Bonding in Clusters. Part 10.† The Nature of the BH Groups in *closo*-Borane Anions. A Study by Vibrational Spectroscopy, Electronic Spectroscopy for Chemical Analysis, and *ab initio* Computation‡

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The i.r. and Raman spectra of $Cs_2B_nH_n$ compounds have been studied, concentrating on the BH stretch vibrational bands which have very much the same energy independent of cluster site or size. Electronic spectroscopy for chemical analysis of the same compounds shows that the charge localised on the boron atoms is essentially independent of the details of cluster bonding. These observations allow the assignment of sp^2 hybridisation to all BH groups in the full set of anions and suggest that the correct starting point for a TSH description of borane clusters is one where each BH fragment makes a constant isolobal contribution to the cage, regardless of cage size. This assignment is consistent with the results of *ab initio* calculations on the *closo* sequence of anions.

Despite the existence for a number of years of Stone's description of the electronic structure of *closo*-borane anions[1,2] and its adoption as a framework for the discussion of borane clusters and related metallo-systems, there have been very liitle experimental data produced to test its validity or accuracy. We have made various theoretical tests of its usefulness[3,4] in earlier papers in this series and have applied it to some experimental data[5,6] with good results. Further data on electronic properties (*e.g.* photoelectron spectra, absorption, spectra, *etc.*) on the anions have, however, proved uninformative, inconclusive, or simply unobtainable. The compounds are of course involatile, which precludes photoelectron spectroscopy (p.e.s.) measurements, and are almost completely transparent in the visible/u.v. absorption region. We are therefore forced to look for secondary sources of experimental information and in this paper we consider the vibrational spectra of the anions $[B_nH_n]^{2-}$ as an indirect measure of their electronic properties. We concentrate on the BH stretching modes as the BH bonding orbitals are closely related to one set of cluster bonding orbitals. We draw attention to a fact available in the literature but apparently not correlated before, simply that the stretching frequencies have much the same energy for the full range of cluster sizes. This is not what would be predicted from one simplified version of Stone's theory and it leads us eventually to an improved starting point for the theory.

Experimental

The caesium salts of the *closo*-borane anions were prepared by literature methods.[7–9] The $Cs_2[B_6H_6]$ was kindly donated by Professor W. Preetz of Kiel University. Infrared spectra of KBr discs and Nujol mull samples were recorded using Mattson Polaris FTIR and Perkin-Elmer 682 spectrometers at both room and liquid-nitrogen temperatures, the latter using a Specac P/N 21000 variable-temperature cell. Raman spectra were measured for room-temperature polycrystalline samples using a Spex Raman spectrometer model 1401 equipped with a Spectra Physics model 165 argon-ion laser. Excitation of the samples was achieved either with the lines of the laser at 514 or 488 nm using incident powers of ≈50 mW. Electronic spectroscopy for chemical analysis (ESCA) spectra were recorded on a AEI ES200 system. *Ab initio* calculations of vibrational frequencies were performed using the CADPAC program[10] on the Cray-1S(ULCC) after initial geometry optimisation using the GAUSSIAN 82 program[11] on a VAX 11/780 computer (Cork).

Stone's Theory and BH *Bonding*.—For an approximately spherical distribution of n(BH) groups we can restrict attention to the B,2s and B,2p_r (r = radially directed) atomic orbitals as these are the only ones concerned with BH bonding. They are quite strongly orthogonal to the B,2p_t (t = tangential to the approximate sphere) orbitals, even those on adjacent B atoms and even in the low symmetry of some of the anions. Stone[1] has shown that n radially directed atomic orbitals produce n molecular orbitals which can be classified as approximate spherical harmonics $S,P,D,\ldots$ in increasing order of energy. In ref. 1 an energy level scheme is drawn up for σ orbitals of purely s character, though expressions for pure p, pure d, and hybrid combinations are also given. Given the energy separation between B,2s and B,2p_r of approximately 7.0 eV (from valence shell ionisation potentials VSIE), it is reasonable to propose Figure 1, in which no s–p mixing has been allowed, as the simplest possible starting point for the construction of the radial molecular orbitals.

The four low-energy S^σ and P^σ molecular orbitals are cluster localised, the S^σ being cluster bonding, the P^σ being bonding/non-bonding depending on cluster size and extent of P^σ/P^π mixing, and the D^σ antibonding.[1,4] The n BH bonding orbitals are formed from S^x, P^x, D^x, and F^x (x indicating *exo*), as shown in Figure 1. It was found in semi-empirical MNDO calculations on *closo*-boranes and carboranes[3] that the S^σ and $P^{\sigma/\pi}$ molecular orbitals (m.o.s) in these molecules had a high B,2s content. As we are taking them to be pure B,2s as a first approximation then these four bonding orbitals 'use up' four B,2s atomic orbitals (a.o.s). Assuming that the n BH bonding orbitals are all similar in any one cluster, the average hybridis-

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† Part 9 is ref. 4.

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

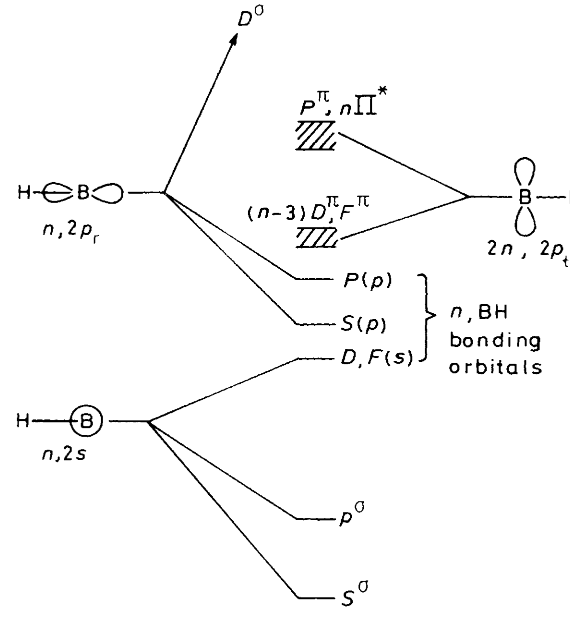

Figure 1. A general orbital diagram for the electronic structure of the *closo*-borane anions based on Stone's theory and allowing no s–p_r mixing

