Bonding in Clusters. Part 6.[1] An Evaluation of Stone's Theory of Bonding in *closo*-Borane Anions, through MNDO Calculations †

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MNDO calculations on *closo*-borane anions are used to assess the accuracy of a recently reported theory of their electronic structure and bonding. The assumptions and results of the theory are found to be fully supported, and parameters are determined that allow molecular orbital energies and composition to be calculated in a manner similar to Hückel theory. The theory is found to be equally applicable to *closo*-carborane molecules, and parameters are determined for these, and also accounts for the *exo*-BH bonding orbitals. The implications of Stone's theory for the bonding of related metal clusters are considered.

The *closo*-borane anions, $B_nH_n^{2-}$ (n = 6—12), exist as regular triangular-faced polyhedra with the n BH groups at the apices of the polyhedra. Many attempts have been made to account for their cluster geometries, particularly why the occupation of $n + 1$ cluster molecular orbitals (m.o.s) produces such regular geometries, whereas occupation of $n + 2$ and $n + 3$ orbitals produce the more open geometries of *nido*- and *arachno*-boranes. An understanding of these anions should explain aspects of metalloborane and metal cluster bonding.

It is known that the availability of two electrons and three orbitals on the BH groups is of fundamental importance, as these groups can be substituted by metallo-groups with similar available electrons and orbitals, without a change in geometry.[2]

In two recent papers Stone[3] developed and applied a simple description of *closo*-borane anions based on their approximate spherical geometries. He successfully explains why $n + 1$ occupied cluster bonding molecular orbitals produce regular triangular-faced polyhedral geometries, and appears to explain how these orbitals are related to the available orbitals in the BH groups. We present here an examination of the assumptions Stone made in developing his description, and of the validity of the resulting energy equations, through MNDO calculations on the anions.

Stone's theory assumes that the boron atoms of the n BH groups are evenly distributed on the surface of a sphere such that all B–B bond lengths are equal and constant, and hence the sphere becomes larger with increasing n, and the angle ω that two adjacent boron atoms subtend with the centre of the sphere becomes smaller. Each BH group has three 'atomic orbitals' available for cluster bonding (one of these is an *sp* hybrid according to Wade[4] and Mingos[2]) and a B–H bonding orbital (B–H antibonding orbitals are ignored); $3n$ cluster molecular orbitals are formed and Stone showed that in the limit of spherical symmetry these are separable into three distinct groups of n orbitals each. One group are LCAO m.o.s of the axial, hybrid σ atomic orbitals directed radially into the sphere, perpendicular to its surface and have regular spherical harmonic properties and are hence labelled S^σ, P^σ, D^σ, *etc.* (given in order of increasing energy). The compound $B_5H_5^{2-}$ has one S^σ, three P^σ, and one D^σ orbitals whereas $B_{12}H_{12}^{2-}$ has one S^σ, three P^σ, five D^σ, and three F^σ orbitals. The other two groups are both composed of the π atomic orbitals of the BH groups, tangential to the surface of the sphere and are distinguished by their parity. The molecular orbitals have the properties of vector surface harmonics, and the even parity set are generally bonding and labelled P^π, D^π, *etc.*, the odd parity set are antibonding and are labelled $\bar{P}^\pi$, $\bar{D}^\pi$, *etc.*

Stone developed energy equations for these three types of molecular orbitals based on Hückel-type approximations for Hamiltonian integrals and the zero-overlap approximation. The molecular orbital energies are expressed as functions of the angle ω, and the energy expressions account for the occurrence of triangular-faced polyhedral geometries in a simple manner which is a major success of the theory. Stone also attempted to determine which $n + 1$ orbitals of the $3n$ are occupied in *closo*-compounds, and implied that they are the S^σ and the n π-type molecular orbitals, with the proviso that the P^π may be displaced by the P^σ by interaction in the lower than spherical symmetry of the molecules.

In our first application of Stone's description to the *closo* systems $B_{10}H_{10}^{2-}$ and $1,10\text{-}B_{10}H_8(N_2)_2$[1] we found from both experiment and theory that in these cases the occupied orbitals are S^σ, P^σ, D^π, and two F^π. We have subsequently investigated the entire set of *closo*-boranes from $B_5H_5^{2-}$ to $B_{12}H_{12}^{2-}$ and present the results here, which include tests of Stone's energy equations and application of the description to *closo*-carboranes.

