Photoelectron Spectra of Sulphidoborons XBS where X = H, F, Cl, or Br[†]

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The photoelectron spectrum of the unstable new sulphidoboron BrBS has been obtained together with new refined measurements on HBS and ClBS. These new data have enabled the series of molecules XBS (X = H, F, Cl, or Br) to be compared so that general trends in the ionisation energies can be investigated as a function of the substituent X. Self consistent field molecular-orbital calculations with a double-zeta basis set have been used to assist in the assignment of the bands in the photoelectron spectra.

Following the original mass spectrometric detection of sulphidoborane HBS by Kirk and Timms[1] in the products of a high-temperature reaction between H_2S and boron, this species was characterised using microwave spectroscopy by Pearson and McCormick,[2] i.r. spectroscopy by Sams and Maki[3] and Turner and Mills,[4] and photoelectron spectroscopy by Kroto *et al.*[5] and Fehlner and Turner.[6] King *et al.*[7] have also been able to observe the emission spectrum of the cation. Using microwave spectroscopy, the methyl analogue, CH_3BS, was subsequently detected in the products of the reaction between the disulphide Me_2S_2 with boron at 1 100 °C.[8]

The disulphide route has proven extremely valuable for producing the halogenated analogues FBS,[9] ClBS,[10] and BrBS[11] which have been detected by both microwave and photoelectron techniques. The emission spectra of the FBS and ClBS cations have also been studied by King *et al.*[12] It has been possible to produce the selenido boron analogue ClBSe,[13] although rather less efficiently.

In this study the photoelectron spectrum of BrBS has been obtained. New improved spectra of HBS and ClBS have been obtained and the results for XBS (X = H, F, Cl, or Br) have been analysed using self consistent field (SCF) molecular-orbital (m.o.) calculations.

Experimental

The compounds were generated using the heterogeneous vapour–solid reaction of the appropriate disulphide (or H_2S in the case of HBS) with crystalline boron chips (Koch-Light) loosely packed in the heated region of a quartz reactor at 1 100 °C. The reactor consisted of a linear quartz tube 300 mm in length and 8 mm internal diameter which was heated over a length of *ca.* 150 mm using an electrical resistance furnace. The compounds were detected when the reaction products were pumped as rapidly as possible into the ionisation chamber of the photoelectron spectrometer. The photoelectron spectrometer was built at Southampton according to the design of Dyke *et al.*[14] Spectra were calibrated with argon and xenon and the resolution was 25 meV. Specific experimental details for each reaction system are given below.

HBS.—Hydrogen sulphide (B. D. H. Ltd.) was admitted into the reactor tube directly from the lecture bottle *via* a Hoke needle valve. The sample pressure was maintained at 100 mTorr.

FBS.—The compound F_2S_2 was synthesised by the reaction of silver fluoride with molten flowers of sulphur,[15] stored in an ampoule, and used without further purification. The vapour pressure of F_2S_2 was readily controlled by holding the ampoule at −130 °C and using a polytetrafluoroethylene (ptfe) 'Rotaflo' valve.

ClBS.—A commercial sample of Cl_2S_2 (B. D. H. Ltd.) was used to generate ClBS. Vapour of Cl_2S_2 was admitted using a ptfe 'Rotaflo' valve to maintain a pressure in the reactor of *ca.* 100 mTorr. This was facilitated by keeping the temperature of the precursor at 0 °C.

BrBS.—The compound Br_2S_2 was synthesised by the reaction of stoicheiometric amounts of bromine and flowers of sulphur in a sealed ampoule at a temperature of 200 °C for 12 h.[16] The product was a dark red liquid which was used without further purification. The vapour pressure of the system was controlled by heating the relatively involatile disulphide to a pressure in the reactor of *ca.* 80 mTorr.

Computational Details

To assist in the assignment of the photoelectron spectra, *ab initio* SCF m.o. calculations were carried out on HBS, FBS, ClBS, and BrBS.