Table 1. Vibrational frequencies (cm^{-1}) of $[BH_4]^-$ calculated with the 4-31G* basis, and BH stretching modes of $[B_3H_8]^-$ calculated with the 4-31G set. The geometry used in the $[B_3H_8]^-$ calculation is a C_{2v} transition state (see discussion in the text)

$[BH_4]^-$		$[B_3H_8]^-$			
Calc.	Exptl.[a]	Calc.	Exptl.[b]	Calc.	Exptl.[b]
2 353.3, a_1	2 314	2 652.5, b_1	2 460	2 567.1, a_1	2 340
2 307.4, t_2	2 298	2 613.0, a_1		2 547.5, b_2	2 310
1 327.9, e	1 255	2 607.7, b_1	2 400	2 310.3, a_1	2 120
1 237.6, t_2	1 131	2 588.2, a_2		2 241.7, b_2	2 080

[a] M. I. Memon, G. R. Wilkinson, and W. F. Sherman, *J. Mol. Struct.*, 1982, **80**, 113. [b] J. Tomkinson, C. J. Ludman, and T. C. Waddington, *Spectrochim. Acta, Part A*, 1979, **35**, 117.

ation of the boron atoms in the bonds should be as in equation (1) *i.e.* varying from sp^2 in $[B_6H_6]^{2-}$, through sp in $[B_8H_8]^{2-}$, to $sp^{1/2}$ in $[B_{12}H_{12}]^{2-}$. This is such a wide variation in hybridisation across the series of anions that even allowing for the simplicity of the assumptions behind Figure 1 we would expect to find observable effects in cluster properties.

$$\frac{n-4}{n}\cdot s + \frac{4}{n}\cdot p \equiv sp^{4/n-4} \qquad (1)$$

A different Tensor Spherical Harmonic (TSH) based scheme has also been employed. Fowler and Porterfield[12] consider the available boron orbitals and divide them into three groups: an *exo*-directed B–H bonding hybrid (which was arbitrarily taken to have sp composition, though any fixed hybrid could have been used), an *endo* cluster-bonding σ hybrid which by subtraction is also sp, and the pair of p_π orbitals tangential to the approximate sphere. The pure σ orbitals produce the S^σ, P^σ, D^σ ... harmonics, of which S^σ is always bonding and P^σ is bonding for n values of about 9 or more. When σ/π interaction is switched on (using the approximate extended-Hückel Hamiltonian to parameterise the matrix elements) the familiar (n + 1) bonding m.o.s of TSH theory are produced. Since this model does not include BH/cluster-localised interactions it would predict something quite different from equation (1), a constant BH hybridisation and therefore a constant BH stretching frequency, independent of n.

Thus we have two distinct descriptions of the BH bonds in a *closo*-borane anion. In one their properties are strongly dependent on cage size, in the other there is little or no variation. The vibrational spectra will be shown to be more consistent with the second viewpoint.

BH *Stretch Frequencies and Hybridisation.*—In a recent publication[13] we have shown that BH stretch frequencies correlate with the nominal hybridisation of the boron atom in the same manner as those of CH in hydrocarbons. The typical values determined were 2 368 cm^{-1} for sp^3, 2 497 cm^{-1} for sp^2, and 2 763 cm^{-1} for sp. The correlation was established and tested for neutral molecules and we now wish to apply it to anions and must therefore justify this extention. We have followed the approach of ref. 13 and performed *ab initio* self-consistent field (SCF) calculations of optimised geometries and vibrational frequencies for $[BH_4]^-$ and $[B_3H_8]^-$ in the 4-31G basis. We expect the calculated frequencies in this basis to be larger than experimental ones by $\approx 8\%$, of which $\approx 3\%$ is accounted for by anharmonic effects in the experimental fundamentals (not present in a purely harmonic calculation) and $\approx 5\%$ is due to the inaccuracy of the calculated harmonic frequencies[14] (use of small basis sets, neglect of electron correlation). We may also expect anions to show deviations from the frequency–hybridisation correlation as the diffuse wavefunctions characteristic of anions imply some movement of electron density away from bonding regions of the molecule. This is shown by the experimental frequencies of $[BH_4]^-$, Table 1, which are significantly lower than those expected for BH bonds on tetrahedral boron in neutral molecules.

Table 1 summarises the calculated results for $[BH_4]^-$. After allowing for an anharmonic correction of $\approx 3\%$, the calculated values for the BH stretch frequencies would be in near perfect agreement with experiment. This implies either that the 4-31G* basis set provides a better representation of anionic systems than of neutrals or that the expected $\approx 5\%$ error is balanced by an additional and opposite error created by the accommodation of the anionic charge. It is not simply an anomaly due to the small size of the molecule since a calculation on CH_4 gave frequencies completely in keeping with our results on other hydrocarbons.[13] Comparing the molecular orbitals of CH_4 and $[BH_4]^-$ we find in the anion a small but distinct increase in population of the polarisation functions of the basis set and, more significantly, a shift towards occupation of the hydrogen atomic orbitals. The second moments of the charge distribution $\langle \Sigma_i e_i r_i^2 \rangle = -32.0\ ea_0^2$ for $[BH_4]^-$ and $-18.6\ ea_0^2$ for CH_4, also consistent with the greater size of the anionic charge cloud, though some of the difference between the two values is attributable to the fact that the bonds are longer in $[BH_4]^-$.

Such effects should reduce in importance with increasing molecular size as the physical excess charge density falls and the anionic charge is more easily accommodated by the basis set. The results for the BH stretching modes of a larger anion, $[B_3H_8]^-$, given in Table 1 seem to bear this out. The frequencies have returned to the expected $\approx 8\%$ overestimate of the observed values and are comparable therefore to the results for neutral systems. We deduce therefore that anionic charge does not invalidate the use of the frequency–hybridisation correlation for large molecules. In this context the *closo*-anions, with four or more heavy atoms, should be large enough.

