Effects of Extra Hydrogens on the Electronic Structures of Five- and Six-vertexed Polyhedral Boranes†

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The effects on the electronic structure of $[B_5H_5]^{2-}$ and $[B_6H_6]^{2-}$ of adding one or two extra hydrogens in terminal and bridging positions have been studied by extended-Hückel molecular-orbital calculations. Trigonal-bipyramidal and square-pyramidal $[B_5H_6]^-$ and B_5H_7 are the five-vertexed species considered; the six-vertexed ones are octahedral, trigonal-prismatic, and capped-square-pyramidal $[B_6H_7]^-$ and B_6H_8. Terminal and edge-bridging sites are preferred for $[B_5H_6]^-$ and $[B_6H_7]^-$ (octahedral) respectively. For polyhedra consisting entirely of triangulated faces there is little site preference for the bridging ligands. However, when a square face is present, there is a marked preference for a bridging ligand to be on an edge of that face. This effect is so marked that the presence of these extra atoms could alter the favoured cluster framework from that of the polyhedral anion to one having a tetragonal face. Generally, adding the extra ligands does not alter the number of bonding orbitals from that in the polyhedral dianion.

IN the previous paper[1] the electronic structures of a number of three- to nine-vertexed $[B_nH_n]^{x+}$ species were investigated by means of extended-Hückel molecular-orbital (EHMO) calculations. Since several transition-metal moieties, *e.g.* C_{3v} $M(CO)_3$ [2] and $M(\eta\text{-}C_5H_5)$,[3] are isolobal with the BH unit, symmetry-based conclusions should be transferable to species of the type $[M_n(CO)_{3n}]^{x+}$. In many examples of cluster compounds the number of ligands is not a multiple of the number of framework atoms and in this situation a distortion of the electronic structure of the frame must occur. The nature of some of these distortions is investigated in this work. One and two extra protons are added in both bridging and terminal positions to $[B_5H_5]^{2-}$ and $[B_6H_6]^{2-}$ species of different geometries. It is hoped to use these as models for isolobal metal carbonyl moieties,[2] *e.g.* $[B_6H_6]^{2-}$ and $[Os_6(CO)_{18}]^{2-}$,[4] B_6H_8 and $[Os_6H_2(CO)_{18}]$,[4] and $[B_5H_6]^-$ and $[Os_5(CO)_{16}]$.[5]

Skeletal electron-counting rules [6,7] have been applied with some success to cluster compounds. The electron counts are derived from the properties of idealised polyhedra and the presence of extra ligands is not considered to affect the preferred geometry of the cluster framework. This assumption is tested in this paper.

CALCULATIONS

These were performed using the same EHMO program as in the previous paper.[1] Burns exponents [8] were used for the hydrogen 1*s* (1.00), boron 2*s* (1.250), and boron 2*p* (1.075) Slater-type orbitals. H_{ii} values were taken from the tables of Basch *et al.*[9] (H 1*s*, −13.60; B 2*s* −15.17; and B 2*p*, −8.31 eV) ‡ and off-diagonal elements calculated by Cusachs' formula.[10] Idealised geometries were used with the nearest-neighbour B–B distances taken as 1.70 Å, terminal B–H lengths as 1.20 Å, and bridging B–H separations of 1.33 Å. Within the terminal BH_2 groups, a B–H–B angle of 120° was assumed. The five idealised B_n structures considered are shown in Figure 1. The positions of the added atoms will be indicated by reference to the numbered atoms of each structure to which they are attached. For example, a B_6H_8 structure with a face-bridging hydride on two *trans* faces of a B_6 octahedron

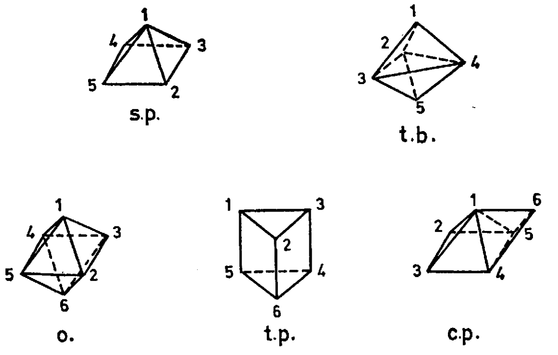

FIGURE 1 The five polyhedra studied: square pyramid (s.p.), trigonal pyramid (t.p.), octahedron (o.), trigonal prism (t.p.), and capped square pyramid (c.p.)

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† No reprints available.

‡ Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

[1] J. Evans, preceding paper.

[2] M. Elian and R. Hoffmann, *Inorg. Chem.*, 1975, **14**, 1058.

[3] M. Elian, M. M. L. Chen, D. M. P. Mingos, and R. Hoffmann, *Inorg. Chem.*, 1976, **15**, 1148.

[4] M. McPartlin, C. R. Eady, B. F. G. Johnson, and J. Lewis, *J.C.S. Chem. Comm.*, 1976, 883.

[5] C. R. Eady, B. F. G. Johnson, J. Lewis, and B. E. Reichert, *J.C.S. Chem. Comm.*, 1976, 271.

