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The Production and Spectroscopic Identification of Bromothioborine, BrB=S from the Thermolysis of 2,4,6-Trisbromo-cyclo-1,3,5-trithia-2,4,6-triborane, $(BrBS)_3$

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Abstract

2,4,6-trisbromo-cyclo-1,3,5-trithia-2,4,6-triborane, $(BrBS)_3$ has been prepared and its thermolysis studied by on line FT-IR and (HeI) photoelectron spectroscopy. The products are compared with the reaction products of dibromodisulphide and boron at high temperatures. *Ab initio* molecular orbital calculations have been carried out, assisting in the assignment of the photoelectron spectrum of $(BrBS)_3$. The 1st ionisation energy of $(BrBS)_3$ is 10.32 eV, due to a doubly degenerate E type orbital originating from ionisation of the lone pairs on sulphur and bromine. ^{11}B NMR spectra of the various boron sulphur compounds prepared are reported, and the IR of B_2S_3 in the gas phase has also been measured.

Introduction

The derivatives of 2,4,6-trisbromo-cyclo-1,3,5-trithia-2,4,6-triborane $(BrBS)_3$ (**I**) (cyclotriborthianes or borthiins) were originally described as 'additive compounds' of formula $B_2S_3{\cdot}BR_3$ (R = Cl, Br) by Stock and Blix [1]. In the same year Stock and Poppenburg [2] reported a compound with formula $B_2S_3{\cdot}H_2S$. More than fifty years later Wiberg and Sturm [3] proposed a cyclic structure for these compounds, reinforced by a Raman study of 2,4,6-tris(hydrothio)-cyclo-1,3,5-trithia-2,4,6-triborane $(-BSH-S)_3$ (**II**) [4]. Compound **II** is of major interest since it can be used as a starting material for the production of other borthiins [4,5], substituted with Cl, Br, I and Me. The unsubstituted parent compounds, $(HBS)_n$ have not been isolated, but mass spectral studies of monomeric HB=S, yielded cyclic species in small proportions [6]. $(-BSH-S)_3$ (**II**) can be produced in small quantities [7] by flowing a mixture of H_2 and H_2S over elemental boron at 800 °C. A similar route has been reported [8] by flowing only H_2S over heated boron in accordance with the equation

$$6H_2S_{(g)} + 3B_{(s)} = (-BSH-S)_{3(g)} + \tfrac{9}{2}H_{2(g)}$$

Analysis of the products showed traces of B_2S_3 and HBO_2 indicating the presence of oxygen containing impurities. A more reliable route to larger quantities of $(-BSH-S)_3$ is the treatment of BBr_3 or BI_3 with H_2S in carbon disulphide [5]

$$6H_2S_{(g)} + 3BBr_{3(\text{solut.})} \xrightarrow[\text{reflux}]{} (-BSH-S)_{3(\text{solut.})} + 9HBr_{(g)}$$

These workers reported two equilibria leading to the trimeric product

$$3BR_3 + 3H_2S = (BRS)_3 + 6HR$$
$$(BRS)_3 + 3H_2S = (-BSH-S)_3 + 3HR$$

It was necessary to work at elevated temperatures to shift the equilibrium to the right hand side. Later work by Bouix and Hillel [9] reported similar results except that they worked at −10 °C obtaining at first $B(SH)_3$ which finally cyclised at room temperature

$$3B(SH)_3 = (-BSH-S)_3 + 3H_2S$$

The reactions of $(-BSH-S)_3$ have been extensively reviewed [10], but contrary to the studies covered therein the only route to $(FBS)_3$ is by thermolysis of various sulphur fluorides with boron [11]. The routes to $(BrBS)_3$ described in the literature are numerous including: (a) treatment of **II** with BBr_3 [12], (b) reaction of BBr_3 with H_2S at low temperature [9], (c) reaction of mercury(II) sulphide with BBr_3 [13], (d) cyclisation of $BBr(SH)_2$ [14, 15].