In Table 1 we have used calculated frequencies for a geometry of $[B_3H_8]^-$ that is not optimal in the 4-31G basis, a method of proceeding that perhaps requires some justification. In common with earlier calculations,[15] we find the C_{2v} geometry of $[B_3H_8]^-$

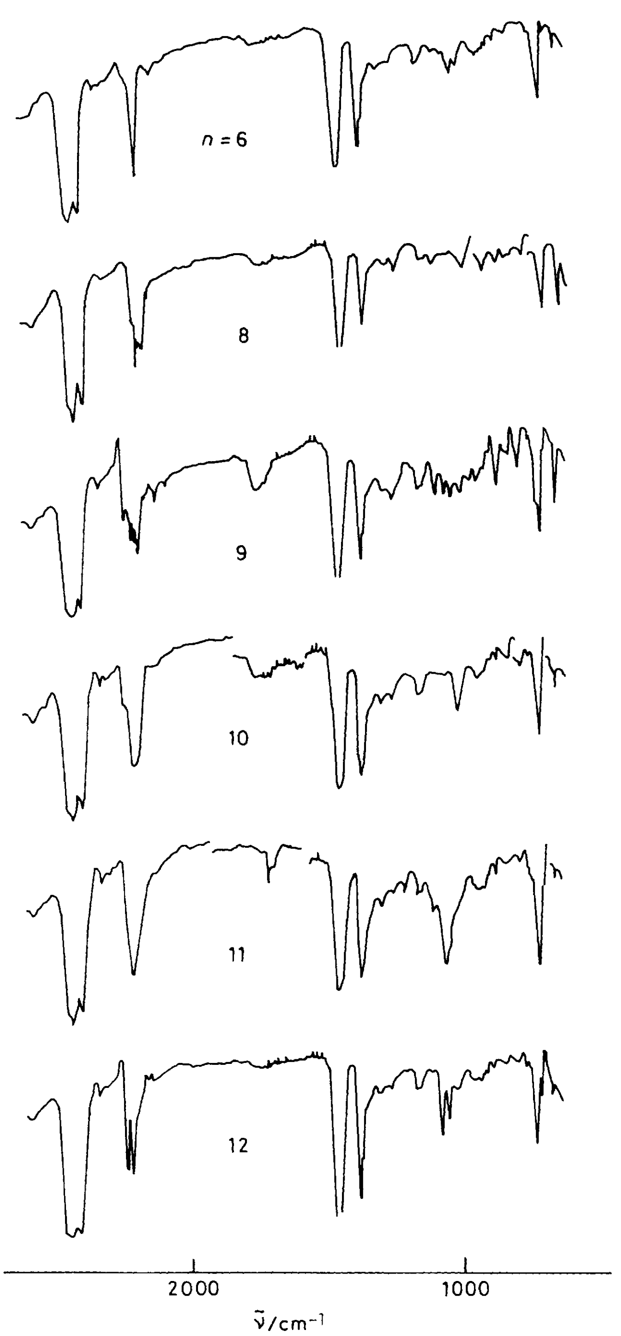

Figure 2. The i.r. spectra at liquid-nitrogen temperature of the $Cs_2[B_nH_n]$ compounds as Nujol mulls

to be a saddle point with one imaginary vibrational frequency (337i in the 4-31G basis). The calculated structure of $[B_3H_8]^-$ is known to be unusually sensitive to the basis set and level of theory employed. There is evidence from ^{11}B n.m.r. studies[16,17] that the molecule undergoes facile rearrangements which permute all the hydrogens and render all the boron atoms equivalent at temperatures above 137 K. The barrier between isomeric structures is therefore low and the potential energy surface locally flat. Experimental *X*-ray diffraction data are compatible with an idealised C_{2v} double-bridged structure[18] and it is likely that the lowest minimum structure has this symmetry. Calculations in small basis sets using PRDDO and *ab intio* SCF methods can give either C_{2v} or C_s global minima,[15] but it is expected that in a sufficiently large basis SCF calculations would predict a C_{2v} structure. Other small boranes with BHB bridges *e.g.* $[B_2H_7]^-$ have shown this problem[19] and addition of polarisation functions to a split-valence basis has been shown to be the cure. Since it is likely that the C_s/C_{2v} energy ordering is incorrect at the 4-31G level we did not pursue the optimisation down to the (probably spurious) C_s minimum. From group theoretical considerations the symmetry-breaking mode of the C_{2v} structure mixes with just one of the BH terminal stretches and one BHB bridging mode. The remaining frequencies would not be greatly altered in the final (C_s) optimum geometry and the above deductions can be considered to be based on the unperturbed modes.

The range of hybridisation predicted in the previous section would be reflected in a range of observed BH absorption frequencies from 2 450 cm^{-1} (sp^2) to some value distinctly larger than 2 800 cm^{-1}, as the larger anions are predicted to have an *s* contribution greater than *sp* where the frequency–hybridisation correlation is varying most rapidly. In fact, as we will describe, there is almost no variation of observed absorption energy with cluster size. Whilst the predictions based on Figure 1 are not expected to be accurate, it is after all a very simple model of the bonding of the anions, it is perhaps surprising that they are so far from correct.

Results and Discussion

(*i*) *Vibrational Spectra.*—Figure 2 shows the i.r. spectra of various caesium *closo*-borates dispersed in Nujol. The spectra were measured at liquid-nitrogen temperature. The spectra of $[B_6H_6]^{2-}$ and $[B_{12}H_{12}]^{2-}$ have both been the subjects of detailed study previously[20,21] as they have very high molecular symmetry which greatly simplifies the analysis. The spectra of the others have been reported only in summaries of experimental procedures. Cooling to low temperature had only a marginal effect on the appearance of the spectra suggesting that the rigid nature of the anionic cages and the high symmetry of the (monatomic) cations produce few low-energy, structure-broadening, modes to be frozen out. Figure 2 shows clearly that the BH stretch absorptions all have very much the same energies for the full range of clusters. We will comment on these spectra, and on Raman spectra of the anions, concentrating on the BH stretch bands but initially consider the spectrum of $[B_9H_9]^{2-}$ in some detail as this is the first time it has been reported in full.

$Cs_2[B_9H_9]$. Figure 3(*a*) shows the i.r. spectrum of this molecule in a KBr pressed disc at liquid-nitrogen temperature and Figure 4(*a*) the Raman spectrum of the pure substance at room temperature. The i.r. spectrum is the most sensitive to temperature of those studied, and shows four well resolved peaks.