Double-zeta contracted gaussian basis sets due to Dunning and co-workers were used throughout: for H we used Dunning's (4*s*/2*s*) contraction of Huzinaga's primitive set (scale factor 1.2);[17] for F, Dunning's (9*s*5*p*/4*s*2*p*) contraction of Huzinaga's primitive set;[17] for Cl, Dunning and Hay's (11*s*7*p*/6*s*4*p*) contraction of Huzinaga's primitive set[18] with the correction noted by Craven *et al.*;[19] and for Br, Dunning's (14*s*11*p*5*d*/8*s*6*p*2*d*) contraction of his own primitive set.[20]

The calculations were all carried out at experimental geometries, specifically: *r*(H–B) = 1.168 99, *r*(B=S) = 1.599 61 (HBS); *r*(F–B) = 1.2833, *r*(B=S) = 1.6062 (FBS); *r*(Cl–B) = 1.658, *r*(B=S) = 1.629 (ClBS); and *r*(Br–B) = 1.8316, *r*(B=S) = 1.608 36 Å (BrBS).

The GAUSSIAN 76 and 82 packages[21,22] were employed. In the calculation on BrBS the level-shifting routines implemented in GAUSSIAN 76 by Dr. R. E. Overill of King's College, London were used.

The ionisation energies (i.e.s) were estimated straightforwardly by Koopmans' theorem.[23] With a double-zeta basis set, this approximation usually overestimates the valence i.e.s by *ca.* 10%.[23] Although absolute accuracy is lacking, the spacings between the calculated i.e.s are normally reasonably accurate and of assistance in interpreting experimental data.[23,24]

[†] *Non-S.I. units employed*: eV ≈ 1.60 × 10^{-19} J, Torr ≈ 133 Pa.

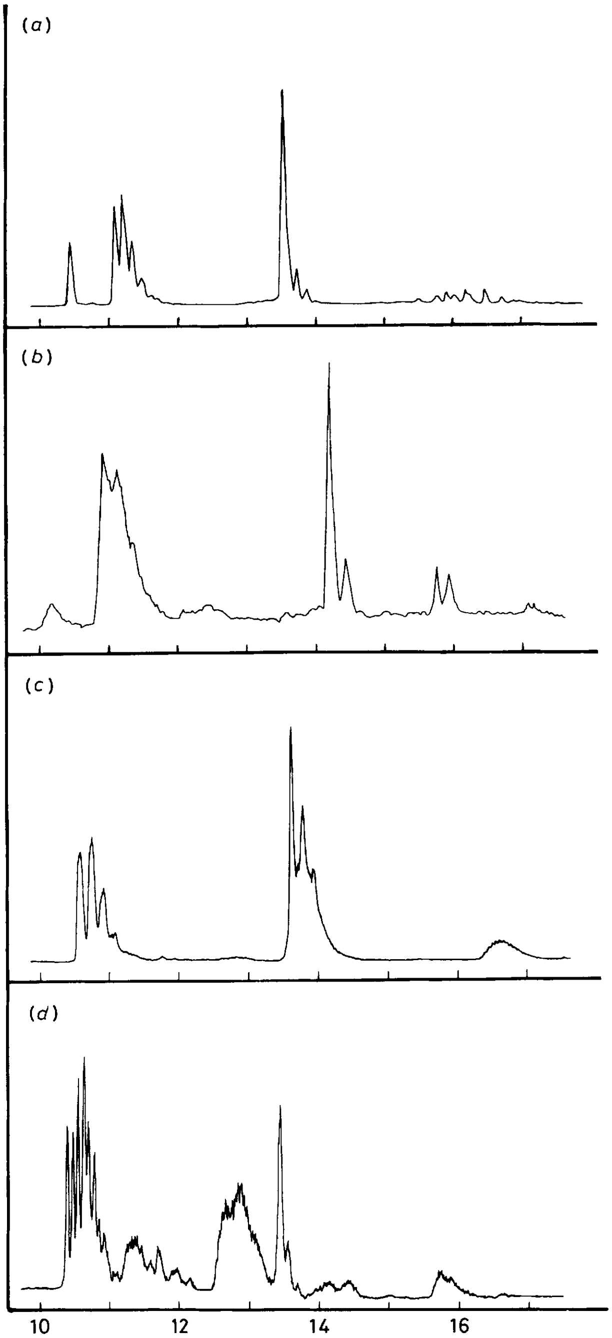

Figure 1. He I p.e. spectrum of (*a*) HBS (the peak at 10.48 eV belongs to H_2S; the third band in the region of 16 eV is weak and overlapped by hydrogen), (*b*) FBS [bands of $(FBS)_2$ appear weakly at 10.1 and 12.4 eV), (*c*) ClBS, and (*d*) BrBS [The features between 11 and 12.3 eV and between 13.9 and 14.5 eV are assigned to the dimer $(BrBS)_2$]

Results and Assignments

In Figure 1(*a*)—(*d*) we show scans of the region between 10 and 18 eV for all four compounds. The individual molecules will be discussed in turn, and reference will be made where appropriate to the corresponding isoelectronic compounds HCP[25] and FCP.[26]

Table.