[6] K. Wade, *Chem. Comm.*, 1971, 792; *Inorg. Nuclear Chem. Letters*, 1972, **8**, 559, 563; *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.

[7] D. M. P. Mingos, *Nature, Phys. Sci.*, 1972, **236**, 99.

[8] G. Burns, *J. Chem. Phys.*, 1964, **46**, 152.

[9] H. Basch, A. Viste, and H. B. Gray, *Theor. Chim. Acta*, 1965, **3**, 458.

[10] L. C. Cusachs and B. B. Cusachs, *J. Phys. Chem.*, 1967, **71**, 1060.

would be denoted by B_6H_8 (o.1,2,3; 4,5,6) and one with edge bridges on two *trans* edges as B_6H_8 (o.2,3; 4,5).

RESULTS AND DISCUSSION

$[B_5H_6]^-$ *Structures involving a* BH_2 *Group*.—The highest-occupied molecular orbitals (h.o.m.o.s) of trigonal-bipyramidal $[B_5H_5]^{2-}$ were calculated to be the $e''(1)$ set at −9.52 eV; the twelfth and thirteenth eigenvalues [$e'(3)$] formed the lowest-unoccupied molecular orbitals (l.u.m.o.s) at −3.95 eV.[1] Four positions of a BH_2 group in $[B_5H_6]^-$ were investigated: in two of these the BH_2 group was in an apical position of the trigonal bipyramid with its plane either parallel with or perpendicular to a side of the equatorial triangle; in the remainder it was in an equatorial position with its plane either parallel with or perpendicular to the equatorial plane of the trigonal bipyramid. In each case the h.o.m.o. had an energy of *ca.* −9.5 eV and there was a gap to the l.u.m.o. of at least 3.05 eV. Thus the total number of bonding orbitals is maintained on adding the extra proton.

TABLE 1

Total energies (eV) for $[B_5H_6]^-$ species

Structure	Point group	Energy	h.o.m.o.	l.u.m.o.
t.b. 1 (BH_2 edge ‖)	C_s	−290.09	−9.51 (a')	−6.14 (a'')
t.b. 1 (BH_2 edge ⊥)	C_s	−290.09	−9.52 (a'')	−6.14 (a')
t.b. 2 (BH_2 axial)	C_{2v}	−288.99	−9.46 (a_1)	−3.95 (b_2)
t.b. 2 (BH_2 equatorial)	C_{2v}	−289.28	−9.29 (a')	−6.24 (b_2)
s.p. 1 (BH_2 ‖ diagonal)	C_{2v}	−287.40	−8.85 (b_1)	−8.31 (b_2)
s.p. 1 (BH_2 edge ‖)	C_{2v}	−287.37	−8.72 (b_1)	−8.31 (b_2)
s.p. 2 (BH_2 axial)	C_s	−288.41	−8.60 (a')	−8.31 (a'')
s.p. 2 (BH_2 equatorial)	C_s	−287.84	−8.55 (a'')	−7.77 (a')
t.b. 1,4	C_s	−289.50	−9.52 (a'')	−4.91 (a')
t.b. 2,3	C_{2v}	−289.48	−9.52 (a_2)	−5.15 (a_1)
s.p. 2,3	C_s	−288.27	−8.83 (a')	−8.31 (a'')
s.p. 1,2	C_s	−287.74	−8.77 (a')	−8.31 (a'')

Square-pyramidal $[B_5H_5]^{2-}$ was calculated to have a half-occupied $e(3)$ set of orbitals at −8.31 eV and the next level was found to be some 6.5 eV higher in energy [$b_1(2)$]. There are 12 orbitals which are bonding in nature and so this anion could readily accommodate an extra electron pair.[1] Four orientations of the BH_2 group (two apical and two as part of the square plane of the B_5 framework) were also considered for this geometry of $[B_5H_6]^-$. The $e(3)$ set was split in each case so that the h.o.m.o. of the monoanion was in the −8.5 to −8.9 eV region (Table 1). There was only a small gap to the l.u.m.o., which again demonstrates the conservation of the number of bonding orbitals.

The trigonal-bipyramidal form of $[B_5H_5]^{2-}$ was found to be 2.10 eV more stable than the square-pyramidal alternative.[1] All the trigonal-bipyramidal arrangements of the isoelectronic $[B_5H_6]^-$ were also more stable than the pyramidal ones. So it seems that, in this case at least, adding an extra terminal ligand does not alter the number of bonding orbitals nor the preferred geometry of the cluster framework.

In both these B_5 geometries a preference was displayed for a particular position of the BH_2 group (Table 1). An apical BH_2 was preferred in the trigonal bipyramid. The two orientations of the apical groups had virtually the same total energy, but when the BH_2 boron was in the trigonal plane the equatorial orientation was favoured (by 0.29 eV). Within the square-pyramidal structure a basal site was preferred for the 'sp^2' boron, particularly with the BH_2 group axially oriented. Whether these site preferences would be universal is dubious, especially considering the small energy differences involved. Indeed, in $[Os_5(CO)_{16}]$,[5] the $Os(CO)_4$ (isolobal with the BH_2 unit) is in an equatorial not an apical site.