The 48 vibrations of the anion in D_{3h} symmetry occur as 32 modes, $6a_1'$, $3a_2'$, $9e'$, $2a_1''$, $5a_2''$, $7e''$ of which the a_2'' and e' modes are i.r. active and the a_1', e', and e'' modes are Raman active. The BH stretches account for the $2a_1'$, $2e'$, $1a_2''$, and $1e''$ modes. The group of absorptions at 2 400—2 500 cm^{-1} in both the i.r. and Raman spectra is clearly due only to these stretches as no overtones or combinations of other modes are possible given the lack of absorption between 1 100 and 2 400 cm^{-1} in both spectra. We therefore expect three stretch absorptions in the i.r. and the presence of four well resolved peaks indicates that one or both e' modes are split by the site symmetry of the molecule. Similarly five Raman absorptions are expected and six peaks are observed. The bands at 2 525 (i.r.) and 2 529 cm^{-1} (Raman) can be taken with reasonable confidence to be due to the same mode, of e' symmetry, as they are well separated from any other bands in both spectra and if they corresponded to different modes the number of peaks would outstrip the number of expected bands by an even larger number. The other e' band

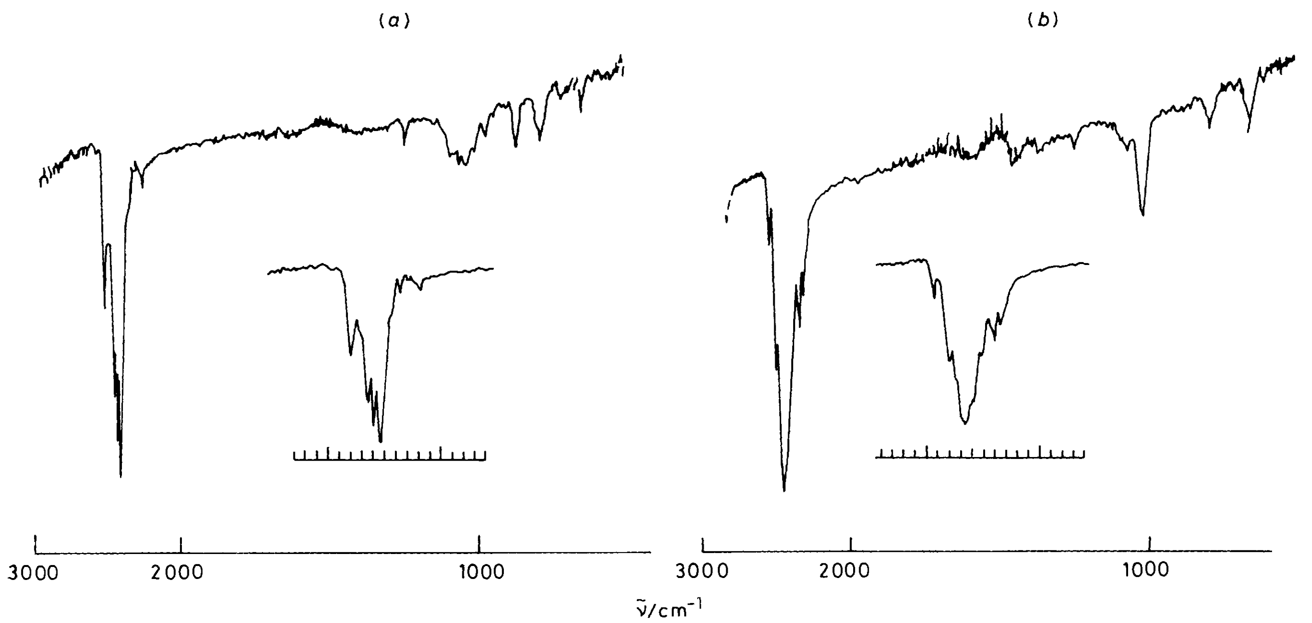

Figure 3. The i.r. spectra at liquid-nitrogen temperature of (*a*) $Cs_2[B_9H_9]$ and (*b*) $Cs_2[B_{10}H_{10}]$ as pressed KBr disks. The inserts show the BH stretch region 2 200—2 600 cm^{-1} in detail

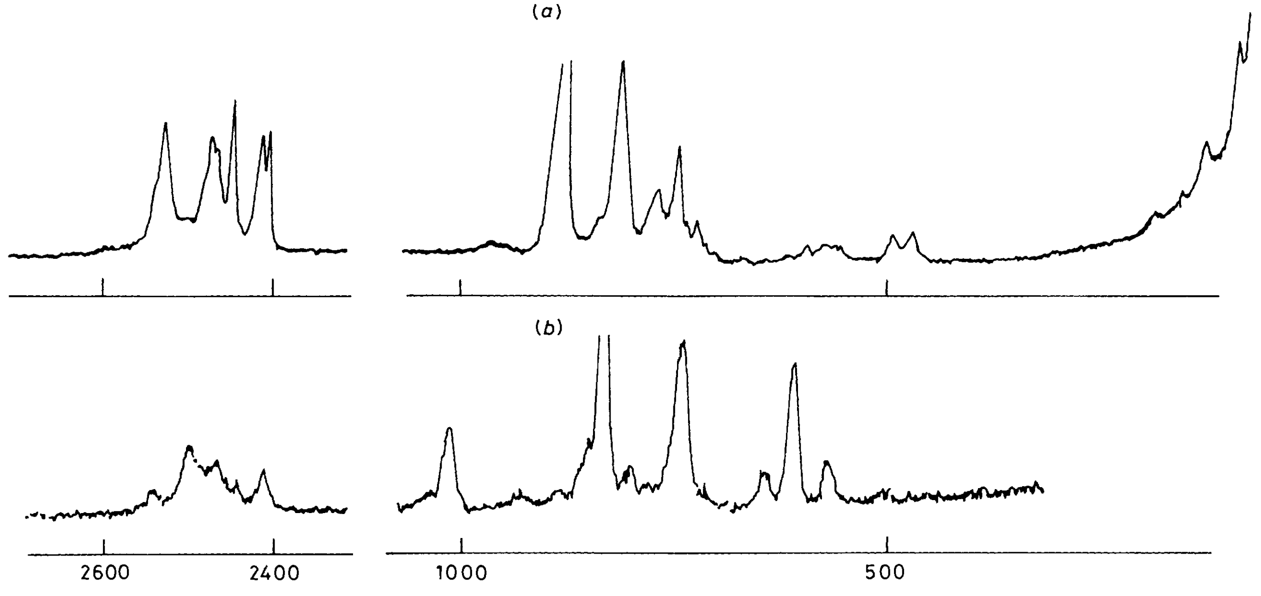

Figure 4. The room-temperature Raman spectra of (*a*) $Cs_2[B_9H_9]$ and (*b*) $Cs_2[B_{10}H_{10}]$ as powders

in the i.r. is then probably the split pair at (2 445 and 2 456 cm^{-1}) which occurs unsplit in the Raman at 2 450 cm^{-1}. This leaves the i.r. band at 2 415 cm^{-1} as the a_2'' fundamental. We propose that the pair at 2 417 and 2 408 cm^{-1}, Raman be assigned to the site-split e'' band and the two bands at 2 467 and 2 475 cm^{-1} to the a_1' absorptions. This is only one of a number of possible assignments but is the one that produces fewest inconsistencies between the two spectra.

