Bonding in Clusters. Part 3.† Protonation of *nido*-Pentaborane(9), *nido*-Hexaborane(10), and *closo*-Hexaborate(6)(2−)

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The bonding and structures of B_5H_9, B_6H_{10}, and $B_6H_6^{2-}$ and the protonated species $B_5H_{10}^+$, $B_6H_{11}^+$, $B_6H_7^-$, and B_6H_8 are analysed with MNDO, Gaussian-80, and self-consistent charge calculations. The known isomer of B_6H_{10} is shown to be more stable than other isomers for which metalloborane analogues are known. The bonding in $B_5H_{10}^+$ can be regarded as a $B_5H_8^+ \cdots H_2$ complex but $B_6H_{11}^+$ prefers a structure with six B–H terminal and five B–H–B bridged bonds. Protonation of $B_6H_6^{2-}$ gives a face-capped $B_6H_7^-$ structure. Diprotonation of $B_6H_6^{2-}$ produces a molecule in which the B_6 octahedral skeleton is entirely disrupted and the molecule is predicted to be highly unstable. Attention is drawn to some of the observed differences in the chemistries of related borane, metalloborane, and metallo-clusters.

In a recent series of publications we have discussed the bonding, structures, and stabilities of metalloborane clusters related to the *nido*-boranes B_5H_9,[1,2] B_6H_{10},[3,4] and the *closo*-borane $B_6H_6^{2-}$.[5] In the process of this work we encountered a number of compounds for which there are no borane equivalents, *e.g.* $[B_5H_{10}Mn(CO)_3]$ and $[B_5H_{10}Fe(\eta^5\text{-}C_5H_5)]$, which are related to unknown isomers of B_6H_{10}; similarly, $[B_3H_5\{Co(\eta^5\text{-}C_5H_5)\}_3]$ and $[Ru_6H_2(CO)_{18}]$ are related to B_6H_8, an unknown *closo* compound. To generate geometries for some of these molecules we determined the precursor borane geometry through the MNDO (modified neglect of differential overlap) calculations of Dewar and Thiel[6] and introduced the subrogating metallo-group in a manner consistent with known borane/metalloborane derivatives.[4] This work has led to a general study of the properties of these boranes, in particular protonation reactions and a comparison of isomer stabilities.

The choice of the MNDO calculation as the method for this study is a logical one. MNDO has recently been extended to cover boron-containing molecules[7] and has been shown to produce geometries and heats of formation in good agreement with experiment. Numerous *ab-initio* calculations on boranes have been reported by Lipscomb and co-workers,[8] including B_5H_9, B_6H_{10}, $B_6H_6^{2-}$, and CB_5H_7[9] of the compounds discussed below. Such calculations have suffered from a neglect of electron correlation which accounts for energies similar in magnitude to the chemical energies producing the effects we discuss here and which is effectively built in to the MNDO calculation through its parameterisation. Many other researchers have used computational methods to investigate boranes at various times. Almost all published work has been concerned with known compounds. In the present study we are primarily investigating boranes whose chemistry is largely unknown or for which only metal-cluster equivalents are known. Thus although our work is clearly an adjunct to that of Dewar, Lipscomb, and others, it is simultaneously quite distinct from theirs and is concerned with previously untreated problems.

The experimental chemist usually approaches the bonding of boranes and related compounds from the simple and powerful methods developed by Wade.[10] These methods allow one to account for the correspondence between cluster bonding units and relates the geometries of clusters, be they boranes, carboranes, metalloboranes, or all-metal clusters. A theoretical basis for these rules has been provided by Hoffmann and co-workers[11] and Mingos[12] through their 'isolobal–isoelectronic' description of cluster bonding units. It is often assumed that the *exo*, *endo*, and bridging ligands $(X)_n$ in a cluster group MX_n are important in determining cluster bonding, and hence stereochemistry, only to the extent by which they influence the number of orbitals and electrons available for cluster bonding. Thus groups such as $-BH_2$ or $-BCO$ both provide three skeletal bonding electrons according to Wade,[10] irrespective of the bonding in each group. Furthermore, in the skeletal electron-counting rules the electron pairs that would be allocated to *endo* M–X or bridging M–X–M bonds are included in the skeletal electron count. However, it has been pointed out in an attempt to systematize borane and carborane structures from empirical observations[13] that bridging and *endo* hydrogens appear to be of primary structural importance. Our calculations show that the positions of *endo* and bridging groups can exert considerable influence on cluster structure.

Below we discuss the protonation of B_5H_9, B_6H_{10}, $B_6H_6^{2-}$ and also the various possible isomers of the B_6H_{10} molecule. Of these, Evans[14] has investigated the protonation of $B_6H_6^{2-}$ using extended-Hückel calculations. In this work, he assumed geometries based on the octahedral $B_6H_6^{2-}$ unit and that protonation would not fundamentally affect the basic structure. This is certainly not the case, but he would not have been able to determine this with the method he employed.

