A Molecular-orbital Evaluation of Skeletal Electron-counting Procedures †

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Extended-Hückel molecular-orbital calculations have been used to follow the changes in electronic structure which occur when idealised borane polyhedra are synthesised from each other by the capping of faces and edges with single BH units or by the mutual approach of two faces. Structures derived from a polygon by face capping maintain the basic electronic structure of the polygon. However, the outcome of the approach of two triangular faces is dependent on their relative orientations. Energies of alternative structures of six-, seven-, and eight-vertexed structures have been calculated for different overall charges. A different structure is favoured for $[B_6H_6]^{n+}$ where $n = 0, -2, -4$, and -6 (bicapped-tetrahedral, octahedral, pentagonal-pyramidal, and trigonal-prismatic respectively). All the stable forms have their bonding orbitals filled and, on that basis, the structures are anticipated by the capping principle. However, eight- and seven-vertexed structures are dominated by dodecahedral and *nido*-dodecahedral forms respectively. Rigorous application of the *debor* and capping principles of the conservation of the number of skeletal bonding orbitals may be misleading in some cases.

SKELETAL electron-counting schemes have considerable utility in rationalising the structures of boranes [1-4] and, to a lesser extent, transition-metal carbonyl clusters.[1-6] These schemes use the capping and *debor* principles which together require that the number of skeletal bonding orbitals is unaffected by the capping of a face or the removal of a vertex. The present study investigates these tenets by means of extended-Hückel calculations (chosen for their economy in such a wide study) on idealised borane polyhedra. The effects of synthesising polyhedra from polygons in other ways, by adding edge-bridging BH units or by the approach of pairs of triangular B_3H_3 and square B_4H_4 moieties, are also considered. During the course of this work the general theoretical basis for the capping and *debor* principles was outlined; [7] this study serves to extend that one. Since transition-metal tricarbonyl moieties of C_{3v} symmetry, and other conical fragments, have been shown to be isolobal with BH,[8,9] conclusions relying heavily on the symmetry and nodal properties of the skeletal orbitals should be appropriate to metal carbonyl clusters. Indeed, the boranes may serve as models for $[\{M(CO)_3\}_m]^{n+}$ species. Extended-Hückel calculations on some of the polyhedra considered have been previously reported,[7,10-12] but these had to be repeated for direct comparison with systems newly studied.

CALCULATIONS

All the calculations were of the extended-Hückel type.[11,13] Basis sets of 1*s* for hydrogen and 2*s* and 2*p* for boron were taken using Burns exponents [14] (H 1*s*, 1.0; B 2*s*, 1.25; and B 2*p*, 1.075) for the Slater-type orbitals. H_{ii} values (H 1*s*, −13.60; B 2*s*, −15.17; and B 2*p*, −8.31 eV) ‡ were taken from published tables of valence-orbital

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† No reprints available.

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

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[11] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, 1962, **36**, 2179.

[12] F. Klanberg, D. R. Eaton, L. J. Guggenberger, and E. L. Muetterties, *Inorg. Chem.*, 1967, **6**, 1271.

[13] R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397.

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

ionisation potentials.[15] Off-diagonal, H_{ij}, elements were calculated using Cusachs' formula (1).[16] Idealised poly-

$$H_{ij} = \tfrac{1}{2}(H_{ii} + H_{jj})S_{ij}(2 - |S_{ij}|) \qquad (1)$$

hedra were utilised and BB and BH bond lengths were taken as 1.70 and 1.20 Å respectively, unless otherwise stated. The structures for which calculations were made are listed in Table 1.

TABLE 1

$(BH)_n$ Structures treated by EHMO calculations

n	Structure	Geometry of boron frame	Point group
1	(1)	Point	$C_{\infty v}$
3	(2)	Triangle	D_{3h}
4	(3)	Square plane	D_{4h}
4	(4)	Tetrahedron	T_d
4	(5)	Triangulated plane	D_{2h}
5	(6)	Trigonal bipyramid	D_{3h}
5	(7)	Square pyramid	C_{4v}
6	(8)	Bicapped tetrahedron	C_{2v}
6	(9)	Octahedron	O_h
6	(10)	Pentagonal pyramid	C_{5v}
6	(11)	Trigonal prism	D_{3h}
6	(12)	Capped square pyramid	C_s
6	(13)	*nido*-Pentagonal bipyramid	C_{2v}
7	(14)	Pentagonal bipyramid	D_{5h}
7	(15)	Capped octahedron	C_{3v}
7	(16)	Edge-bridged octahedron	C_{2v}
7	(17)	Capped trigonal prism	C_{3v}
7	(18)	Capped trigonal prism	C_{2v}
7	(19)	Edge-bridged trigonal prism	C_s
7	(20)	Edge-bridged trigonal prism	C_{2v}
7	(21)	*nido*-Cube	C_{3v}
7	(22)	*nido*-Square antiprism	C_{2v}
7	(23)	*nido*-Dodecahedron	C_s
7	(24)	*nido*-Dodecahedron	C_s
8	(25)	Cube	O_h
8	(26)	Square antiprism	D_{4d}
8	(27)	Dodecahedron	D_{2d}
8	(28)	Bicapped octahedron	D_{3d}
8	(29)	Bicapped octahedron	C_{2v}
8	(30)	Bicapped octahedron	C_{2v}
8	(31)	Bicapped trigonal prism	D_{3h}
8	(32)	Bicapped trigonal prism	C_s
8	(33)	Bicapped trigonal prism	C_{2v}
8	(34)	Capped pentagonal bipyramid	C_s
9	(35)	Tricapped trigonal prism	D_{3h}