$[B_5H_6]^-$ *Species with Bridging Hydrogens*.—Adding a bridging hydrogen to either of the two types of edge of the trigonal bipyramid (t.b.) also leaves the number of bonding orbitals unaltered (Table 1) at 11 and 12

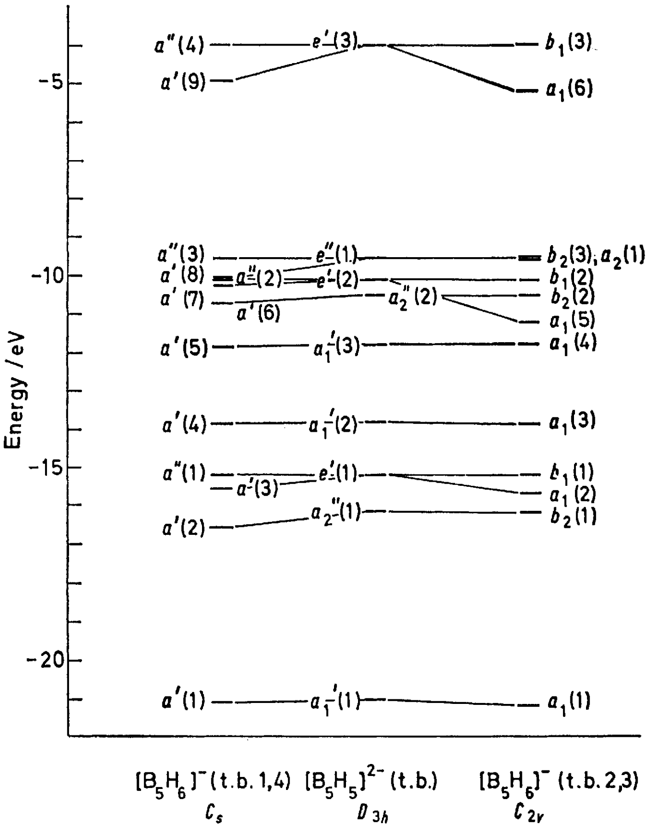
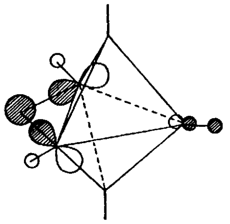


FIGURE 2 Effects of an edge-bridging hydrogen on the energy levels of $[B_5H_5]^{2-}$ (t.b.)

respectively. The former was still the preferred B_5 arrangement. Stacking diagrams are displayed for it in Figure 2. The main interaction of the hydrogen bridging an equatorial edge is with one of the $e'(2)$ set, giving the $a_1(5)$ orbital (1). While none of the individual interactions is quite so marked in the other case (t.b. 1,4), their sum effectively counterbalances that for the equatorial position. There is essentially no preference for either of these sites.


(1) $a_1(5)$

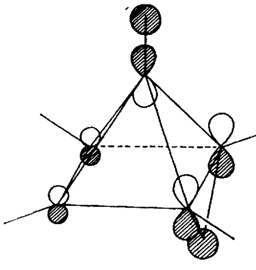

(2) $a'(5)$

Figure 3 shows the stacking diagrams for square-pyramidal (s.p.) $[B_5H_6]^-$. The largest interaction of the bridging ligand is with the $a_1(4)$ orbital of the polyhedral dianion {derived from the $\pi_\perp$ bonding orbital of square-planar $[(BH)_4]^{n+}$ (ref. 1)} giving rise to (2). This forms the basis for the preference for the edge-bridging position below the square plane (0.53 eV); bridging hydrogens on non-trigonal faces of boranes are quite general.[11] The reduced overlap population between the bridging hydrogen and the bridged boron atoms is also larger in that site. (Values of 0.49 for each boron were calculated in s.p. 2,3 as compared with *ca.* 0.40 in s.p. 1,2.)

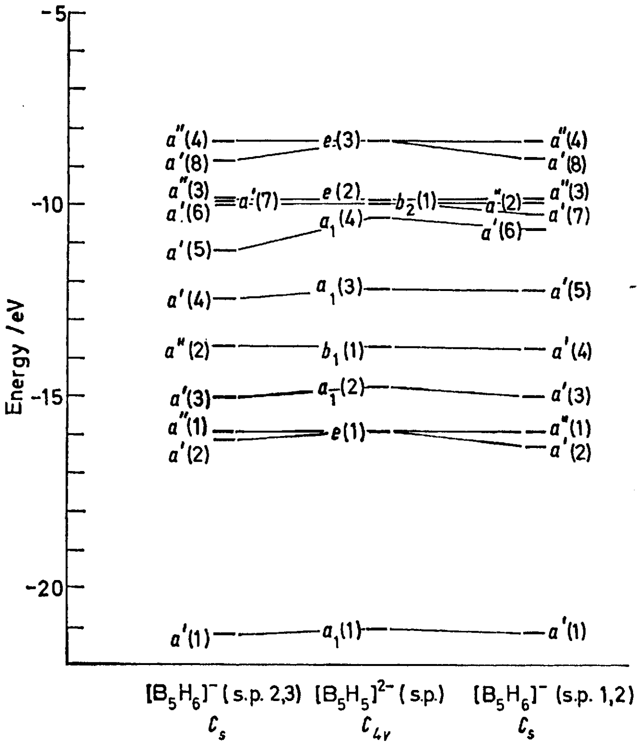


FIGURE 3 Effects of the addition of an edge-bridging hydrogen on the orbital energies of $[B_5H_5]^{2-}$ (s.p.)