CALCULATIONAL METHOD

The MNDO program[15] accepts an approximate geometry and finds an optimised minimum-energy geometry from it provided certain precautions are taken to avoid initial pseudo-minima geometries, not a problem with the molecules we consider. A facility exists for maintaining certain

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† Part 2 is ref. 4.

aspects of the symmetry of the molecule during the calculation. If totally unrestricted variation is allowed, the calculation generally converges on slightly asymmetric geometries. For example, a calculation on B_5H_9 maintaining C_{4v} symmetry gave apical–basal bond lengths of 171.8 pm and basal–basal bond lengths of 186.4 pm, and a $\Delta H_f^\ominus$ of 33.78 kcal mol^{-1}, whereas a calculation without restrictions gave 170.8—171.1 pm, 186.1—186.2 pm, and 31.34 kcal mol^{-1} respectively.* In such cases the differences are clearly insignificant. We have used the symmetry-restricting facility only when restraining molecules to non-minimum energy geometries. MNDO-calculated heats of formation for both known and unknown molecules are listed in Table 1 along with experimental data where available. Calculated bond lengths in B_6H_{10} and its isomers are given in Table 2. The results of other calculations, including SCC (self-consistent charge) Hückel type calculations,[4] are given where relevant in the text, and total overlap populations for B_5H_9, B_6H_{10}, and derived ions are listed in Table 3.

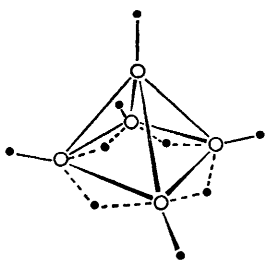
TABLE 1

		$\Delta H_f^\ominus$/kcal mol^{-1}		
Structure	Molecule or ion	MNDO	Expt.	Ref.
(1)	B_5H_9	31.3	17.5	[a]
	$B_5H_9^{+\bullet}$	271.9	249.5	[b]
(2)	$B_5H_{10}^+$	242.3	217 ± 6	20
(3)	B_6H_{10}	18.8	22.7	[a]
(4)	B_6H_{10} isomer	45.0	—	—
(5)	B_6H_{10} isomer	75.5	—	—
(6)	$B_6H_{11}^+$ (all bridged)	210.0	194 ± 8	20
(6a)	$B_6H_{11}^+$ (H_2 at apex B)	247.9	—	—

[a] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, 'Selected Values of Chemical Thermodynamic Properties,' Nat. Bur. Stand., Technical Note 270/3, Washington, D.C., 1968. [b] Calculated using experimental $\Delta H_f^\ominus$ and ionisation potential on B_5H_9.

The MNDO procedure is based on a zero-overlap approximation for the construction of the secular determinant, and its determination of atom charges and comparison of bond strengths is through a Coulson population analysis. Overlap integrals are calculated in order to determine the two-centre resonance integrals, but to use these together with the bond-order matrix to produce a Mulliken overlap-population analysis would be against the basic philosophy of the procedure, and would probably produce misleading information. We have used overlap populations for discussion in all previous papers, and in order to do so here, for convenience and consistency, we have run other calculations not based on a zero-overlap approximation to obtain these data. The other calculations used are either the SCC of Hoffmann and co-workers,[16] with the final geometry of the MNDO program, or in a few cases the Gaussian-80 program (G-80) of Pople and co-workers,[17] which is a full *ab-initio* calculation with complete geometry optimisation. Such a mixing of results from different sources is obviously open to question, particularly in the use of the SCC calculations with the MNDO geometries. However, in all cases the orders of molecular orbitals are the same, the atomic orbital compositions similar, and the molecular orbital energies reasonably comparable. We take the view that after summation over the occupied set of molecular orbitals, any discrepancies between calculational methods are largely averaged out. In the few cases where we have performed both SCC and G-80 calculations on the same molecule this view is borne out.

The criterion for convergence of the SCC calculations has been discussed elsewhere,[2] and the atomic orbital exponents and initial Hamiltonian integral values were those advised by Hoffmann and co-workers.[16] The G-80 program was used with its internal STO-3G basis set [17b] and with Berny optimisation of geometry (a fully analytical method). The atomic orbital exponents used in the MNDO program and the Hamiltonian integral values were those published by Dewar and McKee.[7] Due to the colossal expense of running Gaussian-80 compared with either of the other two programs it has only been used in cases where there was serious doubt about the MNDO optimised geometries. The output geometries (in Z-matrix form) of all MNDO and Gaussian-80 calculations are available, for all species listed in Tables 1—5 which have not been previously calculated, as Supplementary Publication No. SUP 23186 (16 pp.).†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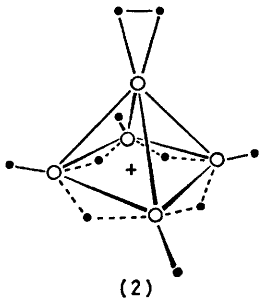

(2)

RESULTS

B_5H_9 ($B_5H_8^+$, $B_5H_9^{+\bullet}$, and $B_5H_{10}^+$).—Our MNDO calculation on B_5H_9 (1) appears to agree in all details with that of Dewar and McKee.[7] The apical–basal bond lengths are 171 pm, and basal–basal 186 pm (experiment: 169 and 180 pm respectively).[18] The calculated charges show a build-up of charge on the apical boron atom (−0.32), partly balanced by its terminal proton (+0.08), the rest of the charge being evenly distributed over the basal B_4H_8 group. The overlap population at the apical BH site is slightly smaller (1.67) than the basal site (2.03), but both approximate the formal two-electron picture suggested by Wade.[10]

