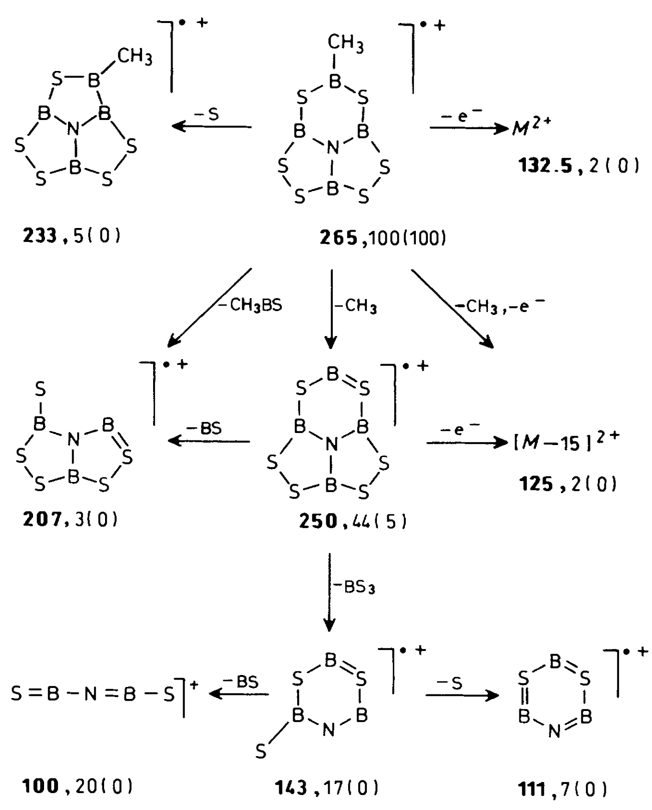


Scheme 5. Fragmentation of compound (**4a**). Paths involving metastable peaks are shown with bold arrows; asterisks indicate the masses of the observed metastable ions. The numbers refer to m/z, the relative intensity at 70 eV and (in parentheses) the relative abundance of the peak at 15 eV. Correct isotopic patterns have been observed. The m/z values are calculated for the isotopes ^{11}B and ^{35}Cl



Scheme 6. Fragments derived from the parent ion of compound (**4e**) observed in the mass spectrum with 70 and 15 eV ionization energy. No metastable peak has been observed. For explanation see Scheme 5

at 1 290 and 1 250 cm^{-1} reported for $N(BX_2)_3$ (X = Cl or Br).[8] The sharp and strong bands are accompanied by a satellite about 50 cm^{-1} to higher frequency due to the presence of ^{10}B.



Scheme 7. Fragmentation of compound (**7**) observed in the mass spectrum with 70 and 15 eV ionization energy. No metastable peak has been observed. For explanation see Scheme 5

Since an analysis of the NB_3 stretching mode and its coupling with other modes has not yet been made, the frequencies should not be taken as a direct measure of bond strengths at the present time. Although the assignment of other specific ring vibrations meets with difficulties, bands in the region 1 100—750 cm^{-1} may arise from such modes. This follows from a comparison with the i.r. data for trithiadiborolanes.[16]

For all the heterocycles studied in this work, electron impact produces the molecular ion in the mass spectra, which is also the parent peak both at 15 and 70 eV. This clearly illustrates the high stability not only of the neutral molecules but also of their radical cations. The ionization process involves removal of an electron from a π-type m.o. (see below). This is substantiated by the formation of doubly charged molecular ions which can be observed in approximately 6 to 1% relative intensity. Such a behaviour is well known for carbocyclic aromatic systems.[17] Compounds (**3**), (**4**), and (**5**) can be regarded as 6π-, 10π-, and 14π-electronic systems and could, therefore exhibit heteroaromaticity.

Degradation of the molecular ion leads to fragments with relative intensities less than 50%. Typically, M^+ of (**4a**), (**4b**) lose the neutral molecules X–B=S[18] (see Scheme 5) followed by extrusion of S_2 and formation of a species XB_2NS^+ which can be regarded as the radical cation of the polyenes X–B=N–B=S. Another fragmentation path involves loss of S_2 and BS_2 leading to the fragment X–B=N=B–X$^+$.

The breakdown of M^+ of (**5**) starts with elimination of S or S_2 followed by a BS_2 fragment. Thus, the most abundant species besides M^+ is the ion $B_2NS_2^+$ which may have the structure S=B=N–B=S$^+$. This same fragment ion (see Scheme 7) is also produced in relatively high abundance (*ca.* 20%) in the fragmentation process of M^+ arising from (**7**). This parent ion

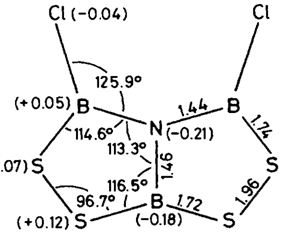


Figure 1. MNDO Geometry optimized structure for compound (**4a**) as calculated by the MNDO-II and PPP methods. Bond lengths in Å