RESULTS AND DISCUSSION

Introduction of Face- and Edge-bridging BH *Units to Polygons.*—Introduction of a face-capping BH unit to a polyhedron does not alter the number of skeletal bonding orbitals, merely stabilising those of σ and π symmetry with respect to the B–H axis.[3,7] The fundamental geometric fragment is often the central polygon and the number of skeletal bonding orbitals is dominated by its properties. Bearing in mind that a BH unit offers fragment orbitals of σ and π symmetry, it is apparent that families of structures built up around a triangle, square, or pentagon should accommodate six, seven, and eight skeletal electron pairs respectively. Another possible orientation for an added atom is bridging an edge. Taking the example of the triangle, this would yield the triangulated structure (5). The orbitals of the cap will again stabilise the $a_1'(\sigma)$, $e'(\pi_{\|})$, and $a_2''(\pi_{\perp})$ levels. However, one of the $e''(\pi_{\perp}{}^*)$ set has δ symmetry with respect to the bridging atom. Thus only five skeletal orbitals would be anticipated. It is apparent that a simple consideration of the symmetries of the interacting units can demonstrate the importance of the orientation of the added BH fragment.

(5)

The limits of these conclusions were tested by extended-Hückel molecular-orbital (EHMO) calculations on appropriate geometries. Figure 1 demonstrates the effect of capping a triangle. On introducing the first cap, *i.e.* $(BH)_3$ to $(BH)_4$, an extra orbital, primarily of BH bonding character, is produced at *ca.* −15 eV. The other effect is stabilisation of the skeletal orbitals, particularly the e'' set. The trend is continued when a second cap is added, yielding a trigonal bipyramid. Even in the bicapped-tetrahedral structure, there are 12 bonding orbitals for the six BH bonds and the B_6 skeleton. At this point two additional, weakly anti-bonding, skeletal orbitals are obtained, suggesting that the limit of the capping principle is being reached. The behaviour of the family of structures derived from the (BH_4) square is shown in Figure 2. The effects of the first two additions are qualitatively the same as in the triangle family. A BH bonding orbital is produced each time and the $\pi_{\perp}$ non-bonding orbital (e_g) is stabilised most. The number of the formally skeletal bonding orbitals is maintained even on two further additions up

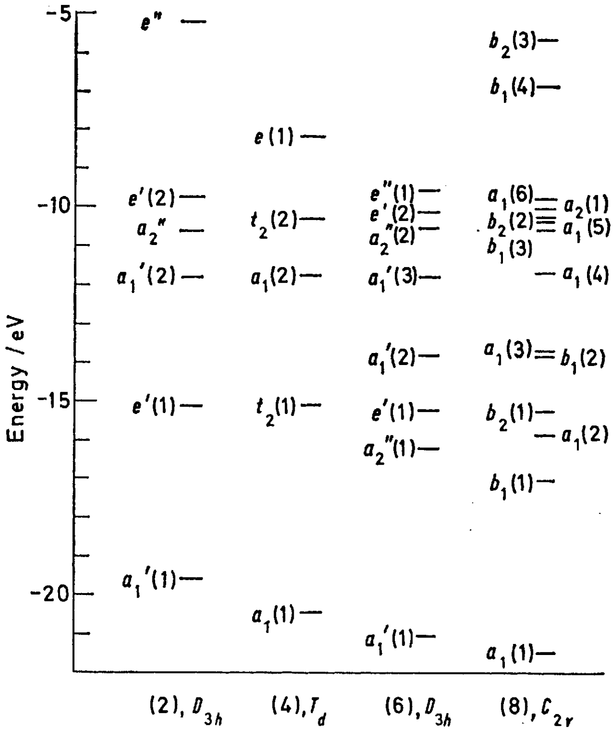

FIGURE 1 Eigenvalues of B_3H_3 and its capped derivatives

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

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

to $(BH)_8$, but by now there is again present a pair of weakly antibonding skeletal orbitals. A qualitatively similar pattern was apparent from calculations on the pentagonal pyramid (10), the pentagonal bipyramid (14), and the capped-pentagonal bipyramid (34).