Calculations and Orbital Assignments

The MNDO calculation of Dewar and Thiel[5] was employed in this paper as we found it to provide excellent geometry and ionisation potential data for the above B_{10} *closo* systems,[1] and Dewar and McKee have shown that it produces good descriptions of other *closo*-borane[6] and *closo*-carborane[7] compounds.[7] Another important feature of this calculation is that it is based on a zero-overlap approximation and is therefore in sympathy with the assumptions used by Stone in developing energy equations.

All calculations, except one, were performed with full optimisation of geometry parameters. For all the boranes and a number of the carboranes the calculations have been reported in varying degrees of detail by Dewar and McKee.[7] All our results agree with theirs in terms of heats of formation and geometries. The exceptional case is $B_9H_9^{2-}$ for which the experimental geometry is not a minimum on the calculated potential energy surface. This problem has been previously discussed by these authors.[7] We calculated a number of geometries for $B_9H_9^{2-}$ all with quite similar heats of formation and the energies of the molecular orbitals were not significantly sensitive to the changes of geometries. We therefore use the results from the optimised tricapped trigonal prism geometry, but any of the others would have given the same results.

The n BH (or CH) bonding molecular orbitals of the $2n + 1$ occupied orbitals are easily identified from their composition. These orbitals are little mixed with the cluster bonding orbitals, and further, their symmetries in high symmetry

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

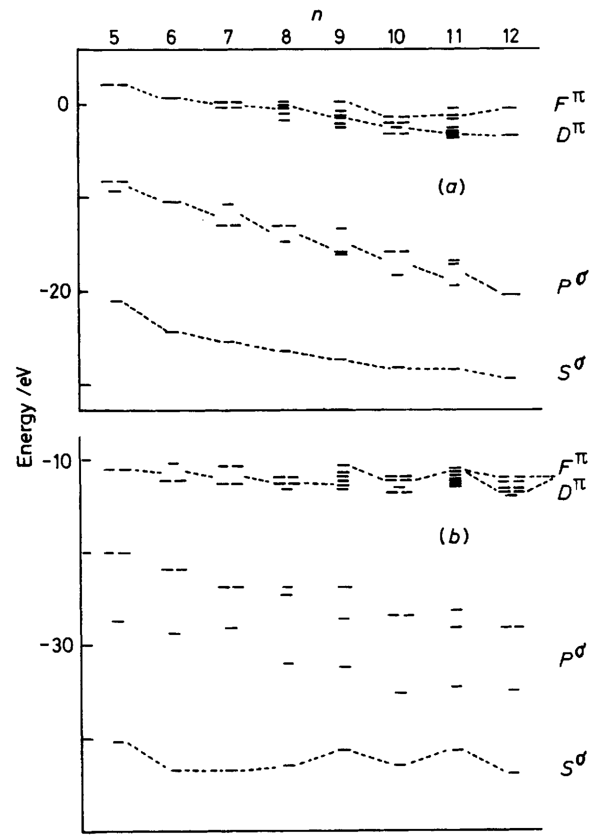

Figure 1. Energies and assignments of the cluster bonding molecular orbitals for (*a*) the *closo*-borane anions, $B_nH_n^{2-}$, and (*b*) the *closo*-carboranes, $C_2B_{n-2}H_n$, with *trans* carbon atoms (n = 5—12)

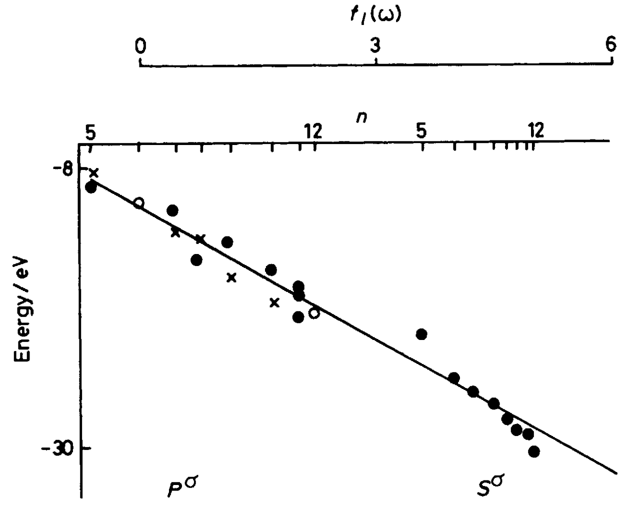

Figure 2. Plot of P^{σ} and S^{σ} molecular orbital energies against $f_l(\omega)$ for the borane anions

molecules provide a secondary check on their compositions. The remaining $n + 1$ orbitals were assigned symmetry labels and their atomic orbital composition inspected. In all molecules four molecular orbitals were found at low energy that were clearly identifiable as Stone's S^{σ} and P^{σ} molecular orbitals. These were lower in energy than the n BH (CH) orbitals and their symmetries correspond to those of the S and P spherical harmonics in the molecular point groups. The $n - 3$ orbitals higher in energy than the BH (CH) orbitals were similarly assigned and identified as the π-type molecular orbitals except for the P^{π} orbitals.