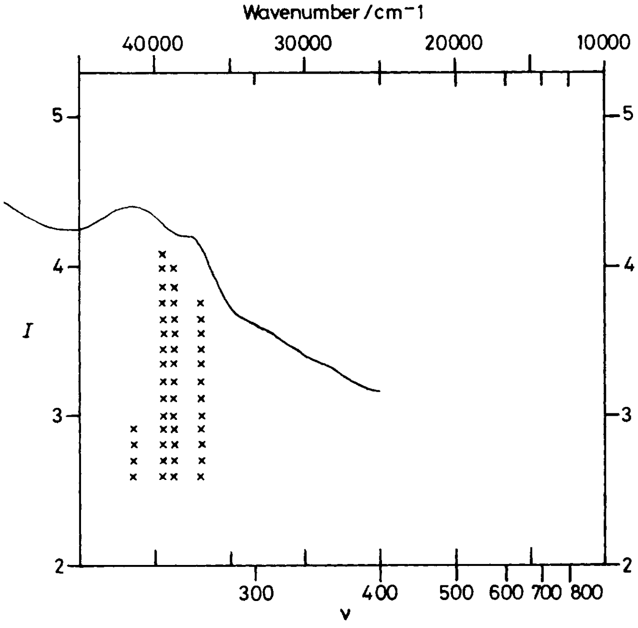


Figure 2. Calculated oscillator strengths and experimental u.v. spectrum of compound (**4a**)

decomposes with loss not only of $(CH_3)B{=}S$ or S but also of CH_3 radicals. This latter process is the only one occurring also at 15 eV ionization energy. Schemes 5—7 illustrate the observed patterns. Additional data are summarized in the Experimental section.

M.O. Calculations, Electronic and He I Photoelectron Spectra

In the absence of *X*-ray structural data for the bicyclic systems (**4**), geometry-optimized m.o. calculations are of importance, especially in view of comparisons with experimental quantities. We chose (**4a**) as the model system since the chlorine substituents are more amenable to calculations. For the latter we used the semiempirical MNDO III[19] and PPP[20] approximations.

The MNDO optimized geometry of (**4a**) (see Figure 1) predicts the molecule to be planar (out-of-plane twist angles 0.2°) with a slight shortening of the B–S and S–S bonds. Such deviations with respect to experimental values have been regularly found when bonds to second-row elements are involved.* There are five doubly occupied orbitals of π type in the molecule (see Figure 1), and this lends support to the view of heteroaromatic character in this molecule. However, the calculated charges, shown in Figure 1, are consistent with polarized, but delocalized π m.o.s in this ring system.

In the PPP calculations the basis was the MNDO optimized geometry and, being restricted to dealing with π orbitals only, counts two electrons each for S, N, and Cl atoms thus giving a total of 14 electrons. These orbitals are depicted in Figure 3. Both methods arrive at the same symmetry for the frontier orbitals.

Figure 2 contains the calculated oscillator strengths for the lowest-energy transitions and their associated calculated wavelengths together with the observed u.v. spectrum. The good agreement between the two sets of data indicates that the u.v. spectrum of compound (**4a**), exhibiting the weakly allowed $\pi^* \longleftarrow \pi$ transition expected for a pseudo-aromatic species, can be well simulated in accord with the calculated planar molecular geometry.

This result can be tested further by He I p.e. spectra. Figure 3 shows that there are three well defined bands at 8.83, 9.71, and 11.0 eV for compound (**4a**). These exhibit featureless profiles thus fitting the ejection of electrons from π-type orbitals, not too strongly involved in bonding. The bands probably arise from the high-lying π-type orbitals of a_2 and b_1 symmetry predicted both by MNDO and PPP methods. The ordering of the energy of these bands is matched with theoretical values with a dephasing of −1.58 eV in the MNDO but only −0.33 eV in the PPP case. All other higher-energy bands cannot be assigned unequivocally.

Molecular Structure of the Tricyclic System (8)

On attempts to obtain single crystals of compound (**4g**), pale yellow plates separated from hexane solutions which proved to be (**8**) by *X*-ray structure analysis. The molecular structure is depicted in Figure 4.

The striking feature of this tricyclic system is the tub conformation of the eight-membered ring reminiscent of the analogous conformation of the eight-membered tetra-azatetraboracines[21] and the dimeric 1,3,2,4-diazastannaboracyclobutane.[22] Annelation of the two five-membered dithiazadiborolidine rings of (**8**) occurs at the BN units of the central $(BNBS)_2$ heterocycle. As can be visualized from Figure 4, the molecule of (**8**) approaches C_2 symmetry. The two five-membered rings are almost planar (maximum deviation of atoms from the mean plane: 0.08 Å), and also the dihedral angles to the connected boron and sulphur atoms demonstrate that these are also almost coplanar with the B_2NS_2 rings (dihedral angles up to 9.6°).

Table 2 contains selected bond lengths and angles. Those which are approximately related by two-fold axes are listed side by side. Most of these pairs can be considered equal in terms of the 3σ criterion. The largest deviations result for the pair N(4)–B(14)/N(8)–B(7) and connected therewith for the bond angles B(3)–N(4)–B(14)/B(9)–N(8)–B(7).