The proton affinity of B_5H_9 has been determined [19] giving a $\Delta H_f^\ominus$ of $B_5H_{10}^+$, one of the more stable gaseous borane cations, Table 1. A structure was proposed for this ion which had the two terminal hydrogen atoms on the apical boron atom involved in a triangular three-centre bond. MNDO calculations agree with this structure, but with the significant feature that the two apical hydrogens are very close to being a hydrogen molecule, structure (2). Calculations with this ($H \cdots H$) molecule oriented over B–B bonds or B atoms of the B_4H_8 base showed no preferential orientation, the values being 242.3 and 242.5 kcal mol^{-1} respectively. The separation of the two hydrogen atoms is 89 pm, both being 133 pm from the apical boron. These values compare with 74 pm in H_2, and commonly found B–H terminal and B–H–B bridging bond lengths of 119 and 135 pm respectively. The apical–basal boron distances are virtually unchanged from B_5H_9 at 169—171 pm, but the basal–basal distances open-up significantly, 187—193

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* Throughout this paper: 1 cal = 4.184 J; 1 eV = 1.602 × 10^{-19} J.

† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

pm. The $B_5H_{10}^+$ molecule may therefore be considered as a charge-transfer complex between a $B_5H_8^+$ ion with C_{4v} symmetry and a H_2 molecule, in which the transfer of charge has proceeded to equal sharing between the two moieties. The H_2 molecule carries a charge of $+0.60$, balanced by a charge of -0.50 on the apical boron. The base of the molecule now carries a $+1.10$ charge (*cf.* $+0.66$ in B_5H_9), which accounts for the lengthening of the basal–basal bonds. Both apical and basal sites have approximately two electrons bonding into the rest of the cluster (Table 3).

TABLE 2

Calculated bond lengths in B_6H_{10}, its isomers, and $B_6H_{11}^+$

	B–B bond (pm)					
Structure	1–2	1–3	1–4	2–3	3–4	4–4′
(3)	180	172	190	187	179	159
(4)	188	175	180	193	186	177
(5)	189	189	189	175	175	175
(6)	180	180	180	181	181	181
(3) (experimental)	174	175	180	180	174	160

A calculation on $B_5H_8^+$ restrained to C_{4v} symmetry exemplifies the changes found with protonation of B_5H_9. The positive charge is now completely localised on the basal B_4H_8 group, the apical boron being virtually neutral. The basal–basal bonds at 197—203 pm are further opened compared with B_5H_9, and the apical–basal bonds shortened at 162—167 pm. Addition of H_2 to this ion clearly has little effect on the basal geometry but reduces the dependence of the apical atom on the base for bonding charge, and charge is simply polarised inside the apical BH_2 unit. It should be noted, however, that the imposed C_{4v} symmetry is not correct according to Wade's rule since $B_5H_8^+$ is the unknown triprotonated *closo*-$B_5H_5^{2-}$ derivative. A trigonal-bipyramidal D_{3h} symmetry is assumed for $B_5H_5^{2-}$.[10]

TABLE 3

Total overlap populations at BH_n unit sites by SCC calculations

(*a*) B_5H_9 derivatives

	Molecule or ion			
	(1)	(2)		
B Site	B_5H_9	$B_5H_{10}^+$	$B_5H_9^{+\bullet}$	$B_5H_8^+$
Apical	1.67	1.94	1.58	2.34
Basal	2.03	1.67, 1.74	1.83	1.70

(*b*) B_6H_{10} derivatives

		Molecule or ion			
		(3)	(4)	(5)	(6)
B Site		B_6H_{10}	B_6H_{10}	B_6H_{10}	$B_6H_{11}^+$
Apical		1.73	1.79	1.63 *	1.95
Basal	B^2	1.71	1.23 *	1.63	1.77
	B^3	1.58	1.70	1.63	1.77
	B^4	1.54	1.72	1.63	1.77

* Hybridisations found were (4) ($s^{0.29}$ $p_x^{0.30}$ $p_y^{0.30}$ $p_z^{0.20}$) with B^2 on y axis, and (5) ($s^{0.35}$ $p_x^{0.22}$ $p_y^{0.49}$ $p_z^{0.49}$) with B(apical) on x axis.

A calculation on $B_5H_9^{+\bullet}$ shows the apical BH unit carries a charge of $+0.10$ while basal BH units carry $+0.15$—0.17; again the base carries the majority of the charge. This ion retains the basic square-pyramidal shape but undergoes a distortion to C_{2v} symmetry, two basal–basal bonds being 174 pm and two 203 pm, with all apical–basal bond lengths 178 pm. The $\Delta H_f^\ominus$ calculated is 272 kcal mol^{-1}, which gives a value for the adiabatic ionisation potential of B_5H_9 of 10.37 eV, in good agreement with the p.e.s. (photoelectron spectroscopy) value of 10.05 eV.[20] In fact the $\Delta H_r^\ominus$ of the protonation of B_5H_9 can be seen from the Figure to be largely accounted for by the introduction of a positive charge on the borane, either by ionisation or removal of a hydride ion.

Both $B_5H_8^+$ and $B_5H_9^{+\bullet}$ attempt to retain the formal two electrons per BH unit even though the addition of the positive charge causes a redistribution of the cluster bonding electron density (Table 3).