Table 2 compares these assignments with the results of a 4-31G* calculation of the vibrational frequencies of the anion and the average error between the two is ≈4%. This, however, does not aid in the assignment of the rest of the spectra. A sharp i.r. band at 885 cm^{-1} could be associated with the most intense Raman band at 884 cm^{-1}. However the calculation does not predict an e' mode within 60 cm^{-1} of this value, well outside a 4% error. A broad i.r. feature between 1 000 and 1 150 cm^{-1}

Table 2. 4-31G* calculated vibrational frequencies of $[B_9H_9]^{2-}$ and experimental assignments of BH stretching modes

Calc.	Exptl*	Sym.	Calc.	Sym.	Calc.	Sym.	Calc.	Sym.
2 612	2 475	a_1'	1 081	a_2''	937	a_1'	711	e''
2 574	2 529	e'	1 073	e'	922	e''	681	a_2''
2 553	2 415	a_2''	1 009	e''	834	a_1'	621	e'
2 548	2 450	e'	1 000	a_2'	825	e'	568	a_1'
2 548	2 467	a_1'	973	e'	824	a_1'	557	a_2''
2 537	2 412	e''	969	a_1''	796	e''	476	e'
1 159		e'	956	e''	772	e'	362	e''
1 088		a_2'	944	a_2''	768	a_2'	139	a_2''

* See text.

could correspond to some four i.r.-active calculated modes of approximately this energy, but three of these should also be Raman active along with one other, yet there are no equivalent Raman bands. If nothing else these difficulties illustrate the improbability of ever achieving a complete analysis of the spectra of these anions.

$Cs_2[B_{10}H_{10}]$ Figure 3(*b*) and 4(*b*) show the i.r. and Raman spectra of this compound under the same experimental conditions as those applying to $[B_9H_9]^{2-}$ above. In D_{4d} symmetry three i.r.-active (one degenerate) and four Raman-active (two degenerate) BH stretch modes are predicted, however, both spectra show many more bands in the 2 450 cm^{-1} region. It is probable that there are multiple site effects operative in this case to produce such a number of bands, particularly in the i.r. spectrum. There is little chance of attempting even a limited analysis of the BH stretches despite the reasonable resolution of the spectra.

$Cs_2[B_{12}H_{12}]$. The i.r. band for BH stretching is split showing peaks at 2 470 and 2 500 cm^{-1} whilst the Raman bands have four maxima at 2 469, 2 479, 2 513, and 2 529 cm^{-1}. The Raman peaks are presumably due to site-group splitting of the degenerate H_g mode of the icosahedral anion by the caesium cations. This also affects the i.r. spectrum which shows a single peak with some cations and the observed double peak with caesium. The spectra have been fully analysed using force field models.[22,23] The high symmetry of the free ion makes it possible to derive analytical results for vibrational frequencies from simple model potentials with few parameters. A new group-theoretical analysis of this case which will correct some details of the results in ref. 23 is in preparation.[24]

$Cs_2[B_6H_6]$. The spectra of this anion are the most studied of the entire set of molecules and our spectra are in complete agreement with those published. The single i.r. band at 2 420 cm^{-1} and Raman bands at 2 466 and 2 470 cm^{-1} correspond to BH stretches t_{1u}, a_{1g}, and e_g respectively and have been reported previously.[20]

$Cs_2[B_8H_8]$ *and* $Cs_2[B_{11}H_{11}]$. The i.r. spectra of both these anions shows single, broad features corresponding to BH stretches. Given the low symmetry of each anion and the probability that site effects will split any degeneracy in $[B_8H_8]^{2-}$, large numbers of modes are potentially active in both spectra, and are simply not resolved. The broad features have maxima at 2 440 cm^{-1} in both spectra. The Raman spectra of both anions were broad and unresolved in the BH region but did show some resolved absorptions in the 800—1 200 cm^{-1} region.

The BH bands covered by this set of data correspond to boron atoms in a wide variety of environments. The boron–boron connectivities vary between four and six and the angle subtended at the centre of the cluster between 90 and 63.4°. The formal charge localised on each BH group also varies from 0.33 e^- in $[B_6H_6]^{2-}$ to 0.16 e^- in $[B_{12}H_{12}]^{2-}$ along the series of anions, yet all BH stretch absorptions fall in a narrow range of energy, 2 440—2 540 cm^{-1}. The BH bonds appear to be unaffected by the details of cluster bonding. Our established correlation between vibrational frequency and hybridisation shows that a frequency of 2 490 cm^{-1} corresponds to a sp^2-hybridised boron atom and that the ± 50 cm^{-1} range implies only small deviation from this nominal hybridisation. The insensitivity of the boron hybridisation to the wide variety of sites clearly indicates that cluster bonding causes only a small perturbation to the ability of a boron atom to take part in a terminal BH bond.