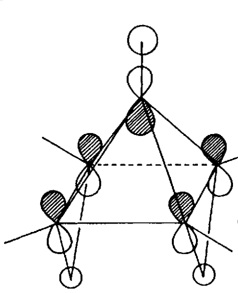
$[B_5H_7]$ *Structures containing two Hydrogen Bridges*.—The number of bonding orbitals was also conserved on adding the second proton to both B_5 geometries. Trigonal-bipyramidal structures were still favoured but the energy gap between the best structure (with bridging hydrogens) was narrowed from 2.10 eV in $[B_5H_5]^{2-}$ through 1.09 eV in $[B_5H_6]^-$ to 0.40 eV in B_5H_7 (Table 2).

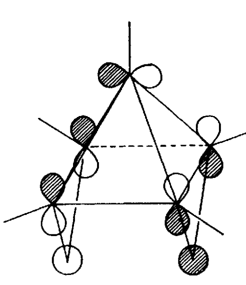
TABLE 2

Total energies (eV) for B_5H_7 species

Structure	Point group	Energy	h.o.m.o.	l.u.m.o.
s.p. 2,3; 4,5	C_{2v}	−292.81	−9.85 (b_1)	−8.31 (b_2)
s.p. 2,3; 2,5	C_s	−291.51	−9.20 (a'')	−8.68 (a')
t.b. 1,2; 3,4	C_s	−293.21	−9.52 (a'')	−5.87 (a')
t.b. 1,4; 2,4	C_1	−293.19	−9.52 (a)	−5.57 (a)
t.b. 2,3; 2,4	C_{2v}	−293.02	−9.52 (a_2)	−5.24 (b_1)
t.b. 1,3; 1,4	C_s	−293.19	−9.88 (a')	−5.13 (a'')
t.b. 1,4; 3,5	C_2	−293.16	−9.89 (b)	−5.36 (b)
t.b. 1,4; 4,5	C_{2s}	−292.80	−9.52 (a_2)	−6.05 (a_1)

This is again due to the preference for the bridging ligand to be associated with the square face. There is comparatively little site preference for the two bridging hydrogens along the edges of the trigonal bipyramid. All the combinations which did not involve placing two bridges along a single edge were considered and only 0.41 eV spanned the total energies of all six structures. Indeed the best four structures were within 0.05 eV of each other. Only positions below the square face of the tetragonal pyramid were investigated since it was apparent that these would be the most favoured. There was a marked preference for the bridging ligands to be placed on *trans* edges of the square plane (1.30 eV). The two orbitals which are mostly responsible for this stable arrangement, (3) and (4), clearly owe their parentage to the $\pi_\perp$ bonding orbital (a_{2u}) and one of the $\pi_\perp$ non-bonding orbitals (e_g) of square-planar $[(BH)_4]^{n+}$.[1] Interestingly, the gap between *trans*- and *cis*-bridged structures is narrowed to 0.56 eV in $[B_5H_7]^{2-}$; the iso-electronic $B_3C_2H_7$ [12] has *cis* bridges but the presence of the carbon atom in the tetragonal plane probably precludes formation of *trans* bridges.


(3) $a_1(4)$


(4) $b_1(2)$

$[B_6H_7]^-$ *Octahedral Species*.—Octahedral $[B_6H_6]^{2-}$ was calculated to have two closely spaced sets of triplets [t_{2g} at −9.91 eV and $t_{1u}(2)$ at −9.85 eV] forming the upper occupied, largely skeletal, orbitals; the l.u.m.o.s

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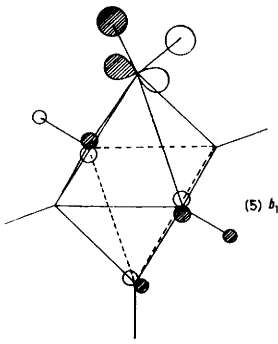
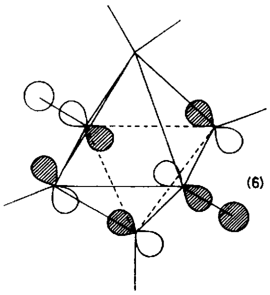
[11] R. W. Rudolph, *Accounts Chem. Res.*, 1976, **12**, 446.

[12] D. A. Franz and R. N. Grimes, *J. Amer. Chem. Soc.*, 1970, **92**, 1438.