		Ionisation energy			Vibrational wavenumber[c]	
		obs.[a] adiabatic	obs.[a] vertical	calc.[b]	p.e.[d]	opt.[e]
HBS	$\tilde{X}\,^2\Pi$	11.10	11.21	11.10	940	984.1
	$\tilde{A}\,^2\Sigma^+$	13.55	13.55	14.10	1 080	1 050.9
	$\tilde{B}\,^2\Sigma^+$	15.84	16.12	18.00	2 250	
FBS	$\tilde{X}\,^2\Pi$	10.91		11.31	1 550	1 721
	$\tilde{A}\,^2\Sigma^+$	14.20		14.93	1 670	1 718
	$\tilde{B}\,^2\Pi$	17.2		20.64		
	$\tilde{C}\,^2\Sigma^+$	19.62		22.85		
ClBS	$\tilde{X}$ $^2\Pi_{3/2}$	10.57	10.73	11.03	1 290	1 348
	$\tilde{X}$ $^2\Pi_{1/2}$	10.60	10.76			
	$\tilde{A}\,^2\Sigma^+$	13.63		14.54	1 260	1 391
	$\tilde{B}\,^2\Pi^+$	13.55	13.72	15.05	1 370	
	$\tilde{C}\,^2\Sigma^+$	16.33	16.68	18.18	520	
BrBS	$\tilde{X}$ $^2\Pi_{3/2}$	10.42	10.57	10.85	1 250	
	$\tilde{X}$ $^2\Pi_{1/2}$	10.50	10.65		1 300	
	$\tilde{A}$ $^2\Pi_{3/2}$	12.49	12.64	13.66	320	
	$\tilde{A}$ $^2\Pi_{1/2}$	12.76	12.85		350	
	$\tilde{B}\,^2\Sigma^+$	13.46	13.46	14.30	970	
	$\tilde{C}\,^2\Sigma^+$	15.54	15.72	17.11		

[a] ±0.05 eV. [b] In eV (double zeta). [c] In cm^{-1}. [d] ±40 cm^{-1}. [e] Refs. 7 and 12.

HBS.—The spectrum shown in Figure 1(*a*) consists of three distinct bands belonging to HBS and a single sharp peak at 10.5 eV which belongs to H_2S. The first band of HBS, with a vertical ionisation energy (i.e.) of 11.2 eV, consists of seven members of a vibrational series separated by 940 cm^{-1}. This band results from the ionisation of an electron from a π(BS) orbital giving rise to a $^2\Pi$ cationic state. The analogous band of HCP (arising from ionisation from the C≡P π orbital) has an energy of 10.79 eV. The vibrational mode excited is likely to be ν_3, which in the neutral molecule is 1 172 cm^{-1}.[4] The second band, at 13.55 eV (compared with 12.86 eV for the second band of HCP), results from ionisation involving a σ orbital and consists of four vibrational components spaced at 1 080 cm^{-1} which is also due to vibration of the B=S group. The region between 15.3 and 17 eV contains the third i.e. of HBS, overlapped by a band due to H_2 which is also formed in the pyrolysis reaction. The third ionisation potential (i.p.) of HBS starts at 15.84 eV and consists of at least six vibrational components with a spacing of 2 250 cm^{-1}. This frequency is the H–B stretching vibration, ν_1, which occurs at 2 736 cm^{-1} in the neutral molecule.[4] The i.e. data and vibrational frequencies together with the results of a double-zeta SCF m.o. calculation are given in the Table.

FBS.—The spectrum of FBS shown in Figure 1(*b*) has been discussed previously.[9] The resulting i.e. data are given in the Table, together with the new theoretical results.

