Bonding in Clusters. Part 9.* The *closo–nido* Relationship; an MNDO Computational Study†

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The role of the four bridging hydrogens, $4H_b$, in the cluster bonding of B_5H_9 is compared with that of S in SB_5H_5, CH^- in $[CB_5H_6]^-$, and BH_2^- in $[B_6H_6]^{2-}$, by analysis of MNDO calculations on the molecules. The four groups are shown to be very similar in their contributions to cluster bonding, and thus B_5H_9 can be considered as a subrogated *closo* system in the same manner as the two heteroborane clusters. This is consistent with the established pattern-recognition procedure for relating *closo* and *nido* boranes and with Wade's rules, simply introducing $4H_b$ as another subrogating moiety. This is further tested by analysis of calculations on the $[B_{11}H_{11}]^{2-}$–$B_{10}H_{14}$ and $[B_7H_7]^{2-}$–B_6H_{10} *closo–nido* pairs and found to be consistently applicable. This approach to the *closo–nido* relationship is compared to previous explanations.

The relationship between *closo* and *nido* boranes has been perceived in a number of ways. For example, an oxidation/reduction connection has been proposed as certain borane and metalloborane reactions can be driven between the two structural types in this way.[1] Lipscomb[2] suggested that the *nido* (and *arachno*) geometries can be derived from the *closo*-$[B_{12}H_{12}]^{2-}$ icosahedral shape; an attractive theory which foundered mainly on the geometry of B_5H_9. The most useful relationship is based on Williams' pattern-recognition theory,[3] whereby the triads, *closo*-$[B_nH_n]^{2-}$, *nido*-$B_{(n-1)}H_{(n+3)}$, *arachno*-$B_{(n-2)}H_{(n+4)}$, are structurally related by the deletion of one and then a second (adjacent) BH^{2-} group from the *closo* geometry, the additional hydrogen atoms being arranged around the vacant sites. This relationship has the advantage that the three molecules are (cluster) isoelectronic as well as being structurally related.

We wish to develop this description using the concepts inherent in Wade's rules,[4] supported by Stone's theory[5] of the electronic structure of *closo* systems. Thus, according to Wade's rules $[B_6H_6]^{2-}$, $[CB_5H_6]^-$, and SB_5H_5 are equivalent *closo* molecules. (Of course, SB_5H_5 is unknown, but related higher nuclearity molecules, SB_9H_9, $SB_{11}H_{11}$, are well known; also $[CB_5H_6]^-$ is unknown, but is simply related to CB_5H_7). The equivalence lies in the 'subrogation' of a BH^{2-} group in $[B_6H_6]^{2-}$ by CH^- and S respectively, the *closo* geometry being preserved. We consider in this paper that B_5H_9 is another equivalent *closo* structure, the BH^{2-} being subrogated by four bridging hydrogens ($4H_b$). The motivation for this approach derives from Stone's work. He has shown from first principles that the approximate spherical shapes of the *closo*-$[B_nH_n]^{2-}$ anions lead to molecular orbitals with atomic-like characteristics which can be usefully described by atomic labels. Maximum stability is achieved when the ratio (number of edges)/(number of apices) (e/n) is a maximum, *i.e.* when the geometry is a triangularly faced polyhedron. In this circumstance ($n + 1$) molecular orbitals are occupied and have atomic character S^σ, P^σ, $(n - 3)(D^\pi, F^\pi)$ (given in order of increasing energy) and where the σ and π labels denote the atomic orbital composition (σ B $2s$, $2p_r$; π B $2p_t$; r = radial, t = tangential to the approximate sphere). We have investigated[6] the validity of Stone's theory and applied it to experimental data on *closo*-B_{10} clusters.[7] For this we used the MNDO calculation[8,9] which agrees remarkably well with experiment, and supports the results of Stone's theory.

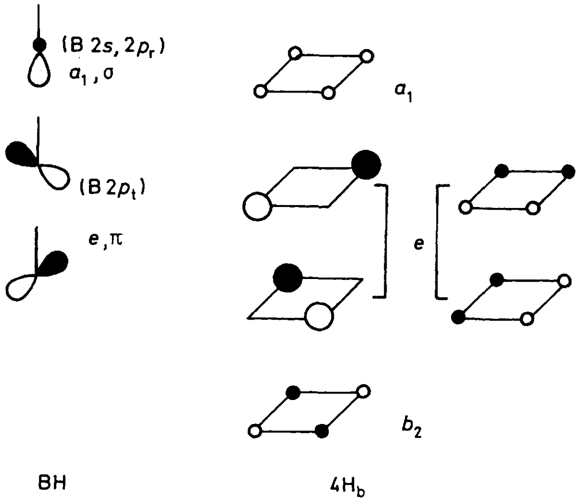

Figure 1. Schematic diagram comparing available cluster bonding orbitals of BH and $4H_b$ groups