(*ii*) *Photoelectron Spectroscopy*.—Perhaps most surprising is the insensitivity of the stretch frequencies to the formal localised charge. Smaller variations of charge in metal carbonyl systems produce very large changes in the stretch frequency of terminally bonded CO ligands which involves one of the strongest bonds in chemistry, yet there is no evidence of an equivalent effect here. A further investigation of this effect was made through the ESCA spectra of the molecules. The B 1*s* ionisation energy has one of the largest chemical shifts, *i.e.* range of values due to chemical environment, in the Periodic Table, namely 193 $\pm$ 5 eV. The spectrum[25] of B_5H_9 illustrates the sensitivity of this ionisation to localised charge. The apical atom of this molecule is calculated to be more negatively charged than the four basal atoms[26] and this is reflected in the ESCA spectrum in two peaks at 196 and 194 eV with a 4:1 intensity ratio. Figure 4 shows the ESCA spectra of the set of *closo*-borane anions. These spectra were internally calibrated by the Cs $4p_{\frac{3}{2}}$ band at 161.3 eV which is very insensitive to environment. All B 1*s* ionisation peaks were single bands with maxima at ≈ 190 eV, varying by no more than ± 0.5 eV and with widths of ≈ 1.5 eV. There was no evidence of any structure distinguishing chemically different sites. The narrowest and most symmetric bands were those for $[B_6H_6]^{2-}$ and $[B_{12}H_{12}]^{2-}$ where all the boron atoms are identical, but those for the other anions were hardly any broader. There is no evidence for a difference in localised charge per boron atom in these spectra and the B_5H_9 spectrum indicates that one should be observed if it exists. This is not because the samples are solid rather than gaseous; we also measured the spectrum of $Cs[B_3H_8]$ which showed a B 1*s* band more than twice as broad as those of Figure 4, presumably hiding unresolved peaks belonging to the two different B sites in the anion.

These spectra can be compared with the calculated orbital energies for the B 1*s* localised 'molecular orbitals' assuming the validity of Koopmans theorem,[27] which is likely to be appropriate here. The equivalent of 'relaxation,' which is the main difficulty with Koopmans theorem when applied to valence levels, is 'shake-up' in the case of inner shells. If shake-up occurs it has clearly observable spectral consequences; these are not found in the present spectra, and so the ionisations of Figure 4 can be compared directly with the calculated orbital energies. These, of course, obey the degeneracies of the molecular symmetry but separate into groups reflecting the chemically distinct sites in the anions. The ion $[B_{12}H_{12}]^{2-}$, for example, is calculated to have all twelve orbitals at a binding energy of 197.2 eV and spread over a range of 0.03 eV, as all the atoms are equivalent; similarly the results for $[B_6H_6]^{2-}$ give an energy of 194.4 eV and range 0.05 eV. The ion $[B_8H_8]^{2-}$ has two distinct groups, four at 195.2 and four at 196.3 eV, $[B_9H_9]^{2-}$ three at 195.4 and six at 196.4 eV, and $[B_{10}H_{10}]^{2-}$ two at 195.8 and eight at 196.7 eV, *i.e* all with ranges of 1.1 eV or less which would not be resolvable given the natural linewidths of the bands. Potentially the most interesting anion here is $[B_7H_7]^{2-}$ as we calculate five B 1*s* binding energies of 194.7 and two of 196.1 eV, a 1.4 eV separation that may be observable. These values do suggest a trend to higher binding energy with increasing cluster size and with increasing boron co-ordination number that is not observed experimentally, but then calculations on the isolated anions do not include the effects of the neighbouring cations which would produce an electrostatic correction to the absolute values. For larger ions the lattice parameters will increase, other things being equal, and therefore the Madelung stabilisation will fall, which may tend to smooth out the variation of core eigenvalues with cage size. We conclude from the theoretical and experimental evidence that the localised charge per boron atom of the *closo*-boranes varies very little with cluster site or size, which concurs with the vibrational spectroscopic result. The variation in formal charge per BH of 0.33—0.16 e^- between the smallest and largest clusters is indeed purely formal.

(*iii*) Ab initio *Calculations*.—To investigate the constant character of the BH bonds across the set of *closo*-boranes in

Table 3. Calculated vibrational frequencies and force constants of the BH stretching modes of the *closo*-borane anions, $[B_nH_n]^{2-}$. The predicted range is found by applying a scaling factor of 0.91 to the raw *ab initio* harmonic frequencies of spectroscopically active modes (*a* indicates i.r. modes only). The force constants *f*(B–H) are found directly from the unscaled *ab initio* second-derivative matrix

n	Basis	*Ab initio* frequencies/cm^{-1}	Scaled range/cm^{-1}	*f*(B–H)/ 10^2N m^{-1}
6	4-31G	2 572.1, a_{1g}; 2 504.1, t_{1u}; 2 490.1, e_g	2 341—	
	4-31G*	2 544.8, a_{1g}; 2 581.8, t_{1u}; 2 469.2, e_g	2 266	3.08
7	4-31G	2 575.8, a_1'; 2 520.9, a_2''; 2 510.8, e_2'	2 294—	3.23 (ap)
		2 503.6, a_1'; 2 487.0, e_2''	2 285^a	3.21 (eq)
8	4-31G	2 589.6, a_1; 2 541.8, b_2; 2 531.8, e	2 313—	
		2 515.6, a_1; 2 511.9, e; 2 510.6, b_2	2 284^a	
9	4-31G*	2 612.9, a_1'; 2 574.3, e'0 2 552.8, a_1'	2 393—	3.30 (ap)
		2 548.1, e'; 2 548.0, a_2''; 2 537.4, e''	2 326	3.36 (eq)
10	4-41G	2 657.1, 2 620.0, b_2; 2 603.1, e_1	2 418—	3.50 (aq)
		2 600.9, a_1; 2 582.9, e_3; 2 579.8, e_2	2 349	3.44 (eq)
		2 584.9, b_2		
12	4-31G	2 686.5, a_g; 2 642.2, t_{1u}; 2 618.2, h_g	2 447—	3.45
		2 610.5, t_{2u}	2 382	

more detail we have performed extensive *ab initio* calculations on the anions using basis sets as similar as practicable to those used in ref. 13. The details of these calculations will be reported elsewhere.[28] They involve full geometry optimisation, starting with the restriction to the idealised symmetry usually attributed to the anions but then checking the nature of the stationary point obtained by calculations of the Hessian matrix, and, if necessary, descending to a lower symmetry. The results agreed well with experimental geometries where available. They were extended to calculate various molecular properties at the optimised geometries, including the vibrational frequencies. Owing to the size of the systems we have had to compromise on a less accurate basis set. 4-31G* and 4-31G sets were tried for $[B_6H_6]^{2-}$ and $[B_9H_9]^{2-}$ and deletion of polarisation functions can be seen from Table 3 to increase the frequencies of the BH stretches by ≈ 20 cm^{-1} (*i.e.* $\approx 1\%$) and has varying small effects on the lower energy modes. The 4-31G set was therefore used for the remainder of the calculations. For all but $[B_9H_9]^{2-}$ this basis reproduces the experimentally observed symmetry of the cluster.