ClBS.—The spectrum of ClBS is shown in Figure 1(*c*) and apparently consists of three bands. The first band, shown under higher resolution in Figure 2(*a*), is a progression of doublets with four components. As in the case of the first i.e. of HBS, this band is expected to arise from removal of an electron from the π orbital localised mainly in the B=S group, the doublet structure resulting from the spin–orbit splitting of the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ cationic states. The vibrational interval observed in both series of components is 1 290 cm^{-1}, which is assigned to ν_3, the B=S stretching frequency. This vibration occurs at 1 458 ($Cl^{10}BS$) and 1 408 cm^{-1} ($Cl^{11}BS$) in the neutral molecule.[27] The second band of this molecule, which starts at *ca.* 13.55 eV and is shown under higher resolution in Figure 2(*b*), appears to consist of two overlapping series of features. The calculations predict two i.e.s in this region originating from the σ(BS) orbital and from a π

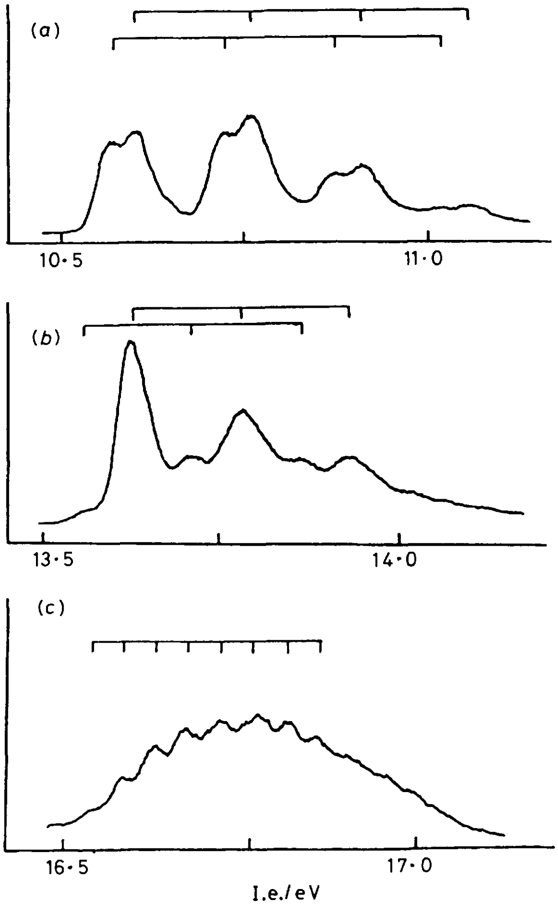

Figure 2. Expansion of (*a*) the first band of ClBS showing the spin–orbit splitting, (*b*) the second and third bands, and (*c*) the fourth band