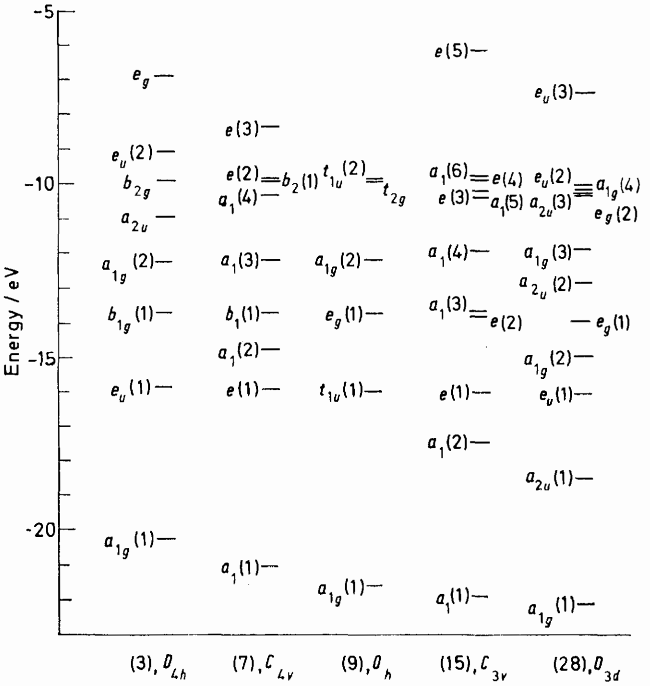


FIGURE 2 Energy levels of square B_4H_4 and its capped derivatives

A comparison between edge- and face-bridging additions to $(BH)_3$ is shown in Figure 3. The addition of the face-bridging unit to give tetrahedral $(BH)_4$ has already been described (see above). The edge-bridged structure (5) of $(BH)_4$ has fewer bonding orbitals and largely follows the qualitative description given above. One of the e'' set is stabilised to yield the b_{2g} orbital. However, there is a complication in the appearance of the $b_{2u}(2)$ level, formally derived from one of the σ^* e_b' set. Evidently it will be difficult to apply a qualitative treatment to larger systems.

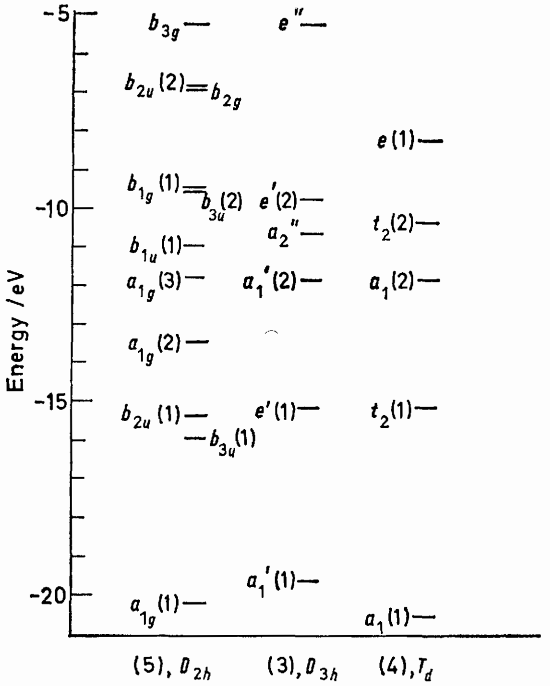


FIGURE 3 Comparison of adding an edge or face bridge to B_3H_3

Formation of Polyhedra from the Interaction of Faces.—Another means of theoretically synthesising three-dimensional structures is by allowing two polygons to interact. The parallel approach of two triangles in a staggered or eclipsed fashion will yield an octahedron and trigonal prism respectively. These two structures are considered to require seven and nine skeletal electron pairs respectively.[1,2] Calculations on the approach of two fixed-geometry B_3H_3 triangles (B–B 1.70, B–H 1.10 Å) from infinity to a B–B nearest-neighbour distance of 1.70 Å were undertaken to probe the reason for this discrepancy in electron requirements. Figures 4 and 5 show the salient features of the orbital energy-level changes on approach. The fates of six pairs of orbitals of the isolated triangles are shown; these six correspond most closely to the six Walsh-type skeletal orbitals of the isolated triangles. (Six pairs of primarily B–H bonding orbitals are omitted. Since they remain bonding in nature throughout the approaches, they have no effect on electron requirements.) Figure 4 represents the eclipsed approach. At an interplane distance of 5.0 Å there is a first-order interaction between the six pairs of