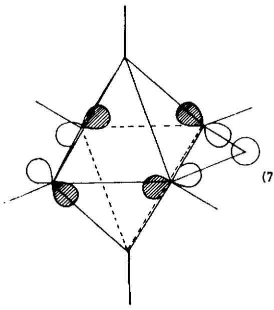
were well removed at -1.81 eV (t_{2u}).[1] Adding an extra hydrogen in terminal (with the BH_2 plane parallel with the diagonal of the central B_4 square), edge-bridging, or face-bridging positions does not alter the number of bonding eigenvalues. The strongest interactions to the extra ligand involve the upper occupied t sets. While the BH_2 group of $[B_6H_7]^-$ (o.1) can stabilise one member of the t_{2g} set to give the $b_1(2)$ orbital, (5) (Figure 4), involvement of the B $2p$ orbital destabilises one of the $t_{1u}(2)$ group to give the $b_1(3)$ level, (6). The edge-bridging ligand participates in the $a_1(5)$ orbital, (7). An orbital of mixed t_{2g} and $t_{1u}(2)$ parentage is largely responsible for the binding of the face-bridging group $[a_1(4)]$, (8). In total the edge-bridging position is 0.38 eV more stable than the face-capping one which in turn is preferred to the terminal site by 0.23 eV; these energy differences result from several contributions, as can be seen from inspection of Figure 4. Although $[B_6H_7]^-$ is not known, the isoelectronic B_5CH_7 has been prepared.[13] It has been reported to have a face-bridging hydride [14] and, since this extra ligand migrates rapidly about part of the octahedral skeleton at 383 K, the energy differences between these types of site are likely to be quite small.[15]



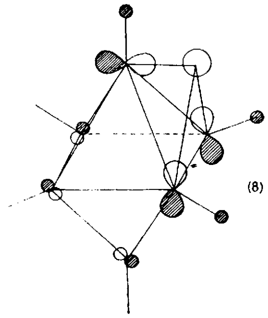
(5) $b_1(2)$



(6) $b_1(3)$



(7) $a_1(5)$



(8) $a_1(4)$

TABLE 3

Total energies (eV) for $[B_6H_7]^-$ species

Structure	Point group	Energy	h.o.m.o.	l.u.m.o.
o.1 (BH_2 diagonal)	C_{2v}	-339.56	-9.00 (a_1)	-4.91 (b_1)
o.2,3	C_{2v}	-340.17	-9.85 (b_1)	-4.07 (a_1)
o.1,2,3	C_{3v}	-339.79	-9.85 (e)	-1.81 (e,a_2)
c.p. 2,3	C_s	-339.06	-8.92 (a')	-5.06 (a'')
c.p. 4,5	C_s	-339.04	-8.89 (a')	-5.30 (a'')
c.p. 3,4	C_1	-338.83	-8.53 (a)	-5.40 (a)
c.p. 1,2	C_1	-338.41	-8.67 (a)	-5.85 (a)
c.p. 4,5,6	C_s	-337.98	-8.83 (a')	-5.06 (a'')
c.p. 1,2,3	C_s	-337.61	-8.53 (a')	-5.06 (a'')
t.p. 1,2	C_s	-338.56	-8.28 (a'')	-7.78 (a')
t.p. 1,5	C_{2v}	-339.35	-8.28 (b_2)	-7.15 (a_2,b_1)

Octahedral B_6H_8 *Species with Two Bridging Hydrogens.*—The number of bonding eigenvalues was maintained on adding the second extra ligand (Table 4). Following the trend set up in the monoanion, structures with two edge-bridging ligands are more stable than ones with one face and one edge bridge (by 0.2—0.4 eV) which in turn are preferred to the ones with two face-bridging groups (by *ca.* 0.35 eV). The energy differences between the various bridging arrangements are not large. This is particularly so when one of the bridging ligands is on a face. Only 0.07 eV separates the three ways of adding a second face bridge and 0.05 eV the two alternative positions for an edge bridge. (This ignores structures in which the edge and face bridges are associated with a common edge.) The largest difference between common types occurs with two edge bridges; the two structures in which the bridges are contained in a B_4H_4 plane (D_{2h} and C_{2v}) are *ca.* 0.2 eV less stable than the two (C_2 and C_s) in which the extra ligands are not coplanar. It was apparent in the $[B_6H_7]^-$ system that the extra ligand stabilised one of the t_{2g} set most. When edge bridges are coplanar they can interact with only one of the t_{2g} set: the symmetric and antisymmetric combinations of the bridging H $1s$ orbitals are involved in the D_{2h} (9) and C_{2v} (10) structures respectively. However, in the other bridge arrangements both symmetric and antisymmetric combinations can each interact with one of the t_{2g} set [the C_s structures' interactions, (11) and (12), are given as examples], and so these out-of-plane arrangements derive extra stability.

Trigonal-prismatic $[B_6H_7]^-$ *and* B_6H_8 *Species.*—Trigonal-prismatic $[B_6H_6]^{2-}$ was found to have an e set [$e'(3)$ at -8.28 eV] constituting its h.o.m.o.s and another [$e''(2)$ at -7.15 eV] its l.u.m.o.s; it is also 1.60 eV less stable than the octahedral form.[1] Two edge-bridging positions were considered for the extra proton in $[B_6H_7]^-$, either one of the edges of a trigonal plane or one between two square faces. Stacking diagrams are presented in

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[13] 'Boron Hydride Chemistry,' ed. E. L. Muetterties, Academic Press, New York, 1975.