The apex deleted in converting a *closo* structure to the related *nido* is invariably that with the highest connectivity.[10] This appears to be in conflict with Stone's (e/n) ratio as a criterion for molecular orbital (m.o.) stability if the bridging hydrogens are considered purely as charge-compensating atoms. This difficulty does not apply when the deleted apex is subrogated and the (e/n) ratio is maintained, as in $[CB_5H_5]^-$ and SB_5H_5. Although such molecules are clearly chemically different from the related borane, one has no difficulty in considering them as *closo* systems. In the following we consider that $4H_b$ is just another Wade's rules subrogand for BH^{2-}, and that B_5H_9 is to all intents and purposes an equivalent *closo* system. We can compare the four groups BH^{2-}, CH^-, S, and $4H_b$ on two bonding criteria; the electron density in which available cluster-bonding electrons reside, and the energy of that density. Figure 1 compares the cluster bonding orbitals of BH^{2-} and the C_4 symmetry group orbitals of $4H_b$. The comparison is least good for the a_1, σ orbitals due to the off-axis locations of $4H_b$, which, however, make the e, π orbitals quite comparable. The CH^- group has orbitals very similar to BH and the $3s$, $3p$ atomic orbitals of S are again similar, although the atomic radius is larger.

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* Part 8, P. Brint, K. O'Cuill, and T. R. Spalding, *Polyhedron*, 1986, **5**, 1791.

† *Non-S.I. units employed:* eV ≈ 1.60×10^{-19} eV, cal = 4.184 J.

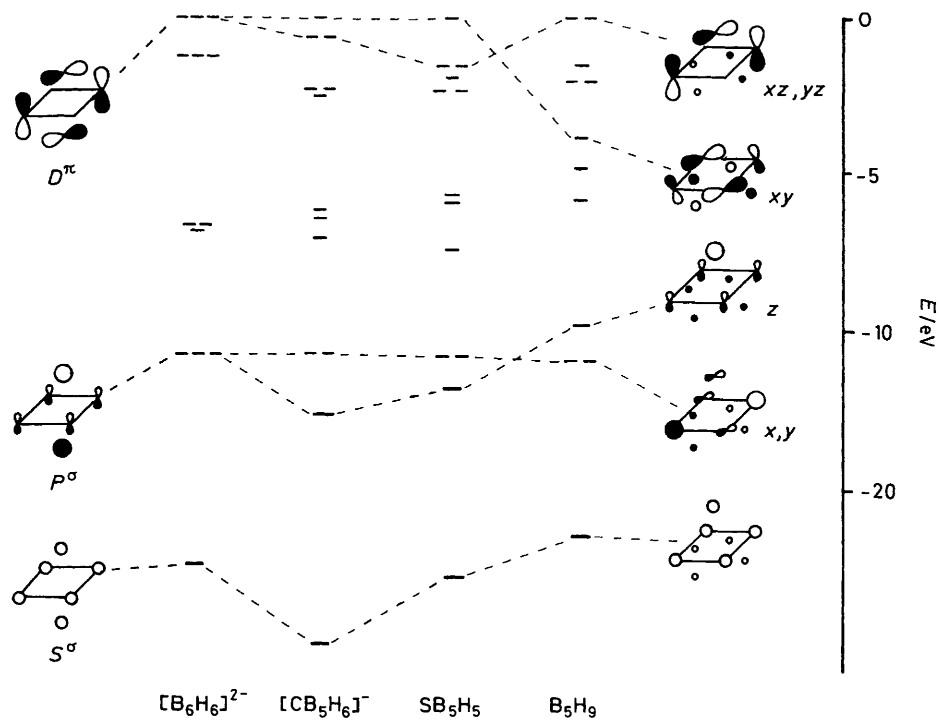


Figure 2. Correlation of the cluster bonding orbitals of $[B_6H_6]^{2-}$, $[CB_5H_6]^-$, SB_5H_5, B_5H_9; add 0.61, −5.16, −11.15, and −11.47 eV to energies respectively. Orbital contributions shown are detailed in Table 1

The energies can be roughly compared from the valence state ionisation energy values used in extended-Hückel theory,[11] B 2*s* −15.2, 2*p* −8.5; C 2*s* − 21.4, 2*p* −11.4; S 3*s* −20.0, 3*p* −13.3; H 1*s* −13.6 eV. The a_1, σ orbital of CH or S has mainly *s* character and its energy therefore differs widely from BH^{2-}, whereas given some energy spread over the $4H_b$ orbitals, presumably $a_1 < e < b_2$, the energy match to BH^{2-} should be quite good. Thus $4H_b$ is potentially an adequate subrogand for BH^{2-} but for rather different reasons than CH^- or S. It also has the b_2 orbital of Figure 1 which has no counterpart in the other groups but which we find to be very important.