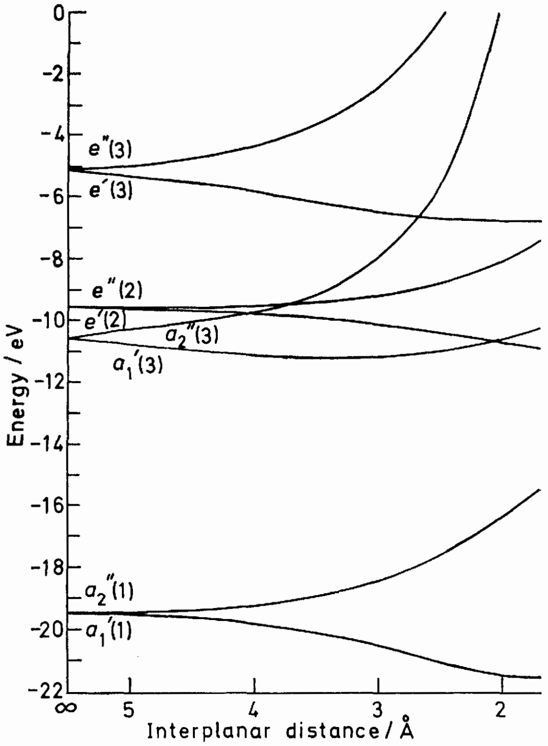


FIGURE 4 Part of the energy-level diagram (D_{3d}) for the vertical approach of two eclipsed B_3H_3 triangles

orbitals to give in- and out-of-phase combinations. As the planes approach further, second-order perturbations give rise to orbital mixing. For example, this is apparent on the $a_2''(1)$ orbital which is initially of B 2*s* character but acquires some H 1*s* density. The strongest interaction is between the π out-of-plane orbitals, and the interplane antibonding combinations, $a_2''(3)$ and $e''(3)$, are greatly destabilised. The energy of the interplane bonding combination $e'(3)$ is lowered but that of the $a_1'(3)$ level is essentially unaltered due to a crossing avoidance. Of the original 12 orbitals at infinite separation, nine are essentially bonding or non-bonding. The behaviour of these six pairs of orbitals on a staggered approach is shown in Figure 5. Generally the curves are similar, showing the destabilisation of the π out-of-plane antibonding combinations [$e_g(3)$ and $a_{2u}(3)$]. The difference lies in the out-of-plane bonding combination $e_u(3)$. Now possessing the same symmetry as the orbital immediately below it, it mixes with the $e_u(2)$ set in a way which is mutually antibonding [in $e_u(3)$] and so is destabilised as the approach is completed. (In the O_h point group, this forms part of the t_{2u} skeletal antibonding set.) Thus there are only seven of the original 12 skeletal bonding orbitals still available. These results are therefore in accord with skeletal electron-counting schemes [1,2] and previously reported calculations on trigonal-prismatic and octahedral structures.[7]

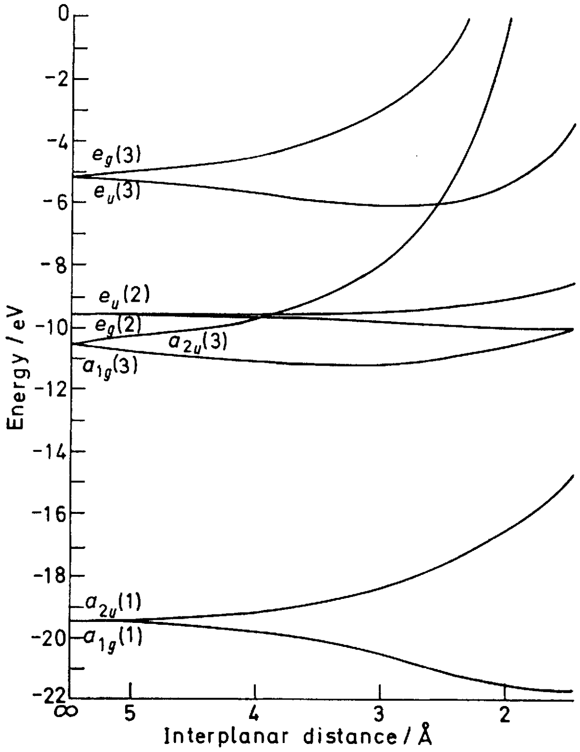


FIGURE 5 Part of the correlation diagram (D_{3d}) for the vertical approach of two staggered B_3H_3 triangles

The eclipsed approach of two fixed-geometry $(BH)_4$ squares was also monitored (B–H 1.10 Å). Figure 6 illustrates the effect on the pairs of four mainly in-plane skeletal bonding orbitals and four out-of-plane π orbitals. Again the interplane antibonding combinations of the $\pi_\perp$ orbitals [$a_{2u}(3)$, $e_g(3)$, and $b_{2u}(2)$] are drastically destabilised. Nine orbitals are bonding in character when the approach is complete and there are a further three [the $e_g(2)$ and $b_{1g}(2)$ which together form the t_{2g} set in the O_h point group] which are very weakly antibonding. So a total of 12 skeletal electron pairs can be housed in a cubic structure. Capping of the square faces would stabilise this uppermost set of three available orbitals and thus make occupancy by 12 skeletal electron pairs more viable.