The sulphur–sulphur bonds in compound (**8**) are longer than those found in 3,4,5-trimethyl-1,2,4,3,5-dithiazadiborolidine[23] and correspond with the S–S bond lengths in bis(dimethylboryl)disulphane.[24] However, the former has been determined at −35 °C while the latter results from an electron-diffraction study. Surprisingly, the two B–S bonds of the five-membered rings differ significantly from one another. The bond lengths for B(5)–S(1) and B(12)–S(11) correspond to B–S distances found not only in the two boron–sulphur compounds referred to[23,24] but also in 3,5-dimethyl-1,2,4,3,5-trithiadiborolane (1.803 Å)[25] or B_8S_{16}.[6] The longer B–S bonds are exhibited by the diethylamino group bearing boron atoms, reflecting strong π-electron donation from this group as evidenced by a short BN

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* This seems to be inherent to the program (personal communication of W. Thiel to P. Kölle); see also P. Kölle, Ph.D. Thesis, University of Munich, 1987.

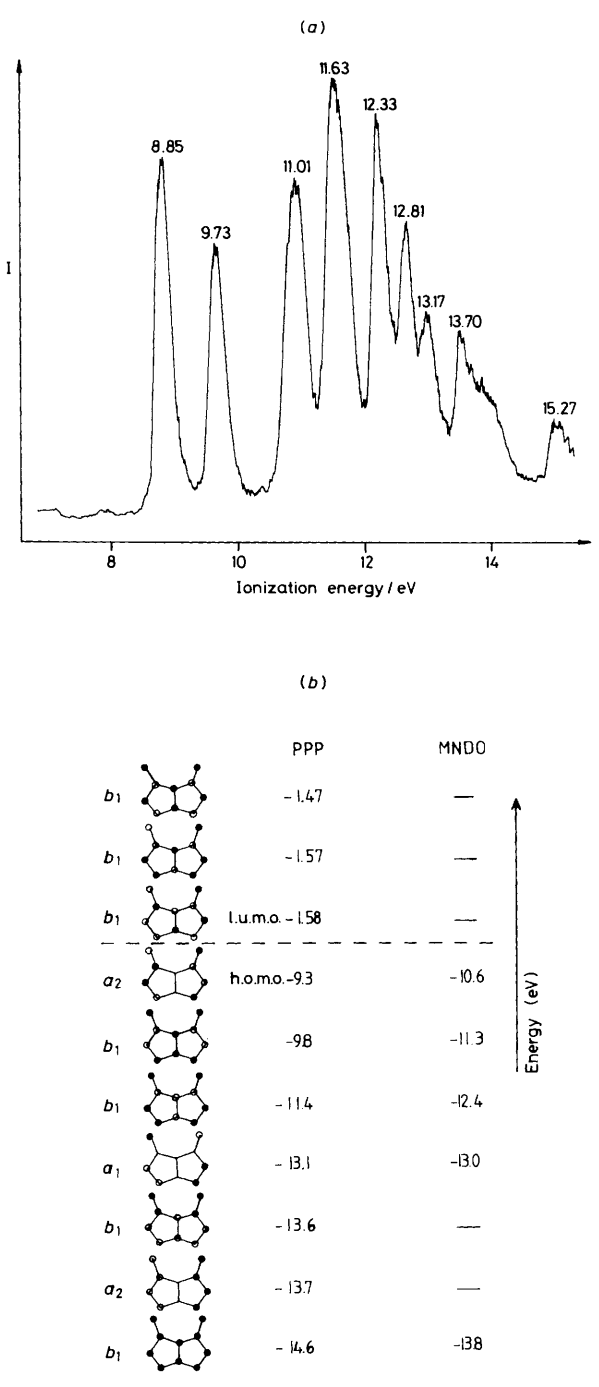

Figure 3. (*a*) He I p.e. spectrum of compound (**4a**). (*b*) PPP- and MNDO-calculated π orbitals for (**4a**), assuming C_{2v} molecular symmetry. The sketches represent only the symmetry and not the magnitude of the calculated eigenvectors. Eigenvectors less than 0.005 have been ignored, l.u.m.o. and h.o.m.o. = lowest unoccupied and highest occupied molecular orbitals

distance. Similar situations are encountered in the dithiadiboretanes $(R_2NBS)_2$.[26] The bridgehead nitrogen atoms each show one short and two longer BN bonds (average 1.419 Å), the latter pointing to the bridgehead boron atom having an environment corresponding to an aminodithioborane. Such units should exhibit comparatively strong B–N π bonding.[23] The other B–N bonds average to 1.478 Å with some larger differences in N(8)–B(7) and N(8)–B(9).

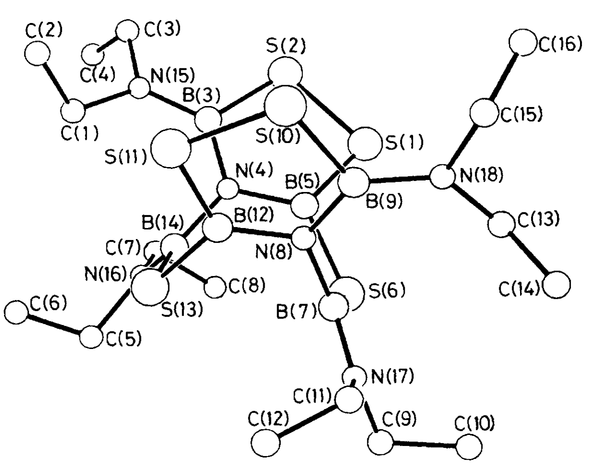

Figure 4. ORTEP plot of the molecular structure of compound (**8**). Hydrogen atoms are not shown for the sake of clarity