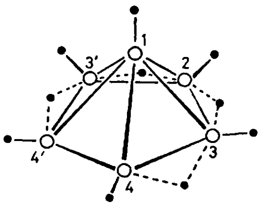
The ability of the B_4H_8 bases of the above molecules to stabilise a positive charge led us to consider the possibility of attack by a proton directly at the base of B_5H_9. This event, unlikely in B_5H_9 as the base is still slightly positively charged, obtains some credence from the existence of $[Fe_5C(CO)_{15}]$, a metal cluster related to B_5H_9, which has incorporated a carbon atom into the basal group. Starting with the proton at the centre of the basal plane, the MNDO calculation produced a very unfavourable geometry ($\Delta H_f^\ominus = 345$ kcal mol^{-1}) with the proton below the plane completing a tetragonally distorted B_5H^+ octahedron with the five boron atoms. The bond distances are apical–basal boron 171 pm, basal–basal boron 192 pm, and basal boron–proton 203 pm.

B_6H_{10} ($B_6H_{11}^+$).—B_6H_{10} is unique among small neutral boranes in having an unbridged basal boron–boron bond, structure (3). This bond provides electron density which can be donated in a Lewis-base manner, and we have previously discussed this in detail.[4] Further, this bond provides the possibility of two other isomers of the molecule, obtained by removing a terminal hydrogen and using it to bridge this bond. The hydrogen atom may come from the apical or basal BH unit. Referring to the three isomers, (3) (the known geometry), (4) (five bridging hydrogens, no terminal hydrogen in position 2), and (5) (five bridging hydrogens, no terminal hydrogen in position 1), the results of MNDO calculations are as follows.

Bond lengths between boron atoms are shown in Table 2 together with experimental values for (3).[21] Obviously, the bond length that changes most between (3) and the other isomers is B^4–$B^{4'}$, as in (3) it is very short (160 pm) due to its unique two-electron–two-centre nature. Otherwise the bonds are little affected in the different geometries. In (5) the basal–basal boron bonds are rather shorter (175 pm) than the average bridge-bonded distance, and the apical–basal rather longer (189 pm), but the differences are not great. The distribution of charge is more significant, and makes an interesting comparison with B_5H_9. Overall the basal groups carry much less charge, being 0.21, 0.38, and 0.08 for (3), (4), and (5) respectively. Charges on BH units in positions 1, 2, 3, and 4 in the three isomers are (3) -0.21, -0.09, $+0.11$, -0.06; (4) -0.38, $+0.26$, -0.02, $+0.04$; and (5) -0.08, 0.00, 0.00, 0.00; the small differences in each molecule being distributed over the bridging hydrogens.

The bare boron atoms of isomers (4) and (5) behave quite differently. In (5) this atom is neutral and compares with the equivalent apical atom in $B_5H_8^+$, whereas in (4) it carries a significant positive charge, balanced largely by a negative charge on the apical BH unit. The charge distribution of (3) is similar to B_5H_9, with its negatively charged apical unit. The base shows some charge separation caused presumably by the excess electron density of the B^4–$B^{4'}$ bond polarising the base. The charge distribution correlates with the variations in apical–basal bond lengths.

The overall population analysis (Table 3) shows in almost all cases approximately two electrons per B site. Position 2 in isomer (4) is an exception, with only 1.2 electrons involved in cluster bonding.



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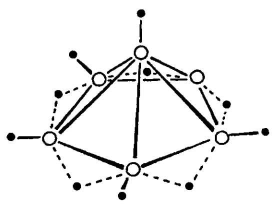

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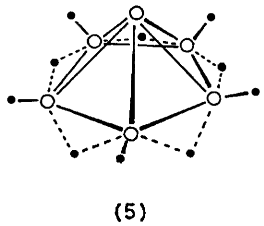

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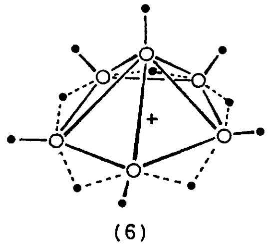

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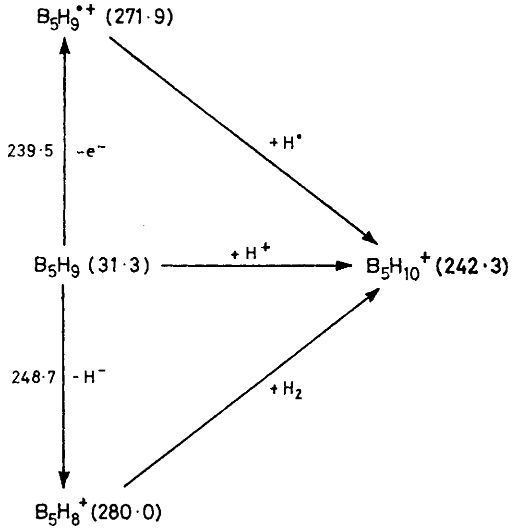
The stabilities shown in Table 1 have no direct explanation from the geometries or charge distributions and must be related to the unsuitability for cluster bonding of the bare boron atoms. The lack of a terminal hydrogen atom removes the directional polarisation of the cluster unit orbitals and the resultant cluster bonding is inefficient. Isomer (5) is the least stable, as the boron atom is required to form five bonds of similar strength under unfavourable conditions, whereas in (4) it has to form two strong bonds (to the bridging hydrogens) and the three weaker ones to adjacent borons. If the boron atom of (4) is replaced by a unit with the correct orbital polarisation, *e.g.* BeX (X = Cl, F, or BH_4),[22] $Mn(CO)_3$,[23] or $Fe(\eta^5\text{-}C_5H_5)$,[24] then this instability is overcome. The same is true of isomer (5) if the B atom is replaced by $Fe(\eta^5\text{-}C_5H_5)$.[24]

Protonation of B_6H_{10}, isomer (3), might be expected to occur at position 1 by comparison with B_5H_9. In fact, the ion $B_6H_{11}^+$ is fairly stable and is known to have five bridged basal bonds (6).[25] The effect of protonation on the bond lengths of the molecule is small, see Table 2. The apical BH unit carries a −0.15 charge, and basal BH units +0.15, mainly on the protons. In many respects this charge distribution is similar to that of B_5H_9 and $B_5H_{10}^+$, with a small apical negative charge and the base carrying the positive charge.