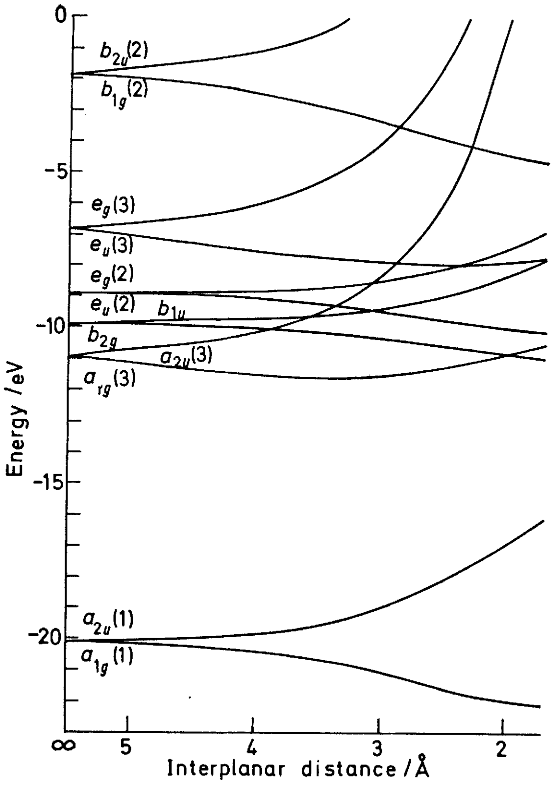
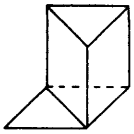


FIGURE 6 Part of the correlation diagram (D_{4h}) for the vertical eclipsed approach of two B_4H_4 squares

Addition of Caps to Larger Systems.—(*a*) *Trigonal prism.* Four capping positions were considered: on a square face (18), a triangular face (17), an edge between two square faces (20), and on the edge of a triangular face (19). The resulting stacking diagrams are displayed in Figure 7. Face capping, either square or triangular, again yielded the same qualitative results as for smaller systems, *i.e.* adding one bonding orbital to accommodate an extra B–H bond. Placing the bridging unit off the edge of a triangular face had more or less the same



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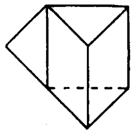


(20)

effect, but in structure (20) an additional orbital, largely skeletal in nature, was encountered in the weakly-antibonding region. The difference between adding face- and edge-bridging units to a polyhedron is again apparent.

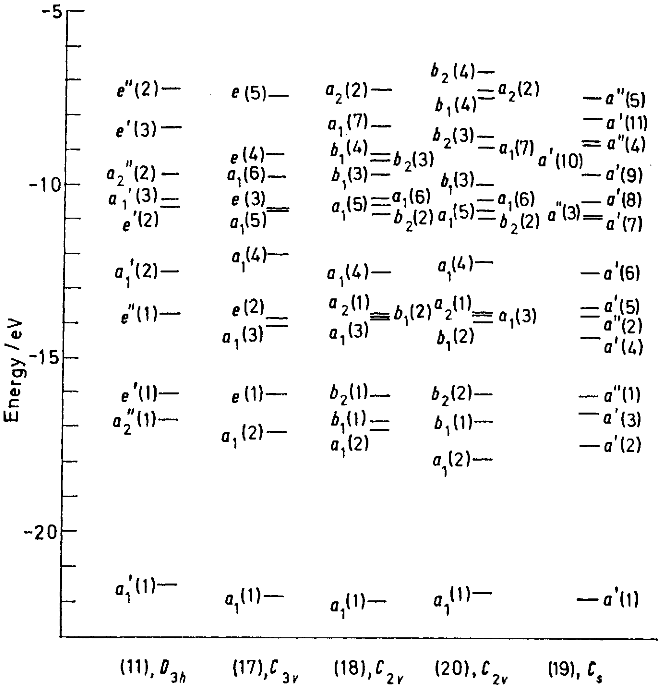


FIGURE 7 Lower-energy levels for trigonal-prismatic B_6H_6 and edge- and face-bridged B_7H_7 derivatives

The nine skeletal bonding orbitals of the trigonal prism result from in- and out-of-phase combinations of the in-plane bonding orbitals of the $(BH)_3$ triangular faces and bonding combinations of the three $\pi_\perp(BH)_3$ orbitals. In neither this nor any of the other cases considered was recourse necessary to occupation of an orbital derived from either the σ^* or $\pi_\parallel^*$ orbitals of the basic polygon or an out-of-phase combination of the $\pi_\perp$ orbitals. However, $[B_9H_9]^{2-}$ has a tenth skeletal electron pair[17] and this has been shown to have a closed-shell configuration.[7]