Table. Values of $f_l(\omega) = (2e/n)\, P_l(\cos\omega)$ for n = 5—12, where e is the number of edges in the *closo* geometry

n	5	6	7	8	9	10	11	12
ω	100	90	84	80.5	75	69.6	65.5	63.4
$f_l(\omega)$	−0.625	0.0	0.45	0.74	1.15	1.67	2.03	2.24
$f_0(\omega)$	3.60	4.0	4.29	4.50	4.44	4.80	4.91	5.00

Figure 1 shows the energies and assignment of the cluster bonding orbitals for the boranes and carboranes. The BH(CH) orbitals are omitted and discussed later.

Results

(*i*) *σ-Type Cluster Orbitals.*—Stone's treatment of the σ-type orbitals leads to equation (1) for the molecular orbital energies, W_l^{σ}, where α^{σ} and β^{σ} have much the same interpretation as the corresponding parameters of Hückel theory. The

$$W_l^{\sigma} = \alpha^{\sigma} + f_l(\omega)\beta^{\sigma} \qquad (1)$$

bonding (resonance) integral β^{σ} is constant across the set of molecules if its component atomic orbitals have little directional polarisation, *i.e.* if the hybrid atomic orbital is predominantly 2*s*. The Table lists the values of ω and $f_l(\omega)$ for values of n = 5—12, and Figure 2 shows the plot of the 32 σ-type molecular orbital energies of Figure 1 against $f_l(\omega)$; the accuracy of the correlation is evident. Linear regression analysis shows a correlation coefficient of 0.988 and determines the values of the parameters $\alpha = -10.94$ eV and $\beta = -3.54 \pm 0.10$ eV.

Clearly Stone's equation is very accurate for these orbitals. The approximate spherical symmetry and the energy separation of these four orbitals from the others prohibits mixing which would increase the scatter. Also the σ hybrid is predominantly 2*s* in composition as is shown by the excellence of the correlation. This is a feature that we have commented on before for *closo*- and *nido*-boranes,[8] and for metalloboranes and metal clusters. Only in molecules with a cluster centre atom, for example, $[Fe_5C(CO)_{15}]$, are the σ atomic orbitals directionally polarised.[8]

When a similar plot as Figure 2 is made for the complete set of *closo*-carboranes a general linear correlation is evident, but the scatter is very large. However if data relating to *closo*-carborane with adjacent carbon atoms are deleted, the remaining 44 data points from 11 compounds give the results shown in Figure 3. Two clear linear correlation lines are evident, one involving one P^{σ} and the S^{σ} orbital per molecule, the other involving the other two P^{σ} orbitals.

The separation of the P^{σ} orbitals into two groups is easily accounted for. For carboranes with *trans* carbon atoms ($1,6\text{-}C_2B_4H_6$, $1,10\text{-}C_2B_8H_{10}$, *etc.*), the diameter through these atoms defines the z axis of the $D_{\infty h}$ distorted sphere. The P^{σ} orbitals are still spherical harmonic in appearance, but the P_z^{σ} orbital is almost exclusively composed of C 2*s* atomic orbitals, whereas the $P_{x,y}^{\sigma}$ orbitals are exclusively B 2*s*. For other carboranes ($1,5\text{-}C_2B_6H_8$, $1,7\text{-}C_2B_8H_{10}$, *etc.*) the diameter through the centre and bisecting the chord between the carbon atoms defines a dihedral axis, z, of the low symmetry distorted sphere. Taking the distortion to be to $C_{\infty v}$ symmetry, then the $P_{x,y}^{\sigma}$ are still spherical harmonic in appearance, but P_z^{σ} can have any axial distribution. It is found that P_z^{σ} in these molecules is again localised on the carbon atoms giving it a