A calculation on an isomer (6a, not shown) of $B_6H_{11}^+$ with two terminal protons on the apical boron produces a structure very similar to $B_5H_{10}^+$, with a H_2 molecule (H–H bond length 80 pm) bonded to $B_6H_9^+$. The $\Delta H_f^{\ominus}$ of this isomer is 248 kcal mol^{-1}, *i.e.* 35 kcal mol^{-1} less stable than the known geometry. Thus it would appear that this molecular complex structure for protonated boranes is the most reasonable one when there is a simple ' apical ' boron atom site in the neutral molecule. It is not found in $B_6H_{11}^+$ due to the presence of the B^4–$B^{4'}$ bond of B_6H_{10} which can be bridged, but may be expected to be applicable to other compounds, particularly *closo*-boranes, in which any of the vertices are in similar bonding situations to the apex of B_5H_9, for example those of $B_6H_6^{2-}$.

$B_6H_6^{2-}$ ($B_6H_7^-$, CB_5H_7, *and* B_6H_8).—The MNDO calculation on $B_6H_6^{2-}$ gave a perfect octahedron (7) with boron–boron bond lengths of 173 pm, and boron–hydrogen bond lengths of 116 pm (experimental: 169 and 119 pm respectively).[26] The BH units carry −0.32 charges, nearly all on the boron atoms. MNDO calculations on $B_6H_7^-$ were started from a geometry with one set of two terminal hydrogens, and a geometry with one edge-bridging hydrogen. Both converged on an identical geometry in which one bond of (7) has broken and caused a severe distortion of the basic octahedron. The extra proton is terminal on atom 2 and pointing over the open B^1,B^2,B^3,B^4 face, but not close enough to constitute a face-capping geometry. This geometry, although believable in terms of the known instability of $B_6H_6^{2-}$ in acid solution, is surprising as intuitively one would expect a geometry similar to that known for the isoelectronic molecule CB_5H_7, *i.e.* an octahedron with a face-capping hydrogen atom.[27] As a check, we performed an MNDO calculation on CB_5H_7 with the result shown [structure (8)] clearly bearing no resemblance to the experimental geometry, and hence removing all confidence in the result for $B_6H_7^-$. We therefore performed *ab-initio* calculations with full geometry optimisation (G-80 calculations) on these molecules. The results for CB_5H_7



Thermochemical cycles relating B_5H_9, $B_5H_8^+$, $B_5H_9^{+\bullet}$, and $B_5H_{10}^+$ (values in kcal mol^{-1})

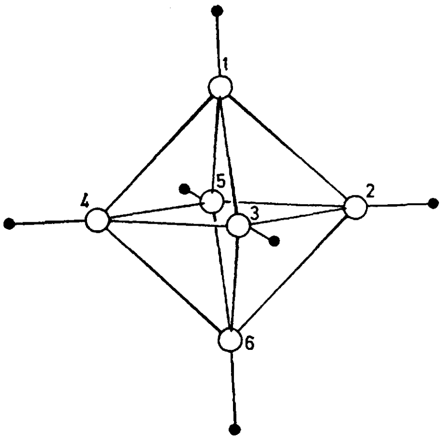
TABLE 4

Calculated (MNDO, G-80) and experimental bond lengths (numbering of atoms as given in diagrams)

		MNDO	G-80	Exp.	Ref.
$B_6H_6^{2-}$	B–B	173	168	169 (1)	26
	B–H	116	116	111 (7)	
$B_6H_7^-$	B^1–H^7		141		
	B^1–B^2		185		
	B^1–B^4		168		
	B^4–B^6		170		
CB_5H_7	B^1–H^7		157		
	B^2–H^7		137		
	B^1–B^2		191	189	27
	B^1–B^3		188	187	
	B^1–B^4		166	170	
	B^3–B^4		167	170	
	B^4–B^5		171	172	
	B^3–C^6		159	160	
	B^4–C^6		163	163	

are compared with experiment in Table 4 and are obviously in excellent agreement. Both CB_5H_7 and $B_6H_7^-$ are found by the G-80 method to be face-capped octahedra (9), exactly as intuitively expected, with atom 6 as C or B.