Calculations

All calculations were performed using the MNDO program as supplied by Quantum Chemistry Program Exchange. The geometries were optimised under restriction to exact molecular symmetry, as this greatly simplifies analysis and assignment of molecular orbitals. The resultant geometries and energies were compared with free varied geometry optimised calculations and the differences were insignificant. Localised orbitals were calculated using the method of Perkins and Stuart.[12]

Results and Discussion

$[B_6H_6]^{2-}$, $[CB_5H_6]^-$, SB_5H_5, *and* B_5H_9.—Figure 2 shows the calculated occupied molecular orbital energies of the four molecules and correlates the seven cluster bonding orbitals. Table 1 shows the composition of the four low-energy cluster orbitals which we have previously argued[13] determine the stability of the *closo* system. The largest variation of S^σ from the $[B_6H_6]^{2-}$ 'standard' is in $[CB_5H_6]^-$, reflecting the greater stability of the CH^- a_1, σ orbital; otherwise this orbital is very similar in all four molecules. The a_1, σ orbital of $4H_b$ is fulfilling most of the role of the BH^{2-} group it subrogates, despite the spatial differences. The P^σ orbitals show much greater variations, the largest being in the $P^\sigma{}_z$ m.o. of SB_5H_5. This orbital is so localised that it is approaching sulphur lone-pair character. In fact, a calculation of localized orbitals for this molecule shows that the sulphur lone pair is 95% S 3*s*, a point we have discussed before.[14] The a_1, σ orbital of $4H_b$ is fulfilling 60% of its role in $P^\pi{}_z$, as its spatial distribution is least appropriate for this orbital. The component of P^π mixed into P^σ is fairly constant across the molecules and can be seen from Figure 2 to enhance the bonding of these formally non-bonding orbitals. The only manner in which $4H_b$ is unusual is that it provides half the P^π component of $P^\sigma(x, y)$ rather than a quarter. As far as these four cluster orbitals are concerned $4H_b$ is an equally adequate subrogand as CH^- and S.

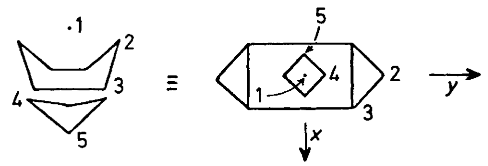
The three D^π m.o.s of $[B_6H_6]^{2-}$ are degenerate and symmetry prohibits any mixing with other orbital types. The C_{4v} symmetry of the other molecules causes splitting (degenerate *xz*, *yz*, non-degenerate *xy*) and allows mixing with BH bonding orbitals. Figure 2 and Table 1 show that these effects are very small in $[CB_5H_5]^-$. In SB_5H_5 a 1.7 eV splitting moves the generate pair close to BH bonding orbitals and strong mixing occurs with a pair 0.7 eV lower in energy. The overall sulphur contribution is much reduced from the $[B_6H_6]^{2-}$ standard. The degenerate pair of B_5H_9 are somewhat mixed with BH bonding orbitals, and we can expect *ca.* 20% contribution per site for comparison with $[B_6H_6]^{2-}$. The $4H_b$ *e*, π orbital contribution is close to this, so the subrogation role is being filled, and considerably more effectively than by S in SB_5H_5. The major difference occurs in the $D^\pi{}_{xy}$ m.o. It is identical in $[B_6H_6]^{2-}$, $[CB_5H_6]^-$, and SB_5H_5 as symmetry prohibits involvement of the deleted site, but in B_5H_9 the orbital undergoes massive mixing with the $4H_b$, b_2 orbital. It is clear that this interaction determines the location of the bridging hydrogens. There is nothing in the composition of the S^σ, P^σ, or $D^\pi{}_{xy,yz}$ orbitals that necessarily makes bond-bridging $4H_b$ preferable to four 'terminal' hydrogens, as the *e* symmetry group orbitals on $4H_b$ corresponding to both arrangements are

Table 1. Comparison of site contributions to the cluster bonding orbitals of $[B_6H_6]^{2-}$, $[CB_5H_6]^-$, SB_5H_5, and B_5H_9

Compound	Site[a]	S^σ	$P^\sigma{}_z$	$P^\sigma{}_{x,y}$	$D^\pi{}_{xy}$	$D^\pi{}_{xz,yz}$
$[B_6H_6]^{2-}$	1	16	30	*b*	25	*c*
Total		94	$60 + 21P^\pi$	*b*	100	*c*
$[CB_5H_6]^-$	1	32	27	0	0	27
	2	9	28	0	0	24
	3[b]	14	2[c]	30	25	24.5
Total		94	$62 + 21P^\pi$	$60 + 36P^\pi$	100	100
SB_5H_5	1	18	62	0	0	15
	2	16	18	0	0	23
	3	16	0	30	25	14
Total		98	$80 + 14P^\pi$	$61 + 35P^\pi$	100	66 + 33BH
B_5H_9	1	11	19	0	45	18
	2	20	35	0	0	30
	3	16	2[c]	34	13.6	17
Total		95	$63 + 24P^\pi$	$67 + 33P^\pi$	100	82 + 17BH

[a] Site 1 is BH, CH, S, or $4H_b$ in the four molecules; site 2 is the BH group opposite to 1; site 3 the equatorial BH groups. [b] Values are identical to those for the related $P^\sigma{}_z$ case. [c] Values are identical to those for the related $D^\pi{}_{xy}$ case. [d] Equatorial BH group contributions are × 4 in non-degenerate orbitals, × 2 in degenerate orbitals. [c] These contributions are impossible in O_h symmetry and arise from $P^\sigma{}_z$–S^σ mixing in C_{4v}.