Experimental

The aim of this work was to produce the trimer of BrBS, $(BrBS)_3$ (**I**) and to study its vapour phase thermolysis by infrared (IR) and photoelectron (PE) spectroscopy. We have accumulated a large collection of data for the conditions of production of the various monomers and of their study by various spectroscopic techniques and the reader is therefore referred to a leading reference for further

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information [16]. $(BrBS)_3$ was synthesised in two stages according to previously published work [5]. The reaction vessel was fitted with 'Clearfit' joints and a 'Safe Lab' greaseless stirrer bearing, since even Fomblin fluorinated grease was attacked during the course of the reaction. A mixture of argon and H_2S was bubbled through a solution of BBr_3 (0.4 mol) in CS_2 over a period of five days, with constant stirring (consuming 200 g, 5.8 mol of H_2S in this time), finally heating under reflux for two days. The solution was cooled to –196 °C and filtered through a glass sinter. The yield was 15 g (0.065 mol, 50.25%) of a colourless solid, $(-BSH-S)_3$. The authenticity of the compound was checked by mass spectrometry, IR and ^{11}B NMR before using it without purification for the next stage. It was dissolved in 60 ml (0.31 mol) of BBr_3 and kept under argon at room temperature for 38 h. The volatile components were trapped at –196 °C and the remaining solid was sublimed under vacuum, yielding 2 g (0.005 mol) of $(BrBS)_3$. This product was characterised by IR, mass spectrometry and ^{11}B NMR.

The thermolysis of Br_2S_2 over heated boron was carried out in a quartz tube 300 mm long of internal diameter 8 mm, heated to 1320 K. The involatile disulphide was warmed until the vapour pressure in the flow system was 11.0 Pa, and then helium carrier gas was admitted to give a total pressure of *ca.* 100 Pa. The products of the reaction were pumped moderately fast through an IR cell of path length 15 cm fitted with KBr windows. The resolution used was 4 cm^{-1} and usually 24 scans were co-added.

For the thermolysis of the trimer, **I**, essentially the same system was used. The involatile solid was placed in a second tube in front of the reactor and warmed to 370 K giving a vapour pressure in the flow system of *ca.* 7.5 Pa. Helium was admitted to give a total system pressure of *ca.* 130 Pa and the reactor heated to 873 K.

The infrared spectrometer used was a Perkin-Elmer 1710 Fourier Transformer instrument fitted with a DTGS detector. The ^{11}B NMR spectra were obtained at 25.669 MHz on a Bruker WP80 and at 115.509 MHz on a Bruker WM360 spectrometer. The mass spectra were obtained on a Kratos MS8080 RF spectrometer and the photoelectron spectra were taken on a Perkin-Elmer PS16/18 spectrometer.

Results and Discussion

IR Studies

The first results to be described are those from the Fourier Transform IR study of the reaction

$$Br_2S_{2(g)} + B_{(s)} \xrightarrow{\Delta H} BrBS_{(g)}$$

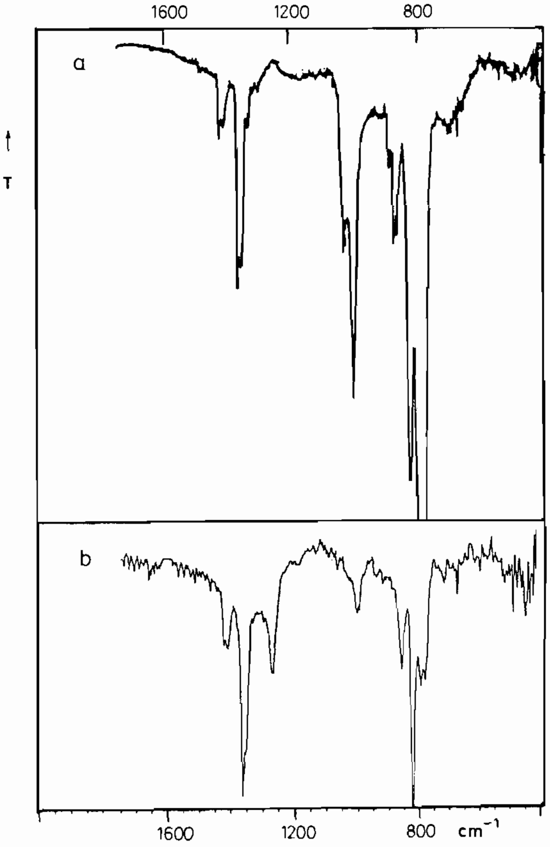


Fig. 1. (a) The IR spectra of BrBS generated by the thermolysis of $(BrBS)_3$, in the ν_1 fundamental region. (b) The IR spectrum of BrBS, generated from dibromodisulphide, in the ν_1 fundamental region.