Conclusions

The spectroscopic data for the bi- and tri-cyclic boron–nitrogen–sulphur heterocycles support their description as heteroaromatic ring systems. Although the condensed tricycle (**5**) could not be well characterized in the solid state, its fragmentation pattern in the mass spectrum indicates a similar behaviour when compared with the other heterocycles in question. On the other hand, the short BN bonds in compound (**8**), taken together with the relatively long BS bonds, are in accord with the presence of strongly π-donating substituents influencing the delocalization of π-electron density within the ring system. We believe this to be the main reason why the diethylamino-substituted bicyclic system (**4g**) is unstable and loses sulphur to give (**8**).

Experimental

General.—All manipulations were performed under an atmosphere of dry dinitrogen; glassware was dried prior to use by heating *in vacuo*. N.m.r. spectra were recorded on a Bruker AC 200 or 200 WP Fourier-transform spectrometer, i.r. spectra as Nujol–Hostaflon mulls between CsI plates on a Nicolet SZDX FT-IR spectrophotometer, mass spectra on a Varian CH7 instrument with electron impact ionization, and u.v. spectra on a Perkin-Elmer 555 spectrophotometer. A Nicolet R3 automated four-circle diffractometer was used for the *X*-ray structure analysis employing graphite monochromatized Mo-K_α radiation and the SHELXTL program package (Version 4.0 as supplied by Nicolet Corp., programs written by Professor G. W. Sheldrick, Göttingen) for structure solution and refinement.

Starting Materials.—The compounds $N[Sn(CH_3)_3]_3$,[27] H_2S_x,[28] $B(CH_3)_2Br$,[29] $Sn(CH_3)_3[N(C_2H_5)_2]$,[30] $N(BCl_2)_3$, $N(BBr_2)_3$,[8] and $Sn(CH_3)_4$[31] were prepared according to literature methods.

Bis(dimethylboryl)disulphane, (**1**).—*Modified preparation*.[9] The compound $B(CH_3)_2Br$ (14.5 cm^3, 18.17 g, 150.2 mmol) was pipetted into a twin-necked flask (50 cm^3) equipped with a solid CO_2-cooled condenser and a dropping funnel. The condenser was cooled to −20 °C (Pr^{i}OH–solid CO_2) and H_2S_x (8.12 cm^3, 13.3 g, 74.6 mmol) was added slowly at room temperature with vigorous stirring. After complete addition of the polysulphane, the mixture was heated to 55 °C in an oil-bath for 4 h; the condenser temperature was maintained between −20 and −25 °C. Isolation of the product was achieved by

Table 2. Selected bond lengths (Å) and angles (°) for compound (**8**) with estimated standard deviations in parentheses

S(1)–S(2)	2.087(4)	S(10)–S(11)	2.074(3)
B(5)–S(1)	1.801(7)	B(12)–S(11)	1.806(8)
B(5)–N(4)	1.420(10)	B(12)–N(8)	1.418(9)
B(5)–S(6)	1.859(10)	B(12)–S(13)	1.845(7)
S(6)–B(7)	1.851(7)	S(13)–B(14)	1.865(8)
N(4)–B(14)	1.470(8)	N(8)–B(7)	1.516(9)
N(4)–B(3)	1.472(11)	N(8)–B(9)	1.455(8)
B(3)–S(2)	1.875(7)	B(9)–S(10)	1.875(8)
B(3)–N(15)	1.401(11)	B(9)–N(18)	1.409(9)
B(14)–N(16)	1.383(8)	B(7)–N(17)	1.384(10)
S(2)–S(1)–B(5)	95.7(3)	S(10)–S(11)–B(12)	95.6(2)
B(3)–S(2)–S(1)	95.8(3)	B(9)–S(10)–S(11)	96.4(2)
S(2)–B(3)–N(4)	113.5(5)	S(10)–B(9)–N(8)	112.6(5)
B(3)–N(4)–B(5)	116.2(5)	B(9)–N(8)–B(12)	117.9(6)
N(4)–B(5)–S(1)	118.4(6)	N(8)–B(12)–S(11)	117.4(4)
S(2)–B(3)–S(15)	118.5(6)	S(10)–B(9)–N(18)	117.3(5)
N(15)–B(3)–N(4)	128.0(6)	N(18)–B(9)–N(8)	130.1(7)
B(3)–N(4)–B(14)	124.0(6)	B(9)–N(8)–B(7)	127.3(5)
B(5)–N(4)–B(14)	117.8(6)	B(7)–N(8)–B(12)	114.8(5)
N(4)–B(14)–S(13)	120.5(5)	N(8)–B(7)–S(6)	119.5(5)
N(4)–B(14)–N(16)	121.1(6)	N(8)–B(7)–N(17)	122.1(5)
S(13)–B(14)–N(16)	118.5(5)	S(6)–B(7)–N(17)	118.4(5)
B(14)–S(13)–B(12)	99.8(5)	B(7)–S(6)–B(5)	102.7(4)
N(4)–B(5)–S(6)	125.5(5)	N(8)–B(12)–S(13)	125.4(5)
S(1)–B(5)–S(6)	115.7(4)	S(11)–B(12)–S(13)	117.2(4)
S(2)–B(3)–N(15)	118.5(6)	S(10)–B(9)–N(18)	117.3(5)
N(4)–B(3)–N(15)	128.0(6)	N(8)–B(9)–N(18)	130.1(7)