Table 2. Comparison of site contributions to the four low-energy cluster bonding orbitals of $[B_{11}H_{11}]^{2-}$ and $B_{10}H_{14}$



Sites (site 1 = $4H_b$ in $B_{10}H_{14}$)

P^σ_y orbitals showing P^π component

Compound	Site	S^σ	$P^\sigma{}_z$	$P^\sigma{}_y$	$P^\sigma{}_x$
$[B_{11}H_{11}]^{2-}$	1	4.0	20.4	0	0
	2	5.9	12.9	12.8	0
	3	7.1	0	4.9	15.8
	4	11.4	0.7	17.6	0
	5	11.4	13.1	0	79
Total		89.5	$74 + 12P^\pi$	$80 + 4P^\pi$	$79 + 9P^\pi$
$B_{10}H_{14}$	1	4.3	14.1	0	0
	2	6.4	11.8	15.4	0
	3	7.7	1.1	6.4	0
	4	11.7	1.5	12.7	14.3
	5	11.0	13.6	0	0
Total		93.3	$72 + 13P^\pi$	$82 + 12P^\pi$	$74 + 15P^\pi$

possible, see Figure 1. The b_2 group orbital, however, is specifically orientated at the bond-bridging positions. The question is whether this extra interaction militates against $4H_b$ being considered as a good subrogand for BH^{2-}. For any axially located subrogand there is no such interaction and subrogation ability is judged on contribution to the S^σ, P^σ, and $D^\pi{}_{xz,yz}$ m.o.s. The $4H_b$ group has already been shown to contribute effectively to these orbitals, rather better than CH^- to S^σ, and certainly better than *S* to P^σ and D^π. As this additional interaction is strongly stabilising, see Figure 1, it can only be considered as enhancing the subrogation ability of $4H_b$. We find our basic premises, that $4H_b$ is an effective subrogand for BH^{2-} and that consequently B_5H_9 has a *closo* electronic structure, are supported by this comparison.

$[B_{11}H_{11}]^{2-}$ *and* $B_{10}H_{14}$.—These two molecules test the comparisons of the previous section as their C_{2v} symmetry is less likely to be a factor in the results than the higher symmetries of the smaller molecules. The C_{2v} symmetry was imposed on the calculations and resulted in only marginal changes from the fully optimised results of Dewar and McKee[15] (differences in $\Delta H^\circ{}_f$ 0.5 kcal mol^{-1}). The four low energy orbitals are again easily identified and their compositions are compared in Table 2. The comparison is even better than in the smaller molecules. The $4H_b$ group almost perfectly replaces the deleted apex. One significant difference is the reduced contribution of $4H_b$ compared with apical BH in $P^\sigma{}_z$, reflecting again the unsatisfactory distribution of the $4H_b$ a_1 group orbital. Another is the amount of P^π mixed into $P^\sigma{}_x$ and $P^\sigma{}_y$ which is larger in

Table 3. Assignments of BH π type occupied orbitals of $[B_{11}H_{11}]^{2-}$, $B_{10}H_{14}$ (H_t = terminal H); add −0.33 and −11.30 eV to energies respectively

$[B_{11}H_{11}]^{2-}$				$B_{10}H_{14}$				
Energy/eV	Symmetry	%H_t	Assignment	Energy	Symmetry	%H_t	%$4H_b$	Assignment
0^a	a_1	12	π	0	b_1	7		π
−1.81	a_2	31	BH π	−0.81	b_2	7	6	π
−1.92	b_2	45	BH	−1.00	a_1	34		BH π
−1.99	b_1	18	π	−1.02	a_2	27		BH π
−2.55	b_1	2	π	−1.35	b_2	31	22	BH
−2.63	a_1	27	BH π	-1.77^b	a_1	12		(BH?)
−2.73	b_2	5	π	-2.30^a	a_2	12	36	π
−3.49	a_1	33	BH	−2.37	b_1	29	6	BH
−4.49	b_2	44	BH	−3.10	b_1	37	11	BH
−5.00	b_1	45	BH	−3.20	a_1	17	19	BH
-5.00^c	a_1	45	BH	−3.70	b_2	37	2	BH
−6.75	a_1	48	BH	−5.42	b_2	39	2	BH
−6.81	b_2	49	BH	−5.89	a_1	26	6	BH
−8.44	b_1	34	BH	−6.38	a_1	37	1	BH
−8.71	a_1	41	BH	−7.93	b_1	14	20	π
−10.07	a_2	26	π BH	−9.25	a_1	16		π BH
−10.13	b_2	23	π	−9.55	a_2	16	12	π
−11.44	a_1	18	π (BH)					

[a] $[B_{11}H_{11}]^{2-}$ a_1 m.o. displaced by stabilised $B_{10}H_{14}$ a_2 m.o. [b] $B_{10}H_{14}$ a_1 m.o. which on symmetry grounds is BH bonding but in fact has little BH component, but is not cluster bonding. [c] $[B_{11}H_{11}]^{2-}$ a_1 m.o. most closely corresponding to apical BH bonding, which has no counterpart in $B_{10}H_{14}$.