[14] E. A. McNeill and F. R. Scholer, *Inorg. Chem.*, 1975, **14**, 1081.

[15] E. Groszek, J. B. Leach, G. T. F. Wong, C. Ungermann, and T. Onak, *Inorg. Chem.*, 1971, **10**, 2770.

TABLE 4

Total energies (eV) for B_6H_8 species

Structure	Point group	Energy	h.o.m.o.	l.u.m.o.
o.1,4;2,3	C_2	−343.67	−9.85 (b,a)	−4.80 (a)
o.1,3;2,3	C_s	−343.63	−9.85 (a',a'')	−4.90 (a'')
o.2,3;4,5	D_{2h}	−343.43	−9.85 (b_{1u},b_{3u})	−5.53 (b_{2u})
o.2,3;2,5	C_{2v}	−343.43	−9.85 (b_1,b_2)	−4.78 (a_1)
o.1,2,3;4,5,6	D_{3d}	−342.87	−9.85 (e_u)	−1.81 (a_{1u},e_u)
o.1,2,3;1,2,5	C_{2v}	−342.92	−9.85 (b_1)	−1.81 (a_2, b_1,a_1)
o.1,2,3;1,4,5	C_{2v}	−342.85	−9.85 (b_2)	−1.81 (a_2,b_1,b_2)
o.1,2,3;5,6	C_s	−343.28	−9.85 (a',a'')	−4.08 (a')
o.1,2,3;2,5	C_1	−343.23	−9.85 (a,a)	−4.13 (a)
c.p. 2,3;4,5	C_s	−343.39	−9.07 (a'')	−5.64 (a')
c.p. 3,4;2,5	C_s	−342.89	−8.53 (a')	−5.76 (a'')
c.p. 2,3;3,4	C_1	−342.55	−8.95 (a)	−5.43 (a)
c.p. 3,4;4,5	C_1	−342.46	−8.90 (a)	−5.60 (a)
c.p. 4,5,6;2,3	C_s	−342.29	−9.09 (a'')	−5.11 (a')
c.p. 4,5,6;4,5	C_s	−341.62	−8.98 (a')	−5.77 (a')
c.p. 1,2,3;4,5,6	C_s	−340.85	−8.84 (a')	−5.06 (a'')
t.p. 1,5;3,4	C_{2v}	−343.60	−8.60 (a_1)	−7.15 (b_1a_1)
t.p. 1,2;5,6	C_{2v}	−342.18	−8.40 (a_1)	−8.28 (b_2)

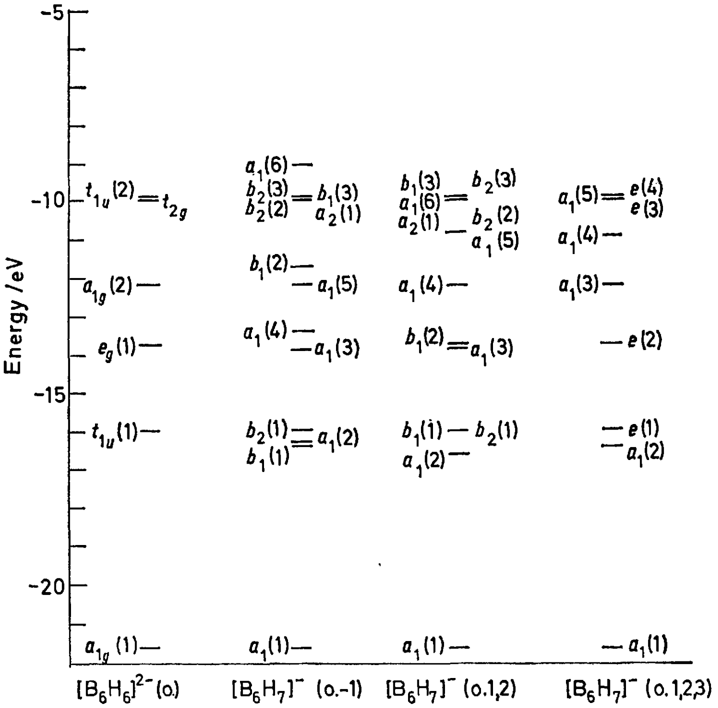
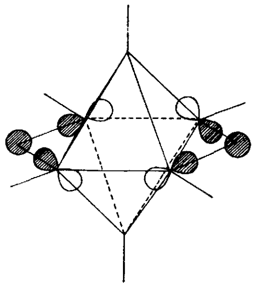
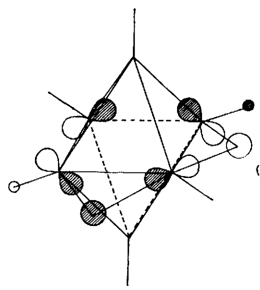


FIGURE 4 Effects of the addition of an extra hydrogen on the orbital energies of octahedral $[B_6H_6]^{2-}$

Figure 3. Placing the extra ligand between the two square faces is preferred by 0.79 eV (Table 4). This preference is the sum of several contributions but the interactions with the frontier orbitals are important.