condensing the volatile fraction of the reaction mixture into a cold trap (–60 °C) *via* a distillation bridge; it was necessary to heat the mixture to *ca.* 100 °C in order to maximize the yield. The product, b.p. 35 °C (665 Pa), was a colourless liquid slightly contaminated with 1,3-dimethyl-2,4,5-trithia-1,3-diborolane. Further purification was found to be unnecessary. Yield: 8.81 g, 79%, ^{11}B N.m.r.: 75.9; lit.,[9] 76.0 p.p.m.

Reaction of $N(BCl_2)_3$ *with* $(CH_3)_2BSSB(CH_3)_2$ (**2**) *in a* 1:1 *Molar Ratio.*—A solution of compound (**2**) (2.60 g, 2.70 cm^3, 18.0 mmol) in pentane (25 cm^3) was added dropwise at –78 °C to a solution of $N(BCl_2)_3$ (4.50 g, 3.0 cm^3, 17.4 mmol) in pentane (35 cm^3) with stirring. A colourless solid precipitated which dissolved on warming to room temperature for 12 h. The solvent was removed *in vacuo* (25 °C, 1.3 Pa) leaving behind a colourless oil. Distillation under reduced pressure at 33 °C (10.8 Pa) yielded 1.95 g of liquid (**3a**) containing 10 mol % $N(BCl_2)_3$ (estimated from the intensities of the ^{11}B n.m.r. signals) and a solid residue 1.0 g (*ca.* 23%) of (**4a**). This solid was sublimed (80 °C, 1.3 Pa). Its n.m.r. data were identical with those of independently synthesized (**4a**) (see below) (Found: B, 13.2; Cl, 49.45; N, 6.5. Calc. for $B_3Cl_4NS_2$: B, 12.85; Cl, 56.20; N, 5.55%). N.m.r.: ^{11}B, δ 45.9, 47.0, and 40.2 p.p.m.; ratio 1:2:0.1; ^{14}N, δ –200 p.p.m.

Reaction of $N(BBr_2)_3$ *with Compound* (**2**) *in* 1:1 *Molar Ratio.*—The compound $N(BBr_2)_3$ (1.86 g, 3.54 mmol) was dissolved in pentane (5 cm^3) and the solution cooled to –78 °C. Compound (**2**) (0.52 g, 3.54 mmol, 0.56 cm^3) dissolved in pentane (5 cm^3) was added slowly from a dropping funnel and a white solid precipitated. After slow (16 h) warming to ambient temperature the solvent was removed and the residue doubly distilled (80 °C, 1.33 Pa) to yield the product (**3b**) as a pale yellow liquid, very sensitive to moisture and contaminated with approximately 20% of starting material. Yield: 1.0 g product. N.m.r.: ^{11}B, δ 47.1 and 41.7 p.p.m., intensity ratio 1:2; ^{14}N, δ –191 p.p.m.

2,8-*Dichloro*-3,4,6,7-*tetrathia*-1-*aza*-2,5,8-*triborabicyclo*-[3.3.0^{1,5}]*octane*, (**4a**).—The compound $N(BCl_2)_3$ (4.5 g, 17.4 mmol) dissolved in toluene (15 cm^3) was added to a solution of compound (**2**) (5.1 g, 34.8 mmol) dissolved in toluene (50 cm^3) at –78 °C with stirring. After slow warming to room temperature the solution was heated to 65 °C for 16 h. A gas evolved which, after isolation in a cold trap (–78 °C), was shown by ^{11}B n.m.r. spectroscopy to be $B(CH_3)_2Cl$. Removal of solvent and sublimation (80 °C, 1.33 Pa) yielded the product (**4a**) as a pale yellow crystalline solid of m.p. 105 °C. Yield: 3.4 g (79%) (Found: B, 13.1; Cl, 28.90; N, 5.65. Calc. for $B_3Cl_2NS_4$: B, 13.20; Cl, 28.85; N, 5.70%). I.r. spectrum: 1 301s (sh) $[\nu_{asym}(^{10}B^{11}B_2N)]$, 1 287vs $[\nu_{asym}(^{11}B_3N)]$, 1 230m (sh) $[\nu_{sym}(^{10}B^{11}B_2N)]$, 1 206s $[\nu_{sym}(^{11}B_3N)]$, 1 121vw, 1 107w, 987w (sh), 977m, 960s, 930w (sh), 915w (sh), 844w, 655n, and 581s cm^{-1}. U.v. spectrum: $\lambda_{max.}$ = 265, 241, and 215 (sh) nm; ε = 13 130 and 18 938 dm^3 mol^{-1} cm^{-1}.