$B_{10}H_{14}$ and mainly due to $4H_b$. Even so the amount of this mixing is much less than in the six-apex molecules. The P^σ orbitals are now significantly bonding on both sides of the nodal plane and the P^π component is not required to give them bonding character as was the case above. These points are illustrated in the diagram associated with Table 2.

Symmetry requires that the B–H bonding orbitals of $[B_{11}H_{11}]^{2-}$ transform as $5a_1$, a_2, $2b_1$, and $3b_2$. As can be seen from Table 3 only nine orbitals with large H contribution can be identified, the other two (a_1 and a_2) being strongly mixed with the π m.o. set. Assigning the symmetry of all orbitals above the lowest four indicates a π set of symmetries, $3a_1$, a_2, $2b_1$, $2b_2$, presumably consisting of D^π ($2a_1$, a_2, b_1, b_2) and $3F^\pi$ (a_1, b_1, b_2). This is supported by Quinn's equation[16] [equation (1)] for the

$$\Gamma_\pi = (\Gamma_\sigma \times \Gamma_{x,y,z}) - \Gamma_\sigma \qquad (1)$$

symmetries of the π m.o.s, which gives, for the 22 π and $\bar{\pi}$ m.o.s, symmetries of $5a_1$, $5a_2$, $6b_1$, and $6b_2$. Using Stone's[10] connection between π and $\bar{\pi}$ orbitals, namely rotation of *p*-orbital contribution by 90°, shows that the change $\pi \longrightarrow \bar{\pi}$ changes $a_1 \longrightarrow a_2$ and $b_1 \longrightarrow b_2$. Thus deleting P^π (a_1, b_1, b_2), $\overline{P^\pi}$ (a_2, b_1, b_2), D^π ($2a_1$, a_2, b_1, b_2), and $\overline{D^\pi}$ (a_1, $2a_2$, b_1, b_2) leaves $3F^\pi$ and $3\overline{F^\pi}$ (a_1, a_2, $2b_1$, $2b_2$) which must be separated as a_1, b_1, b_2 and a_2, b_1, b_2. Hence it is reasonable that the $3F^\pi$ orbitals are the a_1, b_1, b_2 set found in the calculation. Which particular F^π orbitals these are cannot be determined because the symmetry is too low, in fact it is not really possible to distinguish D^π and F^π m.o.s of the same symmetry species.

The situation is more complex in $B_{10}H_{14}$. The 10 B–H orbitals should have $4a_1$, a_2, $2b_1$, $3b_2$ symmetries, but only six of the calculated orbitals have a large terminal H contribution and this is lower than in the corresponding $[B_{11}H_{11}]^{2-}$ orbitals, see Table 2. This leaves a π set of $2a_1$, $2a_2$, $2b_1$, $2b_2$, *i.e.* different from the $[B_{11}H_{11}]^{2-}$ set. The $4H_b$ group has stabilised an a_2 m.o. at the expense of an a_1 m.o. The symmetry is again too low to show whether a P^π or $\overline{P^\pi}$ m.o. has been stabilised or whether D^π or F^π one has been destabilised. The a_2 orbital stabilisation is consistent with the $4H_b$ 'apex'. The $4H_b$ group has an a_2 group orbital which has no counterpart in the BH group and which fills the same role as the C_{4v}, b_2 orbital of $4H_b$ in B_5H_9, and hence stabilisation of an a_2 orbital is to be expected. The a_2 BH, D^π m.o.s of $[B_{11}H_{11}]^{2-}$ are strongly mixed giving one as h.o.m.o.-1 (higher occupied molecular orbital) and one near the low energy of the BH, π set. In $B_{10}H_{14}$ the high energy one is h.o.m.o.-3, the low energy one is the first m.o. above the S^σ, P^σ set, and the extra a_2 m.o. is h.o.m.o.-6, well stabilised and with a 36% $4H_b$ component.