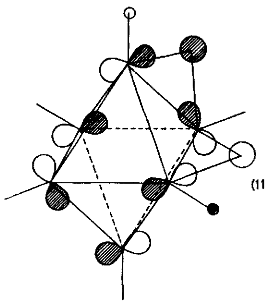


(9) $a_1(4)$

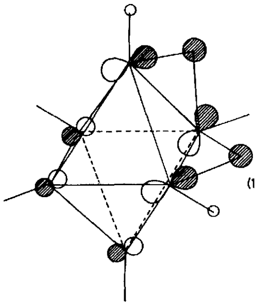


(10) $b_1(2)$

While the t.p. 1,5 form stabilises one of the occupied $e'(3)$ orbitals, the alternative, largely, stabilises one of the $e''(2)$ set which are unoccupied in $[B_6H_6]^{2-}$. The same trend continues as the second ligand is added. Having



(11) $a''(3)$



(12) $a'(6)$

two bridging hydrogens along the edges between the trigonal planes (t.p. 1,5; 3,4) is favoured by *ca.* 1.42 eV compared with the arrangement of a hydrogen along an edge of each trigonal plane (t.p. 1,2; 5,6) (Table 4).

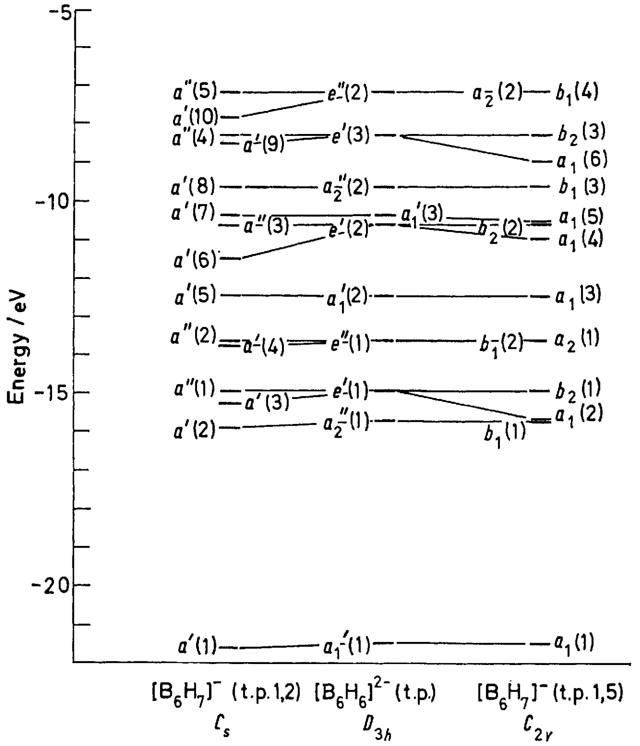
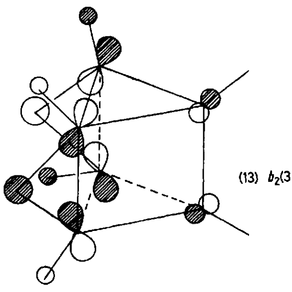
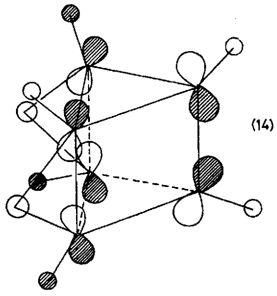


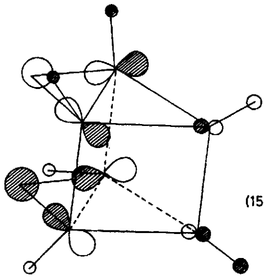
FIGURE 5 Effects of an edge-bridging hydrogen on the orbital energies of $[B_6H_6]^{2-}$ (t.p.)

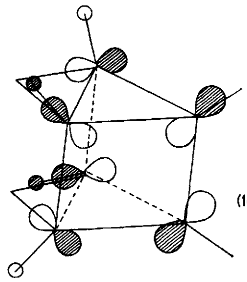
This can largely be ascribed to the same reason. The favoured form can accommodate both symmetric and antisymmetric combinations of the H 1*s* orbitals by interaction with the occupied *e*′(3) set, to give the $b_2(3)$, (13), and $a_1(6)$, (14), levels. Starting from the unoccupied orbital, most of the stabilisation of one of the *e*″(2) set in the trigonal edged form to yield the $b_1(4)$ level, (15), does not contribute to the anion's stability. Also, only one of the *e*″(2) set can interact in this form, the other, $a_2(2)$, (16), being of inappropriate symmetry (δ) to interact with the bridging ligands. If two extra electron pairs were added to yield $[B_6H_8]^{4-}$ the gap between the two alternative bridging modes would narrow to 0.29 eV.