To complete the protonation process to B_6H_8 we proceeded with both MNDO and G-80 calculations and found that they gave slightly different but reasonably related geometries. In the G-80 result, structure (10), the basic octahedron is still discernible but one boron–boron bond has broken (B^1–B^2) and three are very long for unbridged bonds (B^1–B^3, B^1–B^5, B^2–B^3 all >190 pm), in fact the B^1 atom is only significantly bonded to the B^4 atom, and the



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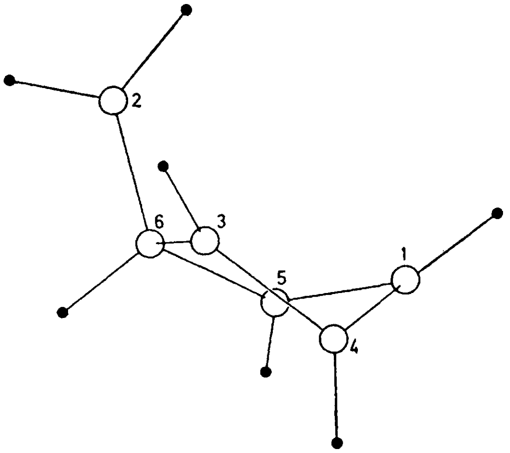

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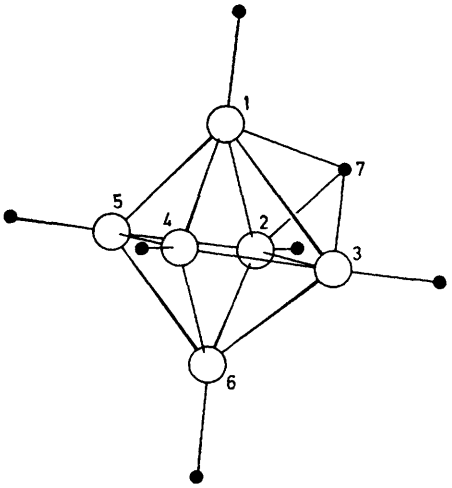

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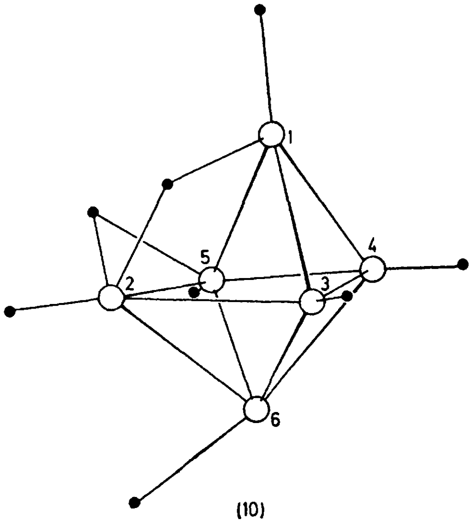

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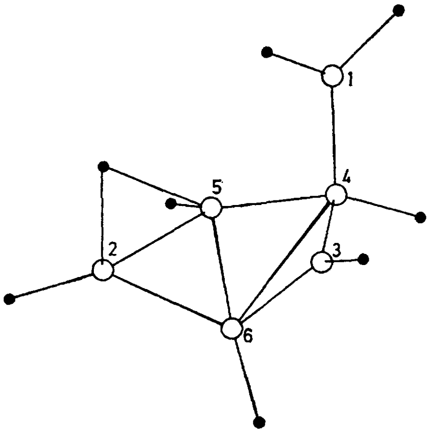

(11)

octahedron is only being maintained by the unusual bridging geometry of H^7. The MNDO geometry (11) relates to (10) as H^7 is now terminal on B^1 and three long bonds have been broken. Given the completely different natures of these two geometry-optimising calculational methods, the correspondence between (10) and (11) is very good and makes the lack of correspondence in the CB_5H_7 and $B_6H_7^-$ geometries even more remarkable.

Comparison of the energies of the structures determined from the calculations is problematic. MNDO is parameterised to calculate $\Delta H_f^{\ominus}$ and G-80 calculates total energies. To connect the latter to a $\Delta H_f^{\ominus}$ is possible but fairly meaningless due to the minimality of the basis set used. So to achieve some comparison we have calculated the energies of all optimised geometries from the two calculations using both methods. These results are shown in Table 5. The Mulliken overlap population analysis of G-80 allows the determination of overlap populations (o.p.s) bonding BH and CH groups into these molecules. We have used this test of bonding in all previous publications in this series. Table 6 summarises the results for $B_6H_6^{2-}$, $B_6H_7^-$, and CB_5H_7. The figure for $B_6H_6^{2-}$ which incidently agrees exactly with the figure obtained from SCC calculations was taken as a standard for a BH unit in these compounds. Table 6 shows that bonding of BH units adjacent to the capping hydrogen of $B_6H_7^-$ is slightly reduced from this figure whilst the other BH units are unaffected. The same applies in CB_5H_7 with an extra general reduction of *ca.* 0.1 for all BH units, the CH unit being almost identical to the standard. The o.p. values for CB_5H_7 are in excellent agreement with those of Lipscomb and co-workers [9] obtained from a different (PRDDO) and approximate *ab-initio* procedure.

TABLE 5

Comparison of energies of optimised geometries from MNDO and G-80 calculations

Geometry Molecule/ calc.	Energy MNDO kcal mol^{-1}	Energy G-80 a.u.*
$B_6H_6^{2-}$/MNDO	33.01	−149.368 43
$B_6H_6^{2-}$/G-80	40.68	−149.384 70
CB_5H_7/MNDO	27.69	−163.245 84
CB_5H_7/G-80	65.25	−163.280 79
$B_6H_7^-$/MNDO	−21.71	−150.165 52
$B_6H_7^-$/G-80	−8.53	−150.205 02
B_6H_8/MNDO	39.3	−150.716 84
B_6H_8/G-80	72.51	−150.740 43

* 1 a.u. = 27.21 eV.