TABLE I. Infrared Spectroscopic Data from the Reaction of Br_2S_2 with Boron

ν (cm^{-1})	Intensity	Assignment
1416	M	P and R branch of $\nu_1(Br-{}^{10}B{=}S)$
1359	S	P and R branch of $\nu_1(Br-{}^{11}B{=}S)$
1026	M	$\nu_1({}^{10}B-{}^{10}B)$ of $B_2S_3Br_2$
994	S	$\nu_1({}^{10}B)$ of $B_2S_3Br_2$
857	M	$\nu_3({}^{10}BBr_3)$
819	VS	$\nu_3({}^{11}BBr_3)$
797	V	$\nu_3({}^{10}B)$ of $B_2S_3Br_2$
519	W	S_n $(n > 2)$ [19]
483	M	
448	W	
425	W	ν_2 of B_2S_3

Figure 1a shows the IR spectrum between 2000–400 cm^{-1} of the products of the above reaction. The observed vibrational frequencies are listed in Table I. Apart from the bands due to the B=S stretching fundamental ν_1 at 1416 and 1359 cm^{-1} ($^{10}B\nu_1$ and $^{11}B\nu_1$ respectively), several other bands are observed.

TABLE II. Infrared Spectroscopid Data from the Thermolysis of $(BrBS)_3$

ν (cm^{-1})	Intensity	Assignment
1407	M	P and R branch of $\nu_1(Br-{}^{10}B{=}S)$
1360	S	P and R branch of $\nu_1(Br-{}^{11}B{=}S)$
1267	M	$\nu_1 + \nu_6$ of B_2S_3
1000	W	ν_1 of $B_2S_3Br_2$
857	M	$\nu_3({}^{10}BBr_3)$
820	VS	$\nu_3({}^{11}BBr_3)$
792	M	ν_3 of $B_2S_3BR_2$
485	VW	S_n ($n > 2$) [19]
471	VW	
444	VW	
443	VW	

These are due to 3,5-dibromo-1,2,4-trithia 3,5-diborolane [17], boron tribromide [18], S_n ($n > 2$) [19, 20] and B_2S_3.

Next the sample of $(BrBS)_3$ was decomposed using the system described above and the IR spectrum of products is shown in Fig. 1b, with the vibrational frequencies listed in Table II. The characteristic ${}^{10}B/{}^{11}B$ bands due to ν_1 of Br–B=S are clearly in evidence together with a new feature at 1267 cm^{-1}. This absorption lies in the expected region for gaseous B_2S_3 [21]. More recent work [22] suggests that this band may be due to overlapping of the fundamentals ν_1 and ν_6 in B_2S_3, and this is supported by comparison with studies on B_2O_3 [23, 24]. However we have not observed the reported shift of this broad feature to lower frequencies ($\nu < 1050$ cm^{-1}) due to deposition of B_2S_3 on the cell windows [25]. When the Br–B=S absorption is examined in more detail under expanded scale, the P and R branch separation of 10 cm^{-1} on the ${}^{10}B$ band yield an approximate value for the rotational constant B of 0.068 cm^{-1} from the approximation

$$\Delta\nu \simeq 2.2\sqrt{BT}$$

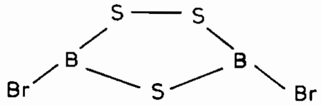
$\Delta\nu$ = P and R separation, T = absolute temperature.

This is in good agreement with previous microwave measurements and with other high resolution studies in progress [26]. After completing the thermolysis reaction, the intermediate trap was carefully warmed and this gave rise to a spectrum with maximum intensities at 1265, 721 and 425 cm^{-1}. Based on the discussion above these bands are attributed to B_2S_3.