One point of interest is that the idealised D_{3h} geometry of $[B_9H_9]^{2-}$ is calculated to be a transition state with the 4-31G basis but to be a stable minimum with 4-31G* (frequencies in Table 2), a measure of the extremely flexible nature of this anion that has been noted before.[26] We assume that the results from 4-31G and 4-31G* are very similar and that therefore when scaling for comparison with experiment a -9% correction to the calculated 4-31G frequencies is appropriate. The raw and scaled results are given in Table 3 for the BH stretching frequencies. The calculated spread of observable frequencies is narrow, as is the experimental range for the 30 different stretch modes, but is in poorer absolute agreement than would be expected from our work on the aminoboranes. The error is not large but corresponds on our correlation to a hybridisation in the range sp^2—sp^4. This is borne out by the Mulliken population analysis. For the aminoboranes the BH bonding overlap density was shared 1:0.88, 1:1.86, and 1:2.62 between B 2*s* and B 2*p* for the geometries corresponding to classical *sp*, *sp*,^{2} and sp^3 hybridisation, whereas for the BH bonds of $[B_6H_6]^{2-}$ (the case in worst disagreement with the correlation) the ratio is 1:4.46. We gave values for the force constants calculated for the various classical hybridisations[12] of BH bonds that were *sp*, sp^2, and sp^3: 4.70 × 10^2, 4.02 × 10^2, and 3.62 × 10^2 N m^{-1}. Table 3 lists the force constants calculated for the various BH bond types in the *closo*-anions, from the second-derivative matrix of the *ab initio* calculations, and again suggests that sp^3—sp^4 hybridisation is applicable to these bonds. Apart from this underestimation of the contribution of the B 2*s* to BH bonding, we consider these calculated results to be in good agreement with experiment and to support our deduction that cluster bonding should be considered as a perturbation to the BH bonding rather than *vice versa*. Table 3 shows some trend of frequency/force constant/hybridisation with cluster size towards increased B 2*s* involvement in the bonding, but not to the extent predicted by the simplified version of Stone's theory given above.

Another less sensitive measure of the electronic structure of a BH bond is its length. Our earlier calculations[13] found a variation of BH bond length with hybridisation; for $sp \longrightarrow sp^2$, $\Delta R = 0.027$ Å; $sp^2 \longrightarrow sp^3$, $\Delta R = 0.016$ Å. Similar changes are found for hydrocarbons.[29] The optimised bond lengths for the anions, by contrast, show little variation across the series. We find *r*(BH) in $[B_nH_n]^{2-}$ to be 1.2095 ($n = 6$), 1.2067 and 1.2091 ($n = 7$), 1.2098 and 1.2064 ($n = 8$), 1.2012 and 1.2002 ($n = 9$), 1.1982 and 1.1961 ($n = 10$), and 1.1942 Å ($n = 12$). This again reflects the relative constancy of the BH hybridisation, though as with the theoretical vibrational frequencies, some trend to increasing B 2*s* content of the BH bond is seen for the larger cages.

Calculations on Anions.—When applying conventional computational methods to geometric and electronic structures of boranes, some thought should be given to the differences between neutral molecules and anions. An isolated doubly charged species is generally unstable with respect to electron loss, although in their solid salts the $[B_nH_n]^{2-}$ ions are stabilised by crystal-field and overlap effects. In a certain sense the results of all *ab initio* calculations on isolated unbound ions are spurious, because in the limit of an infinite basis and an unrestricted Hartree–Fock treatment the dianion configuration would not be the lowest-energy solution of the SCF equations. It is only through the interplay of symmetry, spin, and basis set restrictions that the metastable free-anion electron configuration is produced. Of course, the fact that this is the same as the configuraton of the in-crystal ion means that for practical purposes such calculations often give results which may usefully be compared with experiment. Radom and others[30,31] have noted that geometric parameters of anions can often be calculated quite accurately in modest basis sets, and the present work shows that semi-quantitative results for vibrational frequencies can be obtained. However, it is salutary to remember that one is relying on a deficiency of the 4-31G basis, namely its lack of highly diffuse functions, to simulate the physical effects of in-crystal compression on the ion. To use a limited *ab initio* treatment of free anions to discuss properties of crystal-bound species is in effect to set up a 'model chemistry;' in a better basis the agreement with experiment might well deteriorate unless the crystalline environment were also taken into account in the calculation. One symptom of instability in an anion is the appearance of positive eigenvalue(s) for the highest occupied molecular orbital(s).[32,33] This occurs in some of the 4-31G calculations on *closo*-boranes and will be discussed more fully later.[28] It is possible that the higher *p* content of the *exo* B–H bonding hybrids found in the calculations (sp^{3-4} *vs.* sp^2) is to some extent a consequence of the free ion instability, in that charge density is pushed to the surface of the cluster by electron repulsion which would be partly counterbalanced by the compressive crystalline environment.

In this context it is interesting that monoanions of some $[B_nH_n]^{2-}$ species are known. For example $[B_8H_8]^-$, produced during the synthesis of $[B_8H_8]^{2-}$, gives a red colour to the reaction mixture and can survive as a dopant in the dianion

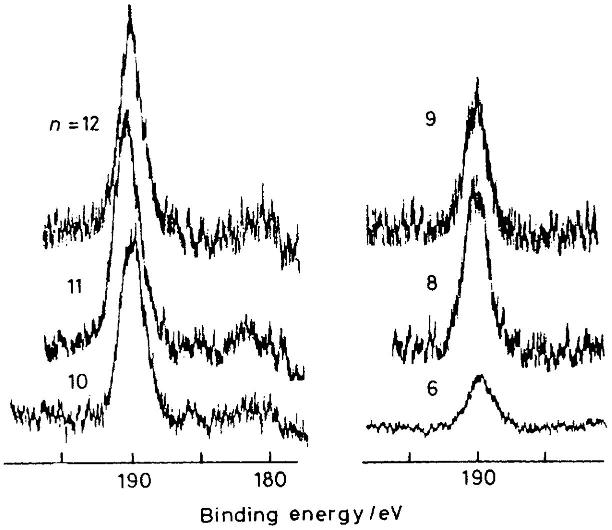

Figure 5. The ESCA spectra of $Cs_2[B_nH_n]$ in the region of the B 1*s* ionisation