2,8-*Dibromo*-3,4,6,7-*tetrathia*-1-*aza*-2,5,8-*triborabicyclo*-[3.3.0^{1,5}]*octane*, (**4b**).—Compound (**2**) (2.0 g, 12 mmol, 2.2 cm^3) dissolved in toluene (10 cm^3) was added to a solution of $N(BBr_2)_3$ (3.17 g, 6.0 mmol) in toluene (10 cm^3) at ambient temperature with stirring. The mixture was warmed to 60 °C for 12 h, after which all volatiles were removed *in vacuo*. The solid crude product was briefly washed with cold pentane (0 °C). Final sublimination (80 °C, 1.3 Pa) yielded the pure product (**4b**) as a pale yellow microcrystalline solid of m.p. 100 °C (decomp.). Yield: 1.5 g (75%) (Found: B, 9.85; Br, 47.9; N, 4.35. Calc. for $B_3Br_2NS_4$: B, 9.9; Br, 47.8; N, 4.2%). I.r. spectrum: 1 278vs,br $[\nu_{asym}(B_3N)]$, 1 205vs (sh) $[\nu_{sym}(^{10}B^{11}B_2N)]$, 1 182vs $[\nu_{sym}(^{11}B_3N)]$, 1 120w (sh), 1 108m (sh), 1 098m, 1 015m, 988s, 969s, 942s, 924vs, 890m (sh), 875m (sh), 806m, 747w, 642n, 631m (sh), and 572vs cm^{-1}. U.v. spectrum: $\lambda_{max.}$ = 270, 244, and 320 nm; ε of the saturated solution, (**4b**) which was only slightly soluble in pentane, was not determined. Mass spectrum [*m*/*z*, relative intensity at 70 eV (15 eV)]: 335, 100 (100); 271, 30 (0); 213, 22 (0); 196, 10 (0); 167.5 (M^{2+}), 1 (0); and 141, 30 (0).

2,8-*Dimethyl*-3,4,6,7-*tetrathia*-1-*aza*-2,5,8-*triborabicyclo*-[3.3.0^{1,5}]*octane*, (**4e**).—The compound $Sn(CH_3)_4$ (1.60 g, 8.96 mmol) was added to a solution of (**4b**) (1.00 g, 2.9 mmol) in toluene (10 cm^3) at –50 °C with stirring. The mixture was warmed slowly to ambient temperature and then heated to 70 °C for 3 d. After removal of the reaction volatiles the residue was doubly sublimed (90 °C, 1.3 Pa) and washed with cold pentane to yield the pure product (**4e**) as a pale yellow microcrystalline solid, m.p. 90 °C (decomp.). Yield: 0.28 g (46%) (Found: C, 11.90; H, 3.05; B, 15.40, N, 6.45. Calc. for $C_2H_6B_3NS_4$: C, 11.75; H, 2.95; B, 15.85; N, 6.85%). I.r. spectrum: 2 950w (C–H stretch), 1 332vs (sh) $[\nu_{asym}(^{10}B^{11}B_2N)]$, 1 318vs $[\nu_{asym}(^{11}B_3N)]$, 1 275vs, 1 246vs, 1 177w (sh), 1 084s (sh), 1 065vs, 1 048s (sh), 954w (sh), 948w (sh), 940s, 887n, 857s, 669w, 641n, and 555s cm^{-1}. U.v. spectrum: $\lambda_{max.}$ = 257 (sh), 240, and 228 nm; ε = 5 730, 8 277, and 7 640 dm^3 mol^{-1} cm^{-1}.

Reaction of Compound (**4a**) *with* $Sn(CH_3)_4$.—The compound $Sn(CH_3)_4$ (0.52 g, 2.9 mmol) dissolved in toluene (4 cm^3) was added to (**4a**) (0.70 g, 2.9 mmol), dissolved in toluene (5 cm^3), at room temperature with stirring. After heating the mixture to 40 °C for 5 h, a sample was taken for n.m.r. analysis. The ^{11}B n.m.r. spectrum showed two peaks (δ 50.2 and 56.1 p.p.m., intensity ratio 1:2) and the ^{1}H n.m.r. spectrum also contained two signals [δ 0.66, $Sn(CH_3)_3Cl$, and 0.97, $B(CH_3)_3$; intensity ratio 3:1]. A further aliquot of $Sn(CH_3)_4$ (1.32 g, 7.4 mmol), dissolved in toluene (5 cm^3), was added to the mixture. After stirring for 4 h at ambient temperature no significant change was observed in the ^{11}B or ^{1}H n.m.r. spectrum. On heating the mixture to 110 °C for 12 h the ^{11}B n.m.r. spectrum showed signals (assignable by comparison with an authentic sample) of the disubstituted compound (**4e**) (^{11}B, δ 56.1 and 57.3 p.p.m., ^{1}H, δ 1.02), contaminated with approximately 10% of (**4c**). A complete separation of the two products was not achieved either by sublimation or fractional crystallization.