We have attempted the on-line gas phase preparation of BrBS by reaction of BBr_3 with mercury(II) sulphide as reported [13], but this failed and only absorptions due to B_2S_3 were observed. Also the analogous reaction with cadmium(II) sulphide was unsuccessful. An attempt at the production of I–B=S by gas phase reaction of BI_3 with H_2S/He also only produced absorptions due to B_2S_3.

From the above results it is possible to formulate a reaction scheme for the reaction of Br_2S_2 with boron to account for the observed products:

$4Br_2S_2 + 4B \longrightarrow$



$+ 2BBr_3 + 5/2S_2$

$$Br_2S_2 + 2B \longrightarrow 2Br{-}B{=}S$$

In comparsion, the thermolysis of the trimer $(BrBS)_3$ may proceed as follows:

$$3(BrBS)_3 \longrightarrow 3Br_2B_2S_3 + BBr_3 + 2B$$

$$(BrBS)_3 \longrightarrow 3BrBS$$

$$(BrBS)_3 \longrightarrow B_2S_3 + BBr_3$$

Assuming a cyclic intermediate arising from reaction of X_2S_2 with boron, S_2 and B–X are formed as initial products. The enthalpy of formation of X–B has values of $\Delta H_{298.15} = -119.7 \pm 10.9$ KJ mol^{-1} [27], $+141.4 \pm 16.7$ KJ mol^{-1} [28] and $+234 \pm 42$ KJ mol^{-1} [28] for X = F, Cl and Br respectively, whereas that of I–B is calculated to have a value of $+305.4 \pm 42$ KJ mol^{-1} [28]. The reaction of X–B with S_2 should then be fast yielding X–B=S and not XSB [16]. There is additional evidence for the production of $Br_2B_2S_3$ detected in the IR as follows

$$2(BrBS)_3 + 3/8S_8 \longrightarrow 3Br_2B_2S_3$$

Photoelectron results

The photoelectron spectrum of the trimer $(BrBS)_3$ (I) was obtained using the direct inlet involatile probe at 335 K and is shown in Fig. 2, with the ionisation energies and assignments collected together in Table III. Molecular orbital calculations were carried out at the SCF level using a double zeta Gaussian basis set (DZ) [29–31] and a double zeta plus polarisation (DZP) basis set. These calculations indicate that 18 two electron orbitals are expected within the HeI region and a brief examination of the spectrum shows that there is a considerable degree of overlapping of bands occurring based on relative intensity considerations.

The first band at 10.32 eV of E symmetry is described as an out of plane lone pair combination of the lone pairs on sulphur and bromine. The next, centred at 10.64 eV and with a greater intensity than that of the first, but somewhat narrower in width is predicted to arise from ionisation of A_2 and A_1 type orbitals described as bromine and sulphur lone pair

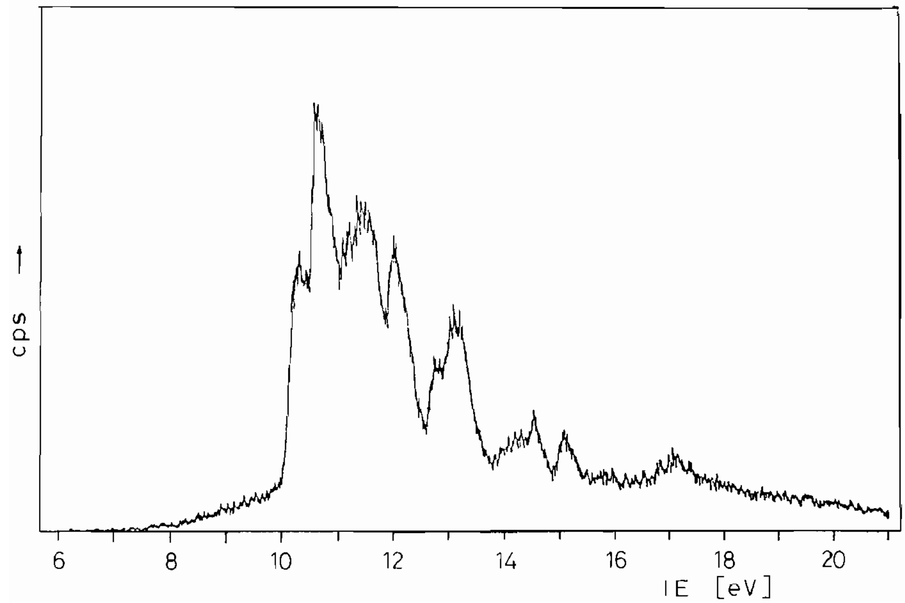


Fig. 2. The photoelectron spectrum of $(BrBS)_3$.