Above the bonding region, the lowest orbital in the trigonal-prismatic structure is the a_2' in-phase combination of the two $\pi_\parallel^*$ orbitals of the individual triangles at 1.46 eV. Figure 8 shows the effect of capping the square faces, ultimately yielding (35). On capping the first face, the nine bonding orbitals undergo a net stabilisation and the a_2' eigenstate is greatly lowered in energy by interaction with a B $2p$ orbital. This trend is continued until after all the three square faces are capped when the $a_2'(1)$ bonding orbital is formed. It is also noteworthy that the $a_2''(3)$ level is only mildly antibonding in (35). This is derived from the out-of-phase combination of the $\pi_\perp$ orbital which is 20.94 eV higher in energy in the trigonal prism. Under some circumstances, the qualitative approach of considering only bonding and weakly antibonding orbitals of the basic polygon will lead to erroneous conclusions. Nevertheless, the scheme is valid over a considerable range of structures and the reasons for the exceptions, as shown by the tricapped-trigonal prism,[7] will probably be apparent from careful inspection.

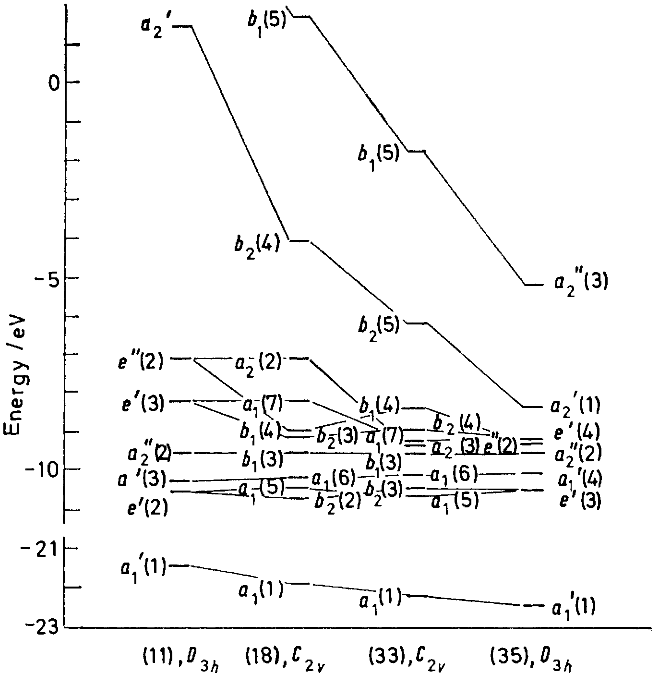
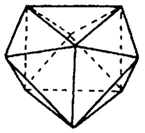


FIGURE 8 Effects of sequentially capping the square faces of trigonal-prismatic B_6H_6 on the lower skeletal-type orbitals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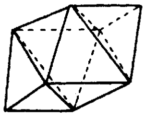
(*b*) *Octahedron.* The differences between the placing of an edge- (16) or face-bridging BH unit (15) on an octahedron are essentially quantitative; in terms of electron counting there is little to distinguish them. Both fit into the broad pattern of conversing the number of skeletal bonding orbitals, but they also stabilise the lowest antibonding orbitals (t_{2u}) of the octahedron. The same general trend is apparent on adding the second face-capping unit in any of the three possible positions so that orbitals of the stabilised t_{2u} set did indeed become occupiable. [The lowest such orbital was at -7.30 (e_u) for (28), -7.22 (a_1) for (29), and -7.73 eV (b_1) for (30).]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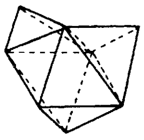
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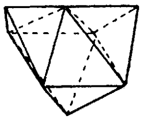
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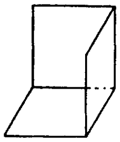
[17] 'Polyhedral Boranes,' eds. E. L. Muetterties and W. H. Knoth, Marcel Dekker, New York, 1968.