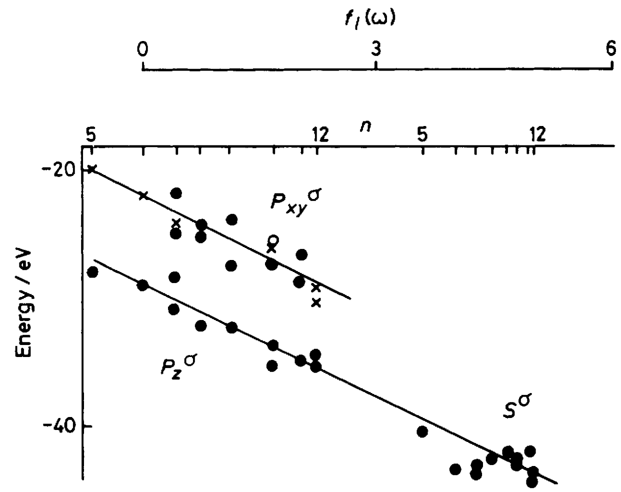

Figure 3. Plot of P^{σ} and S^{σ} molecular orbital energies against $f_l(\omega)$ for the *closo*-carboranes

somewhat *sp* hybrid appearance, whilst $P_{x,y}^{\sigma}$ are predominantly composed of B 2*s* atomic orbitals; $P_{x,y}^{\sigma}$ are the data points of one of the correlation lines.

The P_z^{σ} orbitals correlate with S^{σ} orbitals to form the other line of Figure 3 for a largely fortuitous reason. As shown above the P_z^{σ} orbitals are strongly localised on the carbon atoms, the percentage charge so localised due to this orbital being fairly constant across the group of molecules at 60%. The percentage localised on two boron atoms in the *closo*-boranes by the S^{σ} orbitals is $2/n$ and varies between 40% in $B_5H_5^{2-}$ to 17% in $B_{12}H_{12}^{2-}$. In the *closo*-carboranes the S^{σ} orbitals have larger components on the carbon atoms than on the boron atoms, typically 0.20 compared to 0.10. The percentage of charge localised on the carbon atoms varies between 50% for $C_2B_3H_5$ to 30% for $C_2B_{10}H_{12}$. The $2/n$ variation still applies but is less pronounced and the amount of C 2*s* composition of S^{σ} is similar to that in P_z^{σ}, particularly in the small molecules. The one-centre and two-centre interactions in the two types of orbitals are similar and they correlate together in Figure 3.

The correlation coefficients of the two lines are 0.939 for $P_{x,y}^{\sigma}$ and 0.980 for P_z^{σ} and S^{σ}. The α^{σ} values are -22.00 and -29.20 eV, and β^{σ} values are -3.01 ± 0.25 and -2.94 ± 0.13 eV, respectively. The borane α^{σ} value is considerably higher than the values for the carboranes due to the change from anion to neutral molecule. In the Hückel formalism for $\alpha^{\sigma} = \int \varphi_1 H \varphi_1 d\tau$, φ_1 is the B 2*s* orbital in the higher energy correlation line, and approximates to the C 2*s* in the other. The β^{σ} values from these two lines are the same within statistical variation and are very similar to that from the anions. The Hückel formalism $\beta^{\sigma} = \int \varphi_1 H \varphi_2 d\tau$, has φ_1 and φ_2 on adjacent, bonded atomic centres. Similar values from the *closo*-borane anions and from the $P_{x,y}^{\sigma}$ correlations are expected, φ_1 and φ_2 being a B 2*s* orbital on both centres in both cases. The fact that the same value applies to the P_z^{σ} and S^{σ} correlation when φ is a C 2*s* orbital and φ_2 a B 2*s* shows that the C–B bonds are very similar to the B–B bonds in energy and properties. Clearly the atomic orbitals are distinctly different, having different values of α^{σ}, but the bonding interaction which is of approximately π type is not sensitive to the difference. This result is not surprising, the *closo*-carboranes are known to have properties similar to the *closo*-boranes, however the correspondence of these β^{σ} values is closer than experimental data would suggest. It does correlate however with our *ab initio* calculations on the *closo*-carborane CB_5H_7,[9] where the charge and bonding overlap population of the CH group are almost identical to that of the BH groups. On the other hand, the correspondence does only apply to the σ-type molecular orbitals, and implies nothing about the $n - 3$ π-type orbitals.

(*ii*) *π-Type Cluster Orbitals.*—Stone distinguished two types of interaction due to BH (CH) atomic π orbitals which contribute to the energy of the π-type molecular orbitals. These are illustrated in Figure 4 and the energies due to them are denoted by $F_{(\pi)}^{\pi}$ for the strictly π interaction tangential to the surface of the sphere and perpendicular to the chord connecting the bonded atoms; and by $F_{(\sigma)}^{\pi}$ which, whilst still tangential to the sphere, has the atomic orbitals of the adjacent centres arranged in a σ manner along a great circle of the sphere. He then separated the $F_{(\sigma)}^{\pi}$ integral into a true σ component, along the chord, denoted by F_{σ}^{π} and a π component perpendicular to the chord and directed into the sphere (but not in a radical manner), F_{π}^{π}, Figure 4. These integrals are constant across the set of molecules as the length of the chord is taken as constant. He also assumed that $F_{(\pi)}^{\pi} = F_{\pi}^{\pi}$ as at the atomic level the interactions differ only by a rotation, and developed the energy equation (2), where a_0, a_1, and a_2 are a function of l and ω.