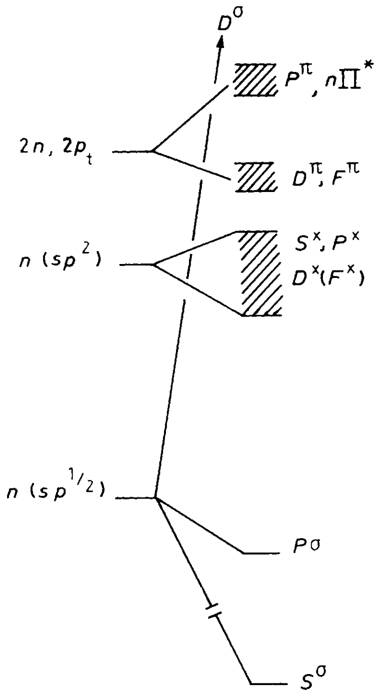

Figure 6. A general orbital diagram for the electronic structure of the *closo*-borane anions allowing for the sp^2 hybridisation of the BH bonds

salt.[34] There is evidence for the production of $[B_{10}H_{10}]^-$ in solutions of $K_2[B_{10}H_{10}]$ under oxidising conditions.[35] Although the radical monoanions would be expected to be more thermodynamically stable in isolation, and possibly in non-polar solvents, the order of stability is reversed in the solid by the gain in Madelung energy for a lattice of more highly charged ions.

Conclusions

The main result from our survey of the experimental and theoretical evidence is that the BH bonds of all *closo*-boranes have very much the same hybridisation and that it is close to sp^2, contrary to the discussion in the Introduction of the B 2*s* content of $S^σ$ and $P^σ$ m.o.s. Perhaps this is not too surprising. The main perturbation experienced by a boron atom in a borane is due to the hydrogen atom bonded to it and features such as cluster bonding cause lower-order corrections to the electronic structure of the BH units. This suggests a better starting point for the construction of an general orbital diagram for *closo*-boranes. VSIE energies, B 2*p* −8.5 eV and B 2*s* −15.2 eV, are taken as guidelines for the atomic orbital energies and maintaining the σ/π separations gives $2n$ $2p_π$ atomic orbitals at −8.5 eV, $n\,sp^2$ hybrids at −11.1 eV, and $n\,sp^{1/2}$ hybrids at −13.1 eV as shown in Figure 6. The $sp^{1/2}$ hybrids directed towards the centre of the cluster interact strongly producing the spread of orbitals from $S^σ$ at ≈18.5 eV below the highest occupied molecular orbital (h.o.m.o.), from our calculations, $P^σ$ orbitals at roughly the energy of the $sp^{1/2}$ hybrids, and the $D^σ$ destabilised into the virtual set as shown. This in many ways resembles Stone's original energy-level diagram for the σ molecular orbitals of the *closo*-borane clusters[1] but now includes the BH bonding orbitals and puts both of these on an energy scale along with the π orbitals. This diagram can also be considered as conforming with ETSH approach of Fowler and Porterfield.[12] If they had taken *endo* $sp^{1/2}$ hybrids rather than *sp* then the cluster orbitals construction from the hybrids would all have been more stable. It is probable that the ETSH $S^σ$ and $P^σ$ m.o.s would then have energies more comparable to those predicted by MNDO and *ab initio* methods for all cluster sizes.

This picture of the electronic structure starts from the pure σ and π combinations of a.o.s. If the radial and tangential local functions are allowed to mix before forming the m.o.s something approaching the 'isolobal' picture of cluster bonding is obtained. If we assume that every B atom donates an sp^2 hybrid to the terminal BH bond, the remaining radial combination is an $sp^{\frac{1}{2}}$ *endo* σ function. From this and the two tangential $p_π$ functions ($p_θ$, $p_φ$) a set of three equivalent hybrids of $sp^{\frac{7}{2}}(\equiv s^{\frac{2}{3}}p^{\frac{7}{3}})$ may be constructed [equation (2)—(4)] which makes angles of $\cos^{-1}(\frac{2}{7}) \approx 73°$ with

$$|h_1\rangle = \frac{\sqrt{2}}{3}|s\rangle - \frac{1}{3}|p_σ\rangle + \sqrt{\frac{2}{3}}|p_θ\rangle \qquad (2)$$

$$|h_2\rangle = \frac{\sqrt{2}}{3}|s\rangle - \frac{1}{3}|p_σ\rangle - \frac{1}{\sqrt{6}}|p_θ\rangle + \frac{1}{\sqrt{2}}|p_φ\rangle \qquad (3)$$

$$|h_3\rangle = \frac{\sqrt{2}}{3}|s\rangle - \frac{1}{3}|p_σ\rangle - \frac{1}{\sqrt{6}}|p_θ\rangle - \frac{1}{\sqrt{2}}|p_φ\rangle \qquad (4)$$

each other, and have major lobes lying on a cone of half-angle $\tan^{-1}(\sqrt{6}) \approx 68°$. This is consistent with the isolobal picture of boranes in which each BH group donates three lobes and two electrons to the cluster bonding. The empirical structural data on *closo*-borane anions are sparse and of rather poor quality, with a few exceptions. The cone half-angles we have been able to abstract from the data are 45 (n = 6), 50 and 52 (n = 8), 51 and 55 (n = 9), 50 and 58 (n = 10), and 58° (n = 12), where pairs of angles refer to four- and five-co-ordinate boron atoms respectively. Their departure from the idealised 68° could be interpreted in terms of different curvatures for the bent ('banana') BB bonds. The half-angles also provide a measure of the extent to which the cluster electron density projects out from the planes of the BBB triangles, and hence may indicate its availability, or more speculatively, may correlate with the reactivity of the anions.

Acknowledgements

We thank Dr. I. T. McGovern of Trinity College, Dublin for the use of his ESCA spectrometer and Professor S. K. F. Kettle, University of East Anglia, for measuring the Raman Spectra. Dr. A. Ceulemans is thanked for useful comments on an early draft of this paper. We also acknowledge the support of the Eolas (Ireland) for grant number NBST 120.86 under the terms of which this work was performed, the S.E.R.C.(U.K.) for a grant of computer time, and University College, Cork for a senior studentship (to B. S.).

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Received 8th December 1988; *Paper* 8/04853C