Removing a Vertex from an Eight-vertexed Polyhedron.—The removal of a BH vertex from a cube, square antiprism, and dodecahedron was evaluated. According to the *debor* principle, this should maintain the number of skeletal bonding orbitals. In cubic $[B_8H_8]^{n+}$ there are 17 orbitals up to -7.82 eV and a t_{2g} set at -6.72 eV. This corresponds to either nine or 12 potentially occupiable skeletal bonding orbitals. Removing a vertex to yield (21) [similar to (19) in geometry] gives rise to 14 eigenvalues up to the first energy and another three (a_1 and e) below the second. Since this would formally correspond to seven and 10 skeletal orbitals respectively, the *debor* principle is violated. The square-antiprismatic arrangement of $[B_8H_8]^{n+}$ has 17 eigenvalues up to -8.70 eV, corresponding to nine skeletal bonding orbitals; the *nido* derivative (22) has 15 eigenvalues up to -8.31 eV and another at -7.23 eV. So there can be thought to be either eight or nine skeletal ' bonding ' orbitals and the *debor* principle may be preserved. Dodecahedral $[B_8H_8]^{n+}$ has 17 eigenvalues up to -8.17 eV, corresponding to an S value (the number of skeletal bonding orbitals) of 9. Removing either of the two types of vertex [giving (23) or (24)] yields 15 eigenvalues up to this energy (S 8) so again the number of skeletal bonding orbitals has not been conserved.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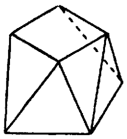
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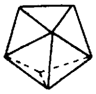
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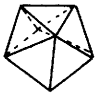
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Relative Stabilities of Alternative Structures.—(*a*) $[B_4H_4]^{n+}$ *and* $[B_5H_5]^{n+}$. Total energies were calculated for three $[B_4H_4]^{n+}$ structures, tetrahedral, square-planar, and triangulated-planar, having the equivalent of four to seven skeletal electron pairs (Table 2). The tetrahedral structure was favoured for $S = 4$ and 6, whilst the square-planar one was preferred when $S = 5$ or 7. In all cases the favoured form would be diamagnetic. There are examples of tetrahedral clusters which have either four, $[Re_4H_4(CO)_{12}]$,[18] or six, $[Ir_4(CO)_{12}]$,[19] skeletal electron pairs and the cyclobutadiene dianion provides an example of a square-planar structure with $S = 7$. Closed-shell configurations were also observed for the favoured $[B_5H_5]^{n+}$ structures (Table 3). While the trigonal-bipyramidal form was preferred for six skeletal electron pairs {*e.g.* $[Os_5(CO)_{15}]^{2-}$},[20] it yielded to the square-pyramidal alternative on addition or loss of an electron pair.

TABLE 2

Total energies (eV) for $[B_4H_4]^{n+}$ species

	n *			
	0	−2	−4	−6
Structure	(4)	(5)	(6)	(7)
(3)	−215.7	−233.8	−247.5	−261.2
(4)	−216.0	−232.3	−248.5	−240.5
(5)	−212.4	−226.0	−239.6	−249.9

* The value of S is given in parentheses

TABLE 3

Total energies (eV) for $[B_5H_5]^{n+}$ species

	n *		
	0	−2	−4
Structure	(5)	(6)	(7)
(6)	−266.8	−258.8	−293.7
(7)	−267.1	−283.7	−300.3

* As in Table 2.

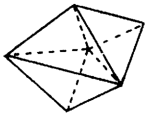
(*b*) $[B_6H_6]^{n+}$. The total energies calculated for the six structures considered for $[B_6H_6]^{n+}$ ($n = 0, -2, -4$, and -6) are presented in Table 4. These overall charges correspond to S values of 6, 7, 8, and 9 respectively. Only 2.4 eV separates the total energies of the six neutral species. The bicapped-tetrahedral structure (8) {as found in $[Os_6(CO)_{18}]$}[21] is calculated to be the most stable. It is not surprising that (13) is only marginally less stable since the two structures are very similar in geometry. One nearest-neighbour link (joining the two six-co-ordinate boron atoms) is expanded from (8) to produce (13). This nearest-neighbour link is unusual in having a reduced overlap population of almost zero in (8) (0.088 4). As more electron pairs are added the structures (not surprisingly) become more differentiated in energy. The octahedral arrangement (9) is favoured for seven skeletal electron pairs {as found for $[B_6H_6]^{2-}$

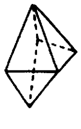
TABLE 4

Total energies (eV) for $[B_6H_6]^{n+}$ species

	n *			
	0	−2	−4	−6
Structure	(6)	(7)	(8)	(9)
(8)	−319.4	−333.1	−343.3	−348.4
(9)	−317.0	−336.7	−340.3	−343.9
(10)	−317.7	−335.0	−352.4	−357.5
(11)	−318.5	−335.1	−349.4	−363.7
(12)	−317.7	−334.7	−344.8	−353.9
(13)	−318.6	−333.7	−348.2	−353.2

* As in Table 2.


(8)


(13)

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(ref. 17) and $[Os_6(CO)_{18}]^{2-}$ (ref. 22)}, the pentagonal pyramid (10) for eight, and the trigonal prism (11) for nine. All the favoured structures had their bonding orbitals totally filled. On that basis, they are the structures one would anticipate on building up the polyhedra by capping the appropriate polygon or bringing together two B_3H_3 faces. They are also in accord with the skeletal electron-counting rules.[1,2] However, the energy differences between alternative forms is often not large and it is apparent that geometries which might be considered ' unlikely ' could exist in other systems.

TABLE 5

Total energies (eV) for $[B_7H_7]^{n+}$ species

	n *			
	2	0	−2	−4
Structure	(6)	(7)	(8)	(9)
(14)	−350.4	−369.1	−385.5	−390.6
(15)	−350.2	−369.8	−381.9	−393.3
(16)	−351.0	−370.5	−381.7	−390.5
(17)	−351.7	−369.7	−384.4	−399.0
(18)	−351.2	−369.2	−385.6	−399.9
(19)	−352.4	−369.7	−385.6	−400.4
(20)	−352.3	−369.3	−384.1	−398.4
(21)	−356.7	−372.3	−386.9	−401.5
(22)	−352.8	−371.6	−388.2	−402.7
(23)	−352.0	−375.4	−392.9	−405.5
(24)	−358.6	−376.6	−394.2	−408.4

* As in Table 2.