Attempted Preparation of Compound (**5**).—For a typical experiment, compound (**2**) (0.45 g, 3.0 mmol) dissolved in toluene (5 cm^3) was slowly added to a solution of (**4b**) (1.0 g, 3.0 mmol) in toluene (5 cm^3) at −10 °C with stirring. After the addition of half of the disulphane derivative a very pale powdery precipitate formed in the yellow solution. After complete addition the mixture was allowed to warm to room temperature and was stirred for a further 48 h. Filtration yielded a pale powder which, before washing, exhibited ^{11}B n.m.r. signals at 62.1, 55.9, and 49.1 p.p.m. in toluene solution (ratio 1:2:1). The filtrate showed similar signals together with peaks at 76.6 [$B(CH_3)_2Br$], 70 (3,5-dimethyl-1,2,4-trithia-3,5-diborolane impurity), and 43 p.p.m. [unreacted BBr groups of (**4b**)]. After repeated washing with toluene the insoluble powder gave a very weak single signal at 56 p.p.m. in hot toluene (80 °C) in the ^{11}B n.m.r. spectrum, assigned to (**5**). Mass spectroscopy of the yellow insoluble powder showed that the solid contained (**4b**) and S_8 as impurities besides (**5**). A complete separation either by solvent extraction (solvents: toluene, CH_2Cl_2, $CHCl_3$, OEt_2, or CS_2) or sublimation (110 °C/0.13 Pa) was not achieved. Yield: 0.2 g of (**5**) (28%) (Found: B, 12.85; N, 5.25. Calc. for B_3NS_6: B, 13.60; N, 5.85%). Mass spectrum [*m*/*z*, relative intensity at 70 eV (15 eV)]: 239, 100 (100); 207, 8 (0); 175, 14 (4); 143, 4 (0); 119.5 (M^{2+}), 6 (0); 111, 4 (0); 100, 25 (0); 57, 15 (0); and 43, 5 (0).

9-*Methyl*-2,3,5,6,8,10-*hexathia*-11-*aza*-1,4,7,9-*tetraboratricyclo*[6.2.1.0^{1,11}]*undecane*, (**7**).—A solution of compound (**2**) (0.41 g, 2.5 mmol) in toluene (5 cm^3) was added to a solution of (**4b**) (0.33 g, 1.0 mmol) in toluene (10 cm^3) at ambient temperature with stirring. After warming the mixture to 70 °C for 36 h, the yellow solution was separated from a small amount of solid which had formed. The ^{11}B n.m.r. spectrum of the solution showed signals at 86.5 [$B(CH_3)_3$], 75.5 [$B(CH_3)_2Br$], 70 (3,5-dimethyl-1,2,4-trithia-3,5-diborolane), 55.8, and 49.7 p.p.m. Removal of all volatiles left a sticky pale yellow solid. After proloned pumping, sublimation of (**4b**) was performed at 110 °C (1.3 Pa). Compound (**7**), m.p. 100—110 °C (decomp.), was isolated as pale yellow needle-like microcrystals from the residue by crystallization from hexane. Yield 0.2 g, (76%) (Found: C, 4.35; H, 1.40; B, 16.1; N, 4.85. Calc. for $CH_3B_4NS_6$: C, 4.55; H, 1.15; B, 16.35; N, 5.30%). I.r. spectrum: 2 954vw (sh), 2 924w, 2 854vw, (C–H stretch), 1 380m (sh), 1 371m (sh), 1 360m (sh), 1 315s (sh) [$\nu_{asym}(^{10}B^{11}B_2N)$], 1 301vs [$\nu_{asym}(^{11}B_3N)$], 1 248m (sh) [$\nu_{sym}(^{10}B^{11}B_2N)$], 1 233s [$\nu_{sym}(^{11}B_3N)$], 1 118w (sh), 1 103w (sh), 1 070w, 1 040w, 1 003m (sh), 982s, 961s, 942m, 816w, 764w, and 576m cm^{-1}.

Table 3. Atomic co-ordinates (× 10^4) of the non-hydrogen atoms of compound (**8**)

Atom	*x*	*y*	*z*
S(1)	5 220(3)	2 029(2)	6 529(1)
S(2)	3 732(3)	911(2)	6 222(1)
B(3)	4 672(10)	−991(8)	6 537(4)
N(4)	6 101(6)	−1 025(5)	6 791(2)
B(5)	6 467(10)	379(8)	6 828(4)
S(6)	8 278(3)	657(2)	7 054(1)
B(7)	8 075(9)	37(7)	7 968(3)
N(8)	6 547(6)	−295(5)	8 349(2)
B(9)	5 311(9)	674(8)	8 815(3)
B(12)	6 365(10)	−1 746(8)	8 252(4)
S(10)	3 753(2)	−294(2)	9 262(1)
S(11)	4 663(2)	−2 293(2)	8 755(1)
S(13)	7 768(2)	−3 155(2)	7 684(1)
B(14)	7 335(10)	−2 383(8)	6 834(4)
N(15)	3 990(6)	−2 186(6)	6 493(3)
N(16)	8 204(7)	−3 113(5)	6 248(3)
N(17)	9 313(6)	−42(6)	8 291(2)
N(18)	5 158(6)	2 164(6)	8 989(3)
C(1)	4 406(9)	−3 642(7)	6 820(4)
C(2)	3 113(11)	−4 062(10)	7 332(4)
C(3)	2 812(10)	−2 050(9)	6 057(4)
C(4)	3 452(12)	−2 808(16)	5 401(5)
C(5)	9 510(10)	−4 436(9)	6 256(4)
C(6)	8 953(12)	−5 794(9)	6 243(5)
C(7)	7 993(9)	−2 616(8)	5 549(3)
C(8)	8 964(11)	−1 490(10)	5 226(4)
C(9)	10 842(9)	237(9)	7 929(4)
C(10)	10 930(10)	1 825(9)	7 977(4)
C(11)	9 257(8)	−478(7)	9 038(3)
C(12)	9 959(10)	−2 102(8)	9 145(4)
C(13)	6 189(8)	3 141(7)	8 666(4)
C(14)	7 140(10)	3 558(9)	9 135(4)
C(15)	3 829(8)	2 878(8)	9 522(4)
C(16)	2 604(10)	4 032(9)	9 244(4)