TABLE III. Photoelectron Assignments for $(BrBS)_3$

Bond	Ionic state	Calculated *IE* (eV)		Assignment	Experimental *IE* (eV)[a]
		DZ	DZP		
1	E	11.46	11.14	out of plane S, Br lone pairs	10.32
2	A_2	11.63	11.45	in plane Br lone pairs	10.64
	A_1	11.73	11.49	out of plane S, Br lone pairs	
3	E	11.92	11.86	Br lone pair	11.2–11.4
	E	12.58	12.51	S, Br lone pair	
4	E	13.15	12.88	S–B–Br π bond	12.05
5	E	14.38	14.12	B–Br σ bond	13.10
	A_1	14.59	14.24	S–B π bond	12.83
6	A_1	15.78	15.69	B–Br σ bond	14.60
	A_1	15.98	15.83	B–S σ bond	
7	A_2	17.30	17.06	B–S σ bond	15.10
8	E	19.81	19.53	B–S σ bond	17.10

[a] Experimental ionisation energies are all ±0.1 eV.

orbitals. Note that the calculations indicate that these two ionic states are almost degenerate giving the appearance of a strong relatively sharp peak. The next band occurring between 11.2 and 11.4 eV has a lower intensity than the previous band but is however much broader, possibly twice the width of the former and is assigned to two E type orbitals which are essentially lone pair in character. The band centred at 12.05 eV has approximately the same intensity as the third but with a much decreased width and is assigned to an E type ring π orbital. The spectrum then shows a gap of about 1 eV before the appearance of another broad band with a maximum at 13.16 eV having a shoulder at 12.83 eV. This orbital consists of the next E type orbital which is boron–bromine σ bonding in nature together with an A_1 type orbital of sulphur–boron π bonding character. The separation of this band from the previous one is nicely represented by the calculations, being 1.17 eV for the DZ and 1.24 eV for the DZP. The calculations once again predict a gap of about 1 eV before the next band centred at 14.60 eV which consists of two A_1 type orbitals, boron–bromine σ bonding and boron–sulphur σ bonding in nature. The re-

TABLE IV. NMR Data

δ (ppm)	Solvent	Compound	δ (ppm) $(CS_2)^a$
54.45	C_6D_6	$(BrBS)_3$	−54
59.06	C_6D_6	$(Br\mathit{B}S)_2BSH$	
47.10	C_6D_6	$(BrBS)_2\mathit{B}SH$	
56.56	CS_2	$(-BSH-S)_3$	−57
61.50	CS_2	$B(SH)Br_2$	−49.8
60.59	CS_2	$B(SH)_2Br$	−56.2

^{a}Refs. 7 and 9.

maining two bands in the spectrum at 15.10 and 17.10 eV are assigned to A_2 and E orbitals respectively, of boron–sulphur σ bonding character.

^{11}*B NMR Studies*

The chemical shifts of the various species identified in the course of this work are listed in Table IV. The sample of $(BrBS)_3$ shows a strong band at 54.45 ppm assigned to $(BrBS)_3$ and a peak at 47.10 which is due to $(Br(BS)_2\mathit{B}SH$. There is also a minor peak at 59.06 ppm assigned to $(Br\mathit{B}S)_2$-BSH. The chemical shifts of a mixture of $(BSH-S)_3$, $B(SH)_2Br$ and $B(SH)_2Br$ were also measured, and these are also given in Table IV. There is good agreement with previous work [7, 9] apart from the values given for $B(SH)Br_2$ and $B(SH)_2Br$, where not only the sign but also the trend is reversed.

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