Correlation of the occupied m.o.s above S^σ, P^σ is possible but very much open to interpretation. Table 3 lists their energies below the h.o.m.o., symmetry species, and assignment, and correlates the m.o.s that have undergone the largest changes. The a_1 h.o.m.o. of $[B_{11}H_{11}]^{2-}$ is the π m.o. displaced by the extra a_2 π m.o. in $B_{10}H_{14}$ and, of course, one a_1 m.o. (corresponding to apical BH bonding) is lost as well. In $B_{10}H_{14}$ only one a_1 m.o. has a large terminal H component, and one which on symmetry grounds should be BH bonding has only a 12% terminal H composition. This should correspond to a change or reduction of BH bonding. The localised orbitals show a change of bonding from 45% B–53% H in $[B_{11}H_{11}]^{2-}$ to 52% B–47% H in $B_{10}H_{14}$, reflecting these differences, but which results in virtually no change in average BH bond length. The dramatic stabilisation of one b_1 π m.o. shown in Table 3 is related to the opening of the 2-position atoms from 2.77 to 3.77 Å on going from $[B_{11}H_{11}]^{2-}$ to $B_{10}H_{14}$. The deletion of the BH apex removes a b_2 $2p_y$ a.o. (atomic orbital) which was directed at the 2-position atoms and a b_1 $2p_x$ a.o. which was directed at no atoms and in fact was little used in bonding (orbital population 0.23 compared to 1.25, 2*s*; 0.78, $2p_y$; 0.72, $2p_z$). The b_1 group orbital of $4H_b$ of $B_{10}H_{14}$ is much better distributed to interact with the 2- and 3-position atoms than is the apical $2p_x$ of $[B_{11}H_{11}]^{2-}$ and hence the b_1 m.o. is stabilised. Correspondingly a b_2 symmetry m.o. is destabilised due to loss of the effectively used apical $2p_y$ atomic orbital.

Therefore as far as these two molecules are concerned the BH^{2-}, $4H_b$ comparison is good for the low energy S^σ, P^σ m.o.s and although the D^π, F^π set is complicated by the low symmetry the orbitals can be correlated. Any significant differences are consistent with the differences in the two subrogating groups and are not large enough to argue against the pseudo-*closo* description.

Table 4. Comparison of site contributions to the cluster bonding orbitals of $[B_7H_7]^{2-}$ and B_6H_{10}

Compound	Site*	S^σ	$P^\sigma{}_z$	$P^\sigma{}_x$	$P^\pi{}_y$	$D^\pi{}_{xz}$	$D^\pi{}_{yz}$	$D^\pi{}_{x^2-y^2,xy}$
$[B_7H_7]^{2-}$	1	15.5	29.3	0		22.3		0
	3	12.8	0	13		11.0		16.5
Total		95	$58 + 21P^\pi$	$65 + 21P^\pi$		100		82.5
B_6H_{10}	1	21.5	34.7	0	0	25	19.7	0
	2	8.3	18.5	0	0	11	5	18
	3	13.2	0	12	12	5.6	5.5	10
Total		96	$53 + 20P^\pi$	$61 + 21P^\pi$	$60 + 19P^\pi$	64	71	68

* Site 1 is the apical BH group, 3 the average contribution of equatorial BH groups, and 2 in B_6H_{10} is $4H_b$.

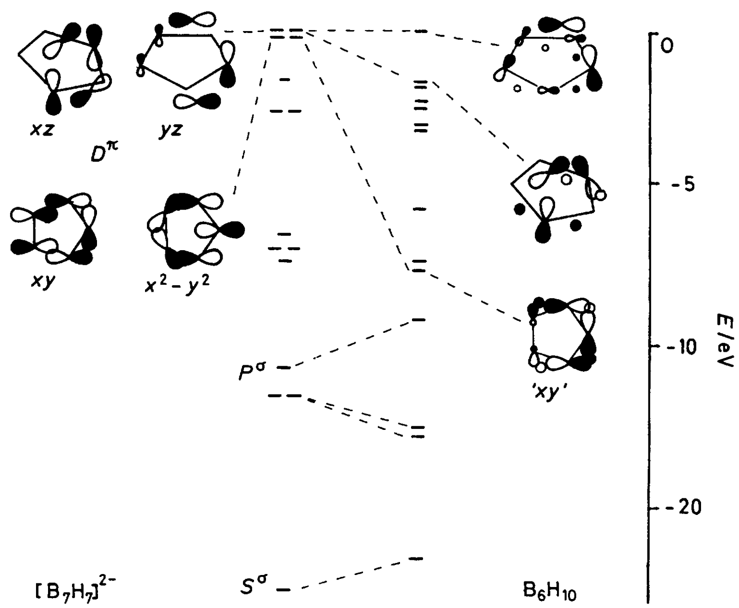


Figure 3. Correlation of the cluster bonding orbitals of $[B_7H_7]^{2-}$, B_6H_{10}: add −0.34 and −10.94 eV to energies respectively. Orbital contributions shown are detailed in Table 4

$[B_7H_7]^{2-}$ *and* B_6H_{10}.—This *closo–nido* pair place the largest demands on the value of the description of $4H_b$ as a pseudo-apex in a *closo* system because there is a large change in symmetry involved, unlike the previous cases. Also $[B_7H_7]^{2-}$ is the least spherical of the *closo* anions, the two apical BH groups being separated by only 2.38 Å (*cf.* B–B bonds of 1.84 Å), giving an oblate, 'strained' geometry, and B_6H_{10} has an almost classical two-electron two-centre bond in its basal plane that is sufficiently electron rich to be involved in donation to Lewis acids.[17]