(13) $b_2(3)$


(14) $a_1(6)$

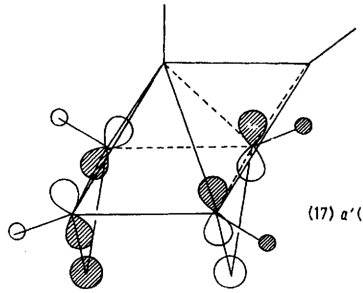
Capped-pyramidal $[B_6H_7]^-$ *and* B_6H_8.—A capped pyramid (c.p.) has similarities to both an octahedron and a trigonal prism. An octahedron and a capped pyramid are derived from a square pyramid by the capping of square and triangular faces respectively. The trigonal prism is converted into a capped pyramid merely by tilting the trigonal faces. These relations are reflected in the electronic structure of capped-pyramidal $[B_6H_6]^{2-}$. It was calculated to be 0.38 and 1.98 eV less stable than the trigonal prism and octahedron respectively.[1] Its h.o.m.o. [*a*′(9)] is at −8.52 eV but the gaps to the first two l.u.m.o.s [*a*″(5) at −5.06 eV and *a*′(10) at −4.53 eV] are intermediate between those of the octahedron and trigonal prism.


(15) $b_1(3)$


(16) $a_2(2)$

Four edge-bridging and two face-bridging positions were considered for $[B_6H_7]^-$ (Table 3). Edge-bridging positions associated with the tetragonal face are again preferred. Placing the bridge on each of the edges split by the mirror plane is equally favoured and a bridge on the edge joining the two tilted faces is *ca.* 0.21 eV less stable. One position associated with the trigonal faces only (c.p. 1,2) was investigated and found to be 0.65 eV higher in energy than the best structure (c.p. 2,3). The two face-bridging sites (c.p. 4,5,6 and c.p. 1,2,3) were found to be less stable still and the total energy spread is 1.45 eV for all the six structures. In all cases the energy of the h.o.m.o. is lowered to some extent and no new bonding orbitals are created.

Addition of the second bridge (Table 4) also followed the trend of conserving the number of bonding eigenvalues. Four structures with edge-bridging ligands on the square face and three with the 4,5,6 face bridged were studied. Total energies now covered a range of 2.54 eV. Bridging *trans* edges of the square face was the best arrangement of those tried with occupancy of the edges shared by the two tilted faces being preferred by 0.50 eV. Evidently, the tilting switches the relative stabilities of the two *trans* edge-bridged structures. The orbital most stabilised by adding the two bridges


(17) *a*′(9)

[a'(9), (17)] bears a strong resemblance to the b_1(2) orbital of the square-pyramidal form of B_5H_7 which most involves the bridging ligands in that species.

Comparison between the $[B_6H_7]^-$ *and* B_6H_8 *Alternative Structures.*—As stated above, in $[B_6H_6]^{2-}$ the stability order for alternative boron geometries is octahedral, then trigonal prismatic, and then capped pyramidal; the energy differences are 1.60 and 0.38 eV between the first and second pair respectively.[1] This stability order is unaltered between the best forms of $[B_6H_7]^-$ for each boron frame (all these have edge bridges), but the gaps in energy between the two pairs are narrowed to 0.82 and 0.29 eV. Once the second extra hydrogen is added, these gaps shrink to 0.03 and 0.21 eV. Evidently, the two structures with square faces become relatively less unstable as extra hydrogens are added; the main difference seems to be between the purely triangulated polyhedron and the others since the differences between the two geometries with square faces vary only slightly. Although the extra ligands do not create any new bonding orbitals, they can effect the relative stabilities of alternative cluster skeletons. There is obviously little to choose between three frameworks in B_6H_8.

There is a balance here between the three frameworks and so the favoured structure in any particular case will depend on subtle quantitative factors. Transition-metal carbonyl chemistry contains examples of these balances: $[M_6(CO)_{18}]^{2-}$, $[M_6H(CO)_{18}]^-$, and $[M_6H_2(CO)_{18}]$ (M = Ru [16] or Os [4]) are isolobal with $[B_6H_6]^{2-}$, $[B_6H_7]^-$, and B_6H_8 respectively. Whilst all the anions have octahedral metal-atom skeletons, the balance is apparently reached when the second bridging ligand is added; the Ru_6 core in $[Ru_6H_2(CO)_{18}]$ is a distorted octahedron,[17] but the osmium analogue has a capped-pyramidal skeleton.[4]

Conclusions.—(1) Adding extra protons (at least to the level of two) does not introduce extra bonding orbitals so, on this criterion, electron-counting procedures should be appropriate when these extra ligands are present. (2) Little site preference was found for edge-bridging ligands on the fully triangulated polyhedra studied, *viz.* the trigonal bipyramid and the octahedron. However, there is a marked preference for bridging hydrogens to be associated with an edge of a square face. (3) The preference of bridges for sites on tetragonal faces favours these more open structures when extra hydrogens are present. For example, trigonal-prismatic and capped-square-pyramidal geometries for B_6H_8 are of very similar energy to the octahedral structure of $[B_6H_6]^{2-}$.

Various approaches to rationalising cluster structures will be compared in a subsequent publication.[18]

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