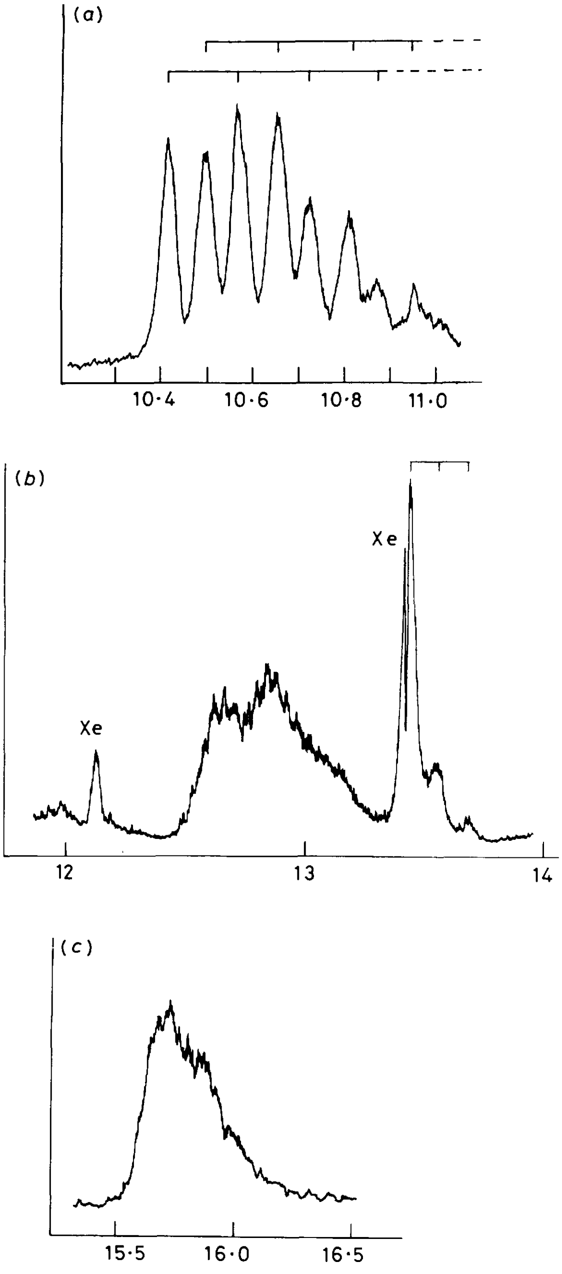

Figure 3. Expansion of (*a*) the first band of BrBS showing the spin–orbit splitting, (*b*) the region 12—14 eV showing the second and third bands (calibration lines of Xe are also shown), and (*c*) the fourth band

lone-pair orbital localised mainly on the Cl atom. The weak feature at 13.55 eV appears to be the first member of a progression consisting of four components with a vibrational interval of 1 370 cm^{-1} which is assigned to the B=S stretching motion. This is overlapped by a stronger and shorter progression of three members commencing with a strong first component at 13.63 eV. The vibrational interval of 1 260 cm^{-1} again belongs to the B=S stretching frequency. The most reasonable interpretation of this is that the weaker progression, adiabatic i.e. 13.55 eV, vertical i.e. 13.72 eV, is the π transition. The σ ionisation is at 13.63 eV and the adiabatic and vertical i.e.s are coincident. This assignment is consistent with the calculations for ClBS, the results of which are also given in the Table. On replacing the fluorine atom in FBS by chlorine to give ClBS one would expect the σ(B=S) orbital to be slightly destabilised on electronegativity grounds, whereas the π (halogen) orbital should show a marked destabilisation, and as discussed above, these two orbitals are almost degenerate. Further confirmation of this assignment is to be found in the consistency of the shape of the band associated with the σ orbital throughout the series shown in Figure 1(*a*)—(*d*). The third region of ionisation, shown under higher resolution in Figure 2(*c*), is due to electron removal from the σ(B–Cl) orbital and consists of at least eight components of spacing 520 cm^{-1}. This vibration belongs to the Cl–B stretching frequency, ν_1, which has been estimated to be 510 cm^{-1} in the neutral molecule.[10] The $B^2\Pi$ state, localised on the chlorine atom does not exhibit resolvable spin–orbit splitting. It is only 0.27 eV in the corresponding orbital in BrBS and would be expected to be lower for Cl than Br ($\zeta \propto Z^2$).

BrBS.—The spectrum of BrBS is shown in Figure 1(*d*). The individual bands are also shown under higher resolution in Figure 3(*a*)—(*c*). The first band consists of two overlapping vibrational progressions associated with the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ cationic states which result from the removal of an electron from the π(B=S) orbital. The spin–orbit splitting is 0.08 eV, significantly larger than in ClBS where it is 0.03 eV. The vibrational intervals are 1 250 cm^{-1} for the $^2\Pi_{3/2}$ and 1 300 cm^{-1} for the $^2\Pi_{1/2}$ states and are assigned to the B=S stretching