The molecular orbital energies and symmetries are correlated in Figure 3. The composition of the low energy S^σ, P^σ m.o.s are given in Table 4 and are largely predictable from their $[B_6H_6]^{2-}$ and B_5H_9 counterparts. The $4H_b$ a_1 group orbital is again found to be poorly adapted to its subrogand role in S^σ and $P^\sigma{}_z$, but to about the same extent as in the smaller molecules. The main problems occur in the D^π m.o.s. The $D_{xz,yz}$ degenerate pair of $[B_7H_7]^{2-}$ can be traced to the two h.o.m.o.s of B_6H_{10}, as shown in Figure 3, but the $4H_b$ group is not involved to anything like the extent expected. This results in a large increase in D^π–BH mixing in these two orbitals. The $D^\pi{}_{x^2-y^2,xy}$ pair of $[B_7H_7]^{2-}$ are only poorly represented by the available atomic orbitals, Figure 3. In fact symmetry and composition rather than orbital distribution are the main sources of the assignment. This is comparable with the $[B_{11}H_{11}]^{2-}$, $B_{10}H_{14}$ situation where the low molecular symmetry prohibits identification of spherical symmetry assignment as D^π, F^π, P^π *etc.* On forming the *nido* compound $D^\pi{}_{xy}$ interacts strongly with the group orbital of $4H_b$ which resembles the b_2 orbital in C_{4v} and is stabilised to become the lowest in energy of the D^π BH m.o.s, and has undergone extensive redistribution in the process, see Figure 3. As the amount of $4H_b$ mixing is much smaller than in B_5H_9, yet the stabilisation is much greater, the magnitude of the stabilisation must derive from this redistribution which removes the 'strain' built into the $[B_7H_7]^{2-}$ geometry. A related effect is that no B_6H_{10} m.o. can be clearly identified as the $D^\pi{}_{x^2-y^2}$ m.o. This spherical symmetry character has been 'smeared out' over a number of m.o.s by the low molecular symmetry.

The canonical SCF m.o.s cannot establish good correspondence between the D^π m.o.s due to change in symmetry. Localised orbitals constructed from the canonical set do show the correspondence. O'Neill and Wade[18] have shown that Lipscomb's *styx* rules predict three two-centre bonds and $(n-2)$ three-centre bonds for $[B_nH_n]^{2-}$, and Perkins and Stuart's localisation procedure[12] provides a comparable 'number of centres' index for the localised orbitals. For $[B_6H_6]^{2-}$ the seven cluster orbitals are calculated as a 3.1—3.2 index of which four are truly three-centre bonding (30% each on the B atoms of a triangular face) and three are predominantly (70%) two-centre

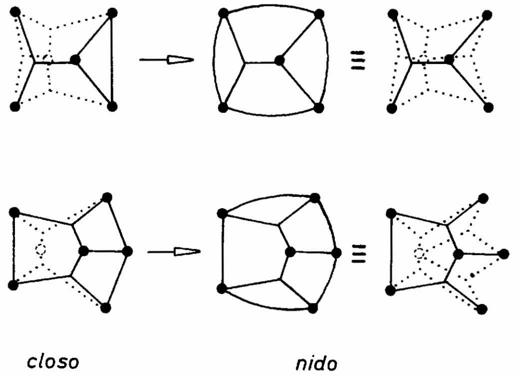


Figure 4. Localised orbitals of $[B_6H_6]^{2-}$, B_5H_9 and $[B_7H_7]^{2-}$, B_6H_{10}, with the *nido* compounds represented both in standard form, and with $4H_b$ as a pseudo-apex

with the balance spread over many centres. For $[B_7H_7]^{2-}$ seven orbitals are 2.8—3.5 index, 3 predominantly two-centre, 4 truly three-centre, and the eighth has a 4.3 index (65% two-centre and the rest very delocalised). The latter is three-centre by *styx* rules but is most easily represented as two-centre. For B_5H_9 the localisation finds three orbitals of 3.2 index of which one is three-centred, and four of 2.7 index all B–H–B bridge bonding, or B, B($4H_b$) three-centred if $4H_b$ is taken as a single apex. B_6H_{10} has one orbital of 2.2 index which is the basal B–B bond, three of 3.1—3.7 index of which one is two-centre, and four of 2.7 index all B–H–B bridging. Figure 4 shows the majority components of all these localised orbitals with the *nido* compounds depicted with $4H_b$ as four bridging hydrogens and as a single apex. The *closo–nido* relationship involves a two-centred bond of the *closo* structure becoming three-centred in the *nido*.

Therefore the S^π, P^π m.o.s of $[B_7H_7]^{2-}$, B_6H_{10} support the pseudo-*closo* description of the *nido* cluster type and in this case, where it is impossible to compare the D^π orbitals, the localised orbitals show that the comparison is consistent.

We feel that there is nothing to be gained from detailed investigation of the other *closo–nido* pairs. $[B_{12}H_{12}]^{2-}$–$B_{11}H_{15}$($[B_{11}H_{14}]^-$) will suffer from the same complexities as $[B_{11}H_{11}]^{2-}$–$B_{10}H_{14}$ in the D^π, F^π orbitals, as will $[B_{10}H_{10}]^{2-}$–B_9H_{13}($B_9H_{12}^-$) and $[B_9H_9]^{2-}$–B_8H_{12} further complicated by the low symmetry of the *nido* species. The $[B_7H_7]^{2-}$–B_6H_{10} pair has both these problems in a more extreme form and yet shows that the pseudo-*closo* description applies, and there is no reason to assume the others will not.