$$W_1^{\pi} = a_0 = a_1F_{\sigma}^{\pi} + a_2F_{\pi}^{\pi} \quad (2)$$

For the D^{π} molecular orbitals we have correlated the W_2^{π} values of Figure 1 with these ω functions and also with the ω functions of the more general equation (3).

$$W_2^{\pi} = b_0 + b_1F_{\sigma}^{\pi} + b_2F_{\pi}^{\pi} + b_3F_{(\pi)}^{\pi} \quad (3)$$

The reason for including this equation is to test the validity of the $F_{(\pi)}^{\pi} = F_{\pi}^{\pi}$ identity. Although valid at the Hartree–Fock level, this identity is questionable in a Hückel-type effective one-electron Hamiltonian level of description. In Hückel theory it is equivalent to assuming 2*p* orbital interactions to be the same in-plane and out-of-plane, which is clearly not the case.

The results of regression analysis of these two equations are as follows. (*a*) For both equations (2) and (3) W_2^{π} is not significantly dependent on a_1 or b_1, and hence the true σ component of $F_{(\sigma)}^{\pi}$ does not contribute to the interactions; (*b*) W_2^{π} correlates strongly with a_2 (coefficient 0.947) but the α^{π} ($= a_0$) and F_{π}^{π} values are rather large, 6.56 and -6.41 eV respectively; (*c*) W_2^{π} correlates well with b_3 (coefficient 0.956) and rather less well with b_2 (0.899). However, whilst the α^{π} and F_{π}^{π} values from the b_2 correlation are similar to those of (*b*) above, from the b_3 correlation the values for α^{π} and $F_{(\pi)}^{\pi}$ are 0.38 and -3.61 eV respectively; (*d*) multiple regression analysis is complicated as the set of molecules do not give a very wide range of ω values and in fact b_2 and b_3 themselves are strongly correlated in the range. Also the lack of correlation with a_1 (b_1) allows an almost free choice of F_{σ}^{π} values, with the α^{π} value simply changing to balance the magnitude of this integral. Further, although the overall correlation is only marginally improved, the accuracy to which the parameters are determined decreases drastically. The only useful result from multiple regression of equation (3) is that F_{π}^{π} and $F_{(\pi)}^{\pi}$ have similar values (-2.5 eV) but with large error ranges on both of them.

The range of b_3 values is more than twice that of the a_2 or b_2 values and it is a similar balance between α^{π} and F_{π}^{π} values, as applies between α^{π} and F_{σ}^{π} values, that is producing the anomalously high parameter values in the latter correlations.

In summary, the analysis suggests that Stone is correct in his $F_{(\pi)}^{\pi} = F_{\pi}^{\pi}$ identity, but that b_3 alone is sufficient to account

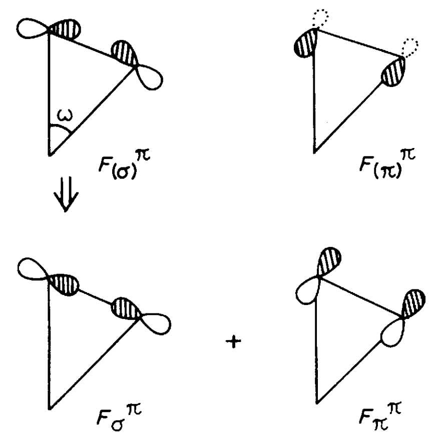

Figure 4. Atomic orbital interactions producing the π molecular orbitals

for the majority of the dependence of W_2^π values on ω, with values $\alpha^\pi = 0.381$ eV and $F_{(\pi)}^\pi = -3.608 \pm 0.196$ eV. This value for $F_{(\pi)}^\pi$ makes even more sense when it is compared with the β^σ value of the previous section. The interactions producing β^σ and F_π^π are very similar, the main distinction being a change from a 2*s* to a 2*p* orbital and a non-radial arrangement of the 2*p* orbitals. Certainly a value of -6 eV for F_π^π is unreasonable on these grounds.

Although the truncated form of equation (3) is sufficient to reproduce the molecular orbital energies, it contains little information on the physics of interaction. Figure 5 shows one of each of the $P^\pi(t_{1u})$ and $D^\pi(t_{2g})$ orbitals of $B_6