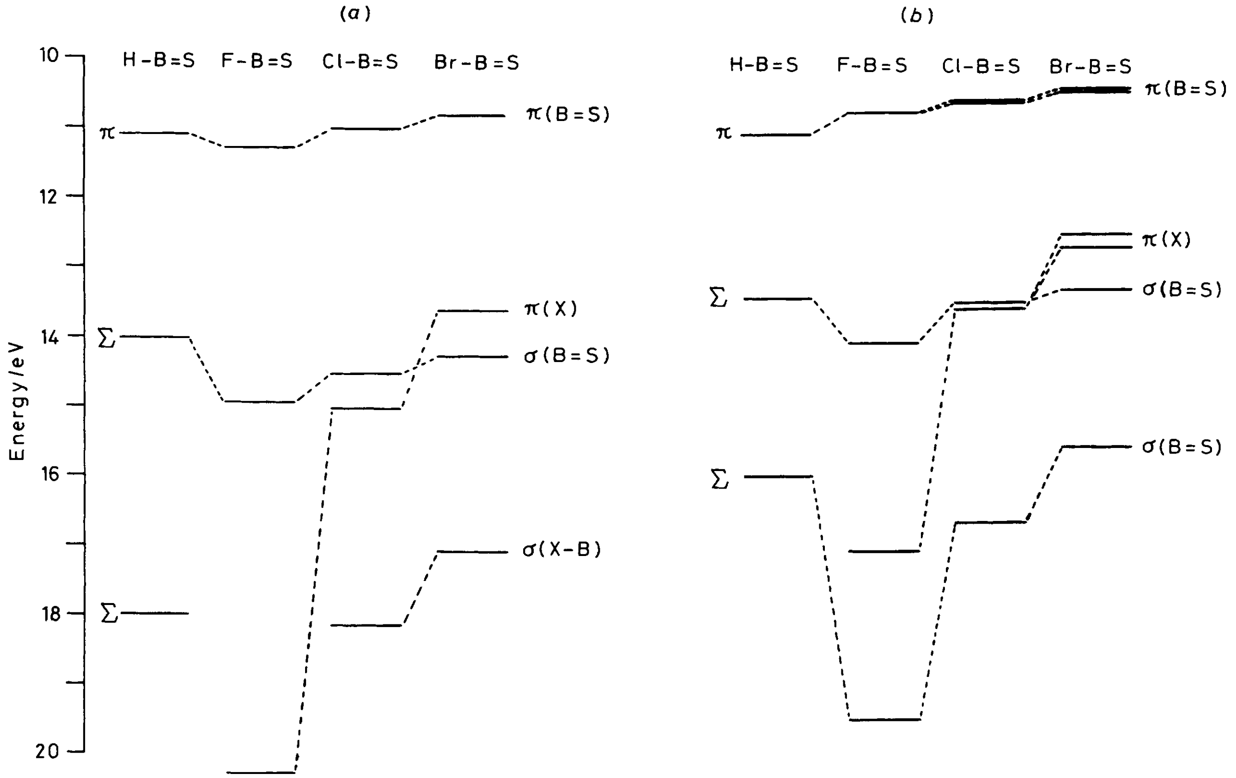

Figure 4. Correlation diagrams of (*a*) the calculated and (*b*) the experimentally determined i.e.s for HBS, FBS, ClBS, and BrBS

frequency, ν_3, which occurs at 1 406 (Br^{10}BS) and 1 348 cm^{-1} (Br^{11}BS).[27] The adiabatic and vertical i.e.s of the two states are 10.42, 10.57 eV and 10.50, 10.65 eV respectively. Between 11 and 12 eV there are some broad features not assignable to BrBS which may be due to polymeric material or other by-products of the pyrolysis reaction, *e.g.* BBr$_3$.[28] The second i.e. of BrBS has an onset at 12.49 eV and under higher resolution appears to consist of two extended overlapping progressions whose maxima are separated by *ca.* 0.20 eV. These two bands are assigned to the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states of the cations which result from electron excitation from the π(Br) lone-pair orbital. The vibrational intervals for these two progressions are 320 cm^{-1} for the $^2\Pi_{3/2}$ state and 350 cm^{-1} for the $^2\Pi_{1/2}$ state and belong to the Br–B stretching motion, ν_1.[29] The third i.e. of BrBS, associated with the σ(B=S) orbital, is predicted by the double-zeta calculations to lie quite close in energy to the π i.e. and the band at 13.46 eV in Figure 1(*d*) is assigned to this excitation. The band is shown in more detail in Figure 3(*b*) and consists of three members of a short vibrational progression with an interval of 970 cm^{-1} which again is due to the B=S stretching frequency ν_3. The fourth i.e. of this molecule occurs as a broad band with an onset of 15.54 and a maximum at 15.72 eV.