Conclusions

The above discussions can be compared with previous attempts to illuminate the electronic properties that underpin the observed *closo–nido* geometry relationship. Stone[10] has presented an approach based on truncated spherical molecules, paralleling his work on the spherical *closo* boranes. This method however does not account for the inconsistencies outlined in our introduction. His approach has much in common with another approach used by a number of authors, particularly Wade,[19] of considering the sequence $[B_{n+1}H_{n+1}]^{2-}$–$[B_nH_n]^{4-}$–B_nH_{n+4} and taking the geometry of the 4– species as indicative of that of the *nido* compound, and the four bridging hydrogens as purely charge compensating ligands on this geometry. This approach has the disadvantage that the critical species $[B_nH_n]^{4-}$ is unobtainable experimentally therefore geometries predicted on the basis of calculations[19b] or empirical (*e.g. styx* rules) methods cannot be checked. The benefit of the approach we describe is that the *nido* compounds fit into an existing scheme for geometry related molecules, namely Wade's rules, and provide no inherent conflict with Stone's description of *closo* electronic structure. Also there is nothing unexpected in William's pattern recognition approach, the *nido* and *closo* geometries look alike because they are fundamentally the same. We cannot explain from the preceding investigation why the BH group subrogated is the one with the most cluster connectivities; however it is quite probable that increasing connectivity is related to decreasing cluster bonding efficiency, and certainly the site produced by deleting this apex provides the most opportunity for maximising interaction with the subrogating $4H_b$ group.

The disadvantage of our approach is that it does not provide a distinct description of *nido* bonding which can be used as a basis for discussing say *nido*-carboranes, -metalloboranes *etc.* These have to be considered as *closo* boranes with two sites subrogated, one by $4H_b$, one by CH or ML_n. The same is true for *arachno* boranes. It is difficult to see how any quantitative description beyond pattern recognition and electron counting (Wade's rules) can be developed. Clearly it is possible to expand the Hückel-type equations given by Stone[5] which assign α(coulombic) and β(resonance) parameters to the integrals in the secular equations for the orbitals, by introducing heteroatom Hückel-type equations, *i.e.* with α and β parameters related to chemically distinct apices. However we have already shown[6] that this is complex enough for the *closo* boranes themselves without the additional problems of heteroatoms. Even if such an approach were developed it is unlikely that its results would be as valuable as SCF calculations on the individual molecules.

References

1 See, for example, N. N. Greenwood and A. Earnshaw, 'Chemistry of the Elements,' Pergamon Press, Oxford, 1984.
2 W. N. Lipscomb, 'Boron Hydrides,' W. A. Benjamin, Inc., New York, 1963.
3 R. E. Williams, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 66.
4 K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.
5 A. J. Stone, *Mol. Phys.*, 1980, **40**, 1339; *Inorg. Chem.*, 1981, **20**, 563.
6 P. Brint, J. Cronin, E. Seward, and T. Whelan, *J. Chem. Soc., Dalton Trans.*, 1983, 975.
7 G. Whelan, P. Brint, T. R. Spalding, W. S. McDonald, and D. R. Lloyd, *J. Chem. Soc., Dalton Trans.*, 1982, 2469.
8 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 5231.
9 W. Thiel, Quantum Chemistry Program Exchange, Indiana State University, Bloomington, 1978, catalogue 11, program 353.
10 A. J. Stone and M. J. Alderton, *Inorg. Chem.*, 1982, **21**, 2297.
11 C. J. Ballhausen and H. B. Gray, 'Molecular Orbital Theory,' W. A. Benjamin, Inc., New York, 1964.
12 P. G. Perkins and J. J. P. Stuart, *J. Chem. Soc., Faraday Trans. 2*, 1982, 285.
13 T. Whelan and P. Brint, *J. Chem. Soc., Faraday Trans. 2*, 1985, 267.
14 J. McCurtain, P. Brint, and T. R. Spalding, *J. Chem. Soc., Dalton Trans.*, 1985, 2591.
15 M. J. S. Dewar and M. L. McKee, *J. Am. Chem. Soc.*, 1977, **99**, 5231.
16 D. B. Redmond, C. M. Quinn, and J. G. McKiernan, *J. Chem. Soc., Faraday Trans. 2*, 1983, 1791.
17 A. Davidson, D. D. Trificante, and S. S. Wreford, *J. Am. Chem. Soc.*, 1974, **96**, 2802.
18 M. E. O'Neill and K. Wade, *Inorg. Chem.*, 1982, **21**, 461.
19 (*a*) K. Wade, 2nd Euchem. Conference on the electronic structure of transition metal complexes, Maynooth, Ireland, 1985; (*b*) P. W. Fowler and W. W. Porterfield, *Inorg. Chem.*, 1985, **24**, 3511.

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