Various important bond lengths for some of these molecules are compared for the two calculations and experiment (where available) in Table 4.

TABLE 6

Overlap populations of bonding BH, CH, and H-capping units in the molecules $B_6H_6^{2-}$, $B_6H_7^-$, and CB_5H_7

Molecule	Unit	Overlap population
$B_6H_6^{2-}$	BH	1.786
$B_6H_7^-$	B^1H	1.620
	B^4H	1.794
	H^7	0.579
CB_5H_7	B^1H	1.519
	B^2H	1.538
	B^4H	1.657
	B^5H	1.621
	C^6H	1.761
	H^7	0.612

DISCUSSION

It is clearly seen that MNDO calculated geometries and $\Delta H_f^{\ominus}$ values on the whole are in good agreement with experiment, Table 1. Further, when the isomers of B_6H_{10} (3)—(5) are considered, a clear trend of stabilities is observed which can be correlated with experimental facts and understood in terms of the bonding requirements of the atoms involved. A structure related to that for $B_5H_{10}^+$, namely borane $\cdots$ H_2, has been calculated by Lipscomb and co-workers [28] for the intermediate BH_5 in a study of the protonation of BH_4^-. Both BH_3 and H_2 sub-units were identified as products from the decomposition of this possible intermediate.

In his comprehensive and stimulating review, Wade [10] considered only known boranes and carboranes with BH− or CH− terminal units. A similar approach was taken by Williams [13] when developing his co-ordination-number pattern recognition theory. Neither considered structures with B units and neither approach can be used to discuss the stability trends in isomers (3)—(5) or metallo-derivatives containing boron equivalents such as the $Mn(CO)_3$ group.

Another problem arises with the protonation of $B_6H_6^{2-}$. The empirical method developed by Wade [10] dealt only with the number of cluster bonding m.o.s and the number of electrons occupying them. Thus, given three orbitals and two electrons per BH terminal unit for cluster bonding, $B_6H_6^{2-}$ will form a possible total of 18 cluster bonding m.o.s of which seven bonding orbitals will be occupied by the 14 electrons available. This system and others with n cluster units and $n + 1$ pairs of electrons are described as *closo*. Addition of protons to $B_6H_6^{2-}$ provides no extra electrons and it is logical to assume that the *closo* description will still hold as was done in the study by Evans.[14]

In the present work, protonation of $B_6H_6^{2-}$ was examined in detail with several geometries through MNDO calculations. A calculation of $B_6H_7^-$ was performed in a geometry with the symmetry restrained to maintain a tetragonally distorted octahedron with two terminal hydrogens on one apical boron, a geometry that may be expected by comparison with B_5H_9 and $B_5H_{10}^+$ (see above). The terminal pair of hydrogens were separated by 185 pm and the B−H distance was 118 pm. Obviously the bonding at the BH_2 site in this structure of $B_6H_7^-$ is not analogous with that in $B_5H_{10}^+$. The instability of this $B_6H_7^-$ structure may be examined by comparison with $B_5H_{10}^+$. As noted above, the B_4H_8 base of $B_5H_{10}^+$ is well able to accommodate a positive charge. The isoelectronic anion $B_5H_8^-$ however undergoes considerable distortion from the C_{4v} symmetry of the parent B_5H_9, involving the opening of the basal–basal boron bond opposite the unbridged basal bond. Thus it would appear that directing excess electronic charge onto the B_4H_8 base is the primary cause of this distortion. Directing a negative charge onto the related B_5H_5 base of this $B_6H_7^-$ geometry also results in the distortion of the molecule. The inability of the MNDO calculation to produce the most probable geometry, *i.e.* H face-capping of $B_6H_7^-$, and the experimental geometry of CB_5H_7 can be explained in terms of the semi-empirical nature of the calculation. The face-capping hydrogen atom of CB_5H_7 is unique in borane and carbaborane chemistry. MNDO is parameterised to reproduce experimental geometries and in order to predict this face-capping geometry, some face-capped molecule would have to have been used in the parameterisation procedure. CB_5H_7 was not used in the procedure, and even if it had been the existence of only one such molecule would probably have been insufficient to bias the program away from the more common bond-bridging hydrogen atom geometry found in borane chemistry. Hence the incorrectness of the MNDO optimised geometries of CB_5H_7 could have been expected even before the calculation was performed. The fact that MNDO and G-80 are in excellent agreement for $B_6H_6^{2-}$ and good agreement for B_6H_8 exemplifies this point. Although the B_6H_8 geometry is obviously unstable, there are no local unusual bonding arrangements of atoms.

The G-80 geometry for CB_5H_7 is in good agreement with that of Lipscomb and co-workers.[9] The face-capping hydrogen atom is closer to B^2 and B^3 than B^1, but quite definitely bonded to all three (o.p.s 0.31, 0.31, and 0.13). The o.p. bonding the CH unit into the cluster is only 0.10—0.15 more than that bonding the BH units, and is the same as that for BH units in $B_6H_6^{2-}$. The CH in the CB_5H_7 cluster is behaving exactly like a BH unit. Interestingly, the CH unit has three bonding electrons associated with it compared to two for BH according to Wade's rules but in the cluster the ' extra ' electron has been delocalised around the molecule exactly as in the case of the two negative charges of $B_6H_6^{2-}$.