In those instances where analogous measurements have been made the photoelectron (p.e.) data are seen to be in good agreement with the more accurate, though less extensive, optical data.[7,12]

Discussion

The calculated and experimental orbital energies are shown in Figure 4(*a*) and (*b*) respectively. The first i.e.s for the sulphidoborons can be assigned, on the basis of the observed patterns and theoretical arguments, to an orbital which has π(BS) bonding character. This orbital shows a gradual destabilisation across the series X = H, F, Cl, Br, with the slight XB antibonding character increasing from F to Br as expected; a trend which is reproduced by m.o. calculations, Figure 4(*a*). The second i.e. of HBS is essentially a lone pair *sp* hybrid localised mainly on the S atom with a small σ(BS) bonding component. The introduction of F tends to stabilise this orbital slightly whereas the effects of Cl and Br are almost negligible. This sulphur *sp* lone-pair orbital is the second i.e. of FBS and is almost degenerate with the third orbital in ClBS and becomes the third orbital in the case of BrBS, Figure 4(*b*). There is some evidence from the theoretical calculation that the F atom has pulled some of the lone-pair electron density into the σ(BS) bonding region. This is a typical σ-acceptor effect as expected for the halogens, F in particular.

The third i.e. of HBS corresponds to the σ(HB) bonding orbital. The energy of this orbital is of course strongly dependent on the atomic orbital on the halogen atom when the H atom is substituted, becoming the fourth i.e. in these cases, and is calculated to lie beyond 24 eV for FBS. The halogen p_π(X) lone-pair orbital which is the third i.e. for FBS crosses over at ClBS to become the second i.e. for BrBS. In general the i.e.s assigned to the lone pairs of the halogen XΠ orbitals are lower in energy than the corresponding orbitals in the HX molecules due to the greater electron-donating ability of the B=S moiety compared with the H atom. The last member of the series is IBS and attempts to detect this molecule have so far not been successful.

These molecules are of interest as reactants because they should be useful ligands, able to form complexes *via* the π system. They would be expected to co-ordinate with transition metals *via* the BS multiple bond, exhibiting analogous behaviour to that shown by the phospha-alkynes.[30] Although there is undoubtedly a triple bond between the carbon and phosphorus atoms in phospha-alkynes, it is not *a priori* clear

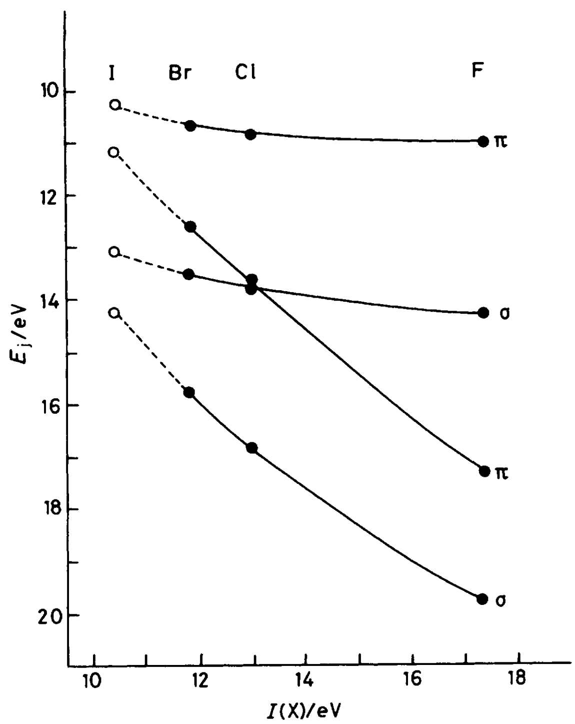

Figure 5. Correlation diagram for the first four orbitals in FBS, ClBS, and BrBS. The experimental ionisation energies are plotted against ionisation energies of the free halogen atoms. The data are extrapolated to predicted values for IBS

whether the boron–sulphur bond of the sulphidoborons is a double or a triple bond. There have been two theoretical studies of the nature of this bond in these molecules,[31,32] both of which indicate that B and S are linked by a triple π dative bond. In the first of these studies Gropen and Wilsøff-Nilssen[31] compared total overlap populations of HBS, H_2BSH, and $H_3B{\cdot}SH_2$. More recently, Nguyen and Ruelle[32] investigated the electron distribution in the bond by a localised orbital analysis and by computation of electrostatic potentials. We have also carried out Mulliken population analyses and obtained similar results as those of Gropen and Wilsøff-Nilssen. It is also feasible that the reactivity could be utilised in the formation of new organic molecules with interesting ring structures involving the BS component.

It has been demonstrated previously[33] that a simple and unambiguous correlation diagram is obtained if the experimental ionisation energies are plotted against the ionisation energies of the free halogen atoms. This is shown for the sulphidoboron series in Figure 5, together with an extrapolation towards the, as yet, unknown IBS species.

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