2,7,9,14-*Tetrakis*(*diethylamino*)-3,5,6,10,12,13-*hexathia*-1,8-*diaza*-2,4,7,9,11,14-*hexaboratricyclo*[9.3.0.0^{4,8}]*tetradecane*, (**8**).—The compound $Sn(CH_3)_3[N(C_2H_5)_2]$ (1.20 g, 5.3 mmol) dissolved in toluene (5 cm^3) was added to a solution of (**4a**) (0.65 g, 2.6 mmol) in toluene (10 cm^3) at 20 °C with stirring. After warming to room temperature the ^{11}B n.m.r. spectrum showed signals at δ 52.4 and 36 p.p.m. indicating that substitution at the boron–chlorine bonds had occurred. The reaction mixture was then warmed to 80 °C with stirring until no more signals attributable to B–Cl bonds of (**4a**) (δ 45—38 p.p.m.) were apparent (*ca.* 72 h); the reaction mixture then exhibited two broad signals at 49.5 and 36.5 p.p.m. (ratio 1:2). Removal of all volatiles from the clear solution and prolonged pumping [to remove $Sn(CH_3)_3Cl$] yielded a solid product coated in a yellow oil. This was dissolved in a toluene–pentane mixture and stored at −15 °C for 2 d. Small crystals of sulphur (*ca.* 50 mg, identified by mass spectrometry) precipitated and were removed by filtration. This process was repeated and the final solution was reduced to *ca.* 1 cm^3. Large yellowish crystals of compound (**8**) formed slowly; these were separated mechanically and washed with pentane. Suitable crystals for *X*-ray structure analysis were grown from a toluene–pentane mixture. Pure crystalline (**8**) is a colourless, extremely hygroscopic, foul-smelling solid which rapidly turns orange on exposure to air. Yield 0.2 g (37%), m.p. 170 °C (decomp.). N.m.r.: ^{11}B (C_6D_6), δ 48.8 and 36.5 p.p.m., ratio 1:2; ^{1}H, δ 1.03 (overlapping triplets) and 3.0 (overlapping quartets); ^{13}C, δ 43.4, 42.7 (CH_2), 15.0, and 14.4 (CH_3); ^{14}N (boryl nitrogen), δ −237.7 p.p.m. I.r. spectrum (Nujol): 1 341m, 1 270m (sh), 1 230s [$\nu_{asym}(B_3N)$], 1 194s, 1 170 (sh), 1 144s, 1 105s, 1 096s, 1 072s, 1 014s, 1 000s, 937m, 900m, 834s, 801s (sh), 783s, 681m, 606m, 579w, 562w, and 541w, br cm^{-1}. Mass spectrum [*m*/*z*, relative intensity at 70 eV (15 eV)]: 574, 31 (0); 545, 6 (0); 502, 100 (0); 486, 26 (0); 470, 10 (0); 427, 14 (0); 387, 10 (0); 272, 18 (0); and 215, 36 (0).

X-*Ray Structure Determination of Compound* (**8**).—$C_{16}H_{40}B_6N_6S_6$, *M* 573.6, crystal size 0.30 × 0.22 × 0.46 mm, triclinic, space group $P\bar{1}$, $a = 9.012(3)$, $b = 9.215(3)$, $c = 19.910\ (7)$ Å, $\alpha = 85.56(3)$, $\beta = 77.97(3)$, $\gamma = 76.08(3)°$ (from the setting angles of 23 automatically centred reflections), $U = 1\ 568.9(9)$ Å^3, $Z = 2$, $D_c = 1.214$ g cm^{-3}.

Data collection. ω-scan, two standards measured after every 48 intensity recordings, scan speed 2—29.3° min^{-1} for ⩽150 and $\geqslant 2\,500$ Hz, scan width 1.2°, signal-to-background ratio 1:1, 2θ range 2—48° in $h \pm k \pm l$, 5 523 measured reflections, 5 055 unique of which 3 519 were considered observed $[I \geqslant 2\sigma(I)]$.

Structure solution. Direct methods, all non-hydrogen atoms refined anisotropically; hydrogen positions calculated and included as rigid methyl and methylene groups in the final steps of refinement. 321 Parameters refined to $R = 0.080$ and $R' = 0.08$ $[R = \Sigma(|\Delta F|)/\Sigma(F_o)$, $R' = \Sigma(w^{\frac{1}{2}}|\Delta F|)/\Sigma(w^{\frac{1}{2}}|F_o|)$, $1/w = \sigma^2 F + 0.0006\ F^2]$, largest $\Delta/\sigma = 0.082$ Å, largest residual electron density 0.42 e Å^{-3}. Final atomic co-ordinates are summarized in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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