Certainly for CB_5H_7 and $B_6H_7^-$, protonation of the strictly *closo* compounds ($B_6H_6^{2-}$, $CB_5H_6^-$) has not significantly affected the structure of the compounds, and the electron-pair/structure relationship is maintained.

Some supposedly analogous metal clusters show quite different bonding situations.[29-31] The reported *X*-ray and neutron diffraction-determined structure of $[Ru_6H(CO)_{18}]^-$ locates the H atom at the centre of the Ru_6 octahedron,[29] similarly in $[Co_6H(CO)_{15}]^-$,[30] but $[Os_6H(CO)_{18}]^-$ has a face-capping H atom.[31] The Ru–Ru bond lengths in the ordered crystals of $[Ru_6H(CO)_{18}]^-$ are 284—292 pm,[29] slightly longer than those in $[Ru_6(CO)_{18}]^{2-}$ (280—289 pm) and shorter than for $[Ru_6H_2(CO)_{18}]$ (287 or 295 pm).[32] A calculation of $B_6H_7^-$ with the extra proton at the centre of the molecule produced a very unfavourable ($\Delta H_f^{\ominus} = 199$ kcal mol^{-1}) octahedral geometry with very long boron–boron bonds (202 pm). The difference in stabilities of the species is most probably related to the greater ability of the metallo-group to accommodate the bond-length change without loss of bonding overlap compared to that of the BH cluster group.

In the study of diprotonation of $B_6H_6^{2-}$ we performed calculations with B_6H_8 restricted to retain a basic octahedral shape, either tetragonally or trigonally distorted, in order to compare to the geometries considered by Evans [14] with one found to be the most stable. Forcing pairs of hydrogen atoms on opposite borons produced a structure with $\Delta H_f^{\ominus} = 116.9$ kcal mol^{-1}; forcing bond-bridging hydrogen atoms on opposite bonds gave $\Delta H_f^{\ominus} = 114.4$ kcal mol^{-1}. These geometries are clearly too unstable to be of interest. Forcing opposite-face H-capping produced a structure with $\Delta H_f^{\ominus} = 61.3$ kcal mol^{-1}, only 22 kcal mol^{-1} more than the found geometry. The details of this geometry are interesting. Uncapped faces have boron–boron bond lengths of 167 pm, whereas for capped faces they are 200 pm. The boron-capping hydrogen distances are 150 pm. The effect of capping these faces is to weaken considerably the boron–boron cluster bonding whilst not replacing it with efficient capping bonds. Although fairly stable, the molecule finds bond-breaking and distortion of the geometry energetically favourable.

Allowing a complete geometry optimisation in the diprotonation of $B_6H_6^{2-}$ produces a disruption of the molecule whichever calculation one accepts, and the electron-pair/structure relationship no longer holds. This correlates with the known instability of $B_6H_6^{2-}$ in acid solution.[33] It is not possible to clearly predict the products of this disruption; (B_5 and B_1)- or (B_2 and B_4)-containing molecules all seem possible. However, it is possible that $B_6H_6^{2-}$ is stable in acid if the protonation proceeds only as far as $B_6H_7^-$.

Once again, the analogous metallo-clusters bond quite differently. An expansion of the capped cluster Ru–Ru bonds occurs in $[Ru_6H_2(CO)_{18}]$.[29] The two opposite Ru_3 faces which are H-capped have bond lengths of 295 pm. These faces are held together by bonds 287 pm long. The osmium analogue is unique with a capped square-pyramidal structure and the hydride ligands probably located at edge-bridging positions.[31] Thus comparison shows that metallo-units can adapt successfully to structures where BH units cannot. This finding is fully in accord with the respective chemistries of $B_6H_6^{2-}$ and $[M_6(CO)_{18}]^{2-}$ (M = Ru or Os). The borane anion is stable to base but hydrolyses in aqueous acid to H_2 and boric acid.[33] The metal hydride clusters are prepared from either $[M_6(CO)_{18}]^{2-}$ or $[M_6H(CO)_{18}]^-$ by the action of concentrated sulphuric acid.[34,35] It is therefore obvious that a number of significant differences are present in the bonding of $B_6H_6^{2-}$ and $[M_6(CO)_{18}]^{2-}$. Indeed, in the series $[M_6(CO)_{18}]^{2-}$, $[M_6H(CO)_{18}]^-$, and $[M_6H_2(CO)_{18}]$ (M = Ru or Os) it has been shown that no two analogous clusters possess the same overall geometry even though they have the same number of formally cluster-bonding electrons.[34,35]

Although B_6H_8 is unstable, several metallo-boranes have been structurally and chemically characterised, including $[B_4H_6\{Co(\eta^5\text{-}C_5H_5)\}_2]$ [36] and $[B_3H_5\{Co(\eta^5\text{-}C_5H_5)\}_3]$.[37] N.m.r. evidence and structure analysis of $[B_4H_6\{Co(\eta^5\text{-}C_5H_5)\}_2]$ by *X*-ray methods indicated that the non-BH terminal hydrogen atoms were associated with the two adjacent Co_2B faces. In the Co_3 compound both non-terminal hydrogen atoms were apparently associated with the Co_3 face. The choice of H–metal face-capping instead of H–boron face-capping is significant and once again reflects the different bonding abilities of BH (or CH) units and metallo-units. Work is in hand to analyse other cluster structures and to study the protonation reactions experimentally.

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