(*c*) $[B_7H_7]^{n+}$. Table 5 contains the total energies calculated for 11 structures for different overall charges; these charges correspond to six to nine skeletal electron pairs. Electron-counting procedures would predict bicapped-trigonal-bipyramidal, capped-octahedral, pentagonal-bipyramidal, and *nido*-dodecahedral structures for $S = 6, 7, 8$, and 9 respectively.[1-5] It is evident that the calculations favour the *nido*-dodecahedral structure (24) in all cases; this geometry is equivalent to a capped-octahedral structure in which one of the edges of the capped face has been elongated. It is thus not unlike the geometries found for $[Os_7(CO)_{21}]$ (S 7) [21] and $[Os_7(CO)_{21}]^{2-}$ (S 8).[23] However, a distorted pentagonal-bipyramidal geometry has been proposed for $[B_7H_7]^{2-}$,[17] and (24) bears little resemblance to this.

TABLE 6

Total energies (eV) for $[B_8H_8]^{n+}$ species

	n *					
	2	0	−2	−4	−6	−8
Structure	(7)	(8)	(9)	(10)	(11)	(12)
(25)	−404.5	−420.2	−435.8	−449.3	−462.7	−476.1
(26)	−403.4	−420.8	−438.2	−449.0	−459.9	−447.4
(27)	−408.7	−427.4	−443.7	−457.4	−465.1	−472.8
(28)	−402.5	−417.5	−431.7	−438.1	−445.5	−448.1
(29)	−402.6	−417.0	−430.0	−441.2	−446.1	−442.5
(30)	−402.3	−417.8	−431.6	−442.0	−445.2	−439.2
(31)	−403.2	−418.8	−434.4	−439.3	−444.2	−446.5
(32)	−402.0	−419.7	−434.6	−444.3	−451.1	−453.8
(33)	−400.8	−418.8	−435.7	−448.1	−451.7	−445.3
(34)	−401.8	−418.8	−432.1	−439.6	−444.5	−442.2

* As in Table 2.

(*d*) $[B_8H_8]^{n+}$. Calculated energies for different structures are listed in Table 6. Apart from $[B_8H_8]^{8-}$, predicted to have a cubic structure (out of those geometries considered), the dodecahedral form (27) was found to be the most stable. This is the geometry determined for $[B_8H_8]^{2-}$ in the crystal.[12] It is apparent that dodecahedral (27), square-antiprismatic (26), and cubic (25) forms are preferred to structures obtained by capping an octahedron, trigonal prism, or pentagonal bipyramid.

Conclusions.—The following general conclusions concerning the molecular orbitals of borane skeletons and the application of electron-counting procedures seem warranted.

(1) In relatively simple cases, the orbital properties of the polyhedral frame can be readily related to the basic polygon of the structure. (2) While addition of an edge-bridging BH unit often does not alter the number of skeletal bonding orbitals, such an addition to the edge of a triangle or to the edge of a trigonal prism between two square faces gives rise to an extra orbital in the weakly-antibonding region, so such structures, (5) and (20), may possess an extra electron pair. (3) In-phase combinations of the π orbitals of the two faces of both a trigonal and tetragonal prism give rise to occupiable orbitals. However, in the trigonal antiprism at least, the in-phase combination of the face's π^* orbitals is also destabilised in the antiprism, so reducing the potential electron occupancy by two electron pairs. (4) While exceptions to the capping principle were normally found after two or three BH units had been added, some exceptions were found to the *debor* principle after removal of the first vertex, *viz*. from the cube and dodecahedron. (5) The favoured arrangement of four,- five-, and six-vertexed species is dependent on the electron occupancy. In general, the most stable form has all its bonding orbitals occupied and is in accord with experimentally determined structures. Eight- and seven-vertexed systems were calculated to be dominated by the dodecahedron and its *nido* derivative, a distorted capped octahedron, respectively.

This paper has dealt with idealised $[B_nH_m]^{x+}$ ($m = n$)

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[23] B. F. G. Johnson, J. Lewis, and G. M. Sheldrick, personal communication.

systems. The effects of the distortions produced when m is greater than n are investigated in the following paper [24] and the general conclusions will be subsequently applied to transition-metal carbonyl clusters.[25]

I thank the Council of the Royal Society for support in the form of a Pickering Research Fellowship, and Professor J. Lewis and Dr. B. F. G. Johnson, University Chemical Laboratory, Cambridge, where these calculations were performed, for their help and encouragement.

[7/781 *Received, 6th May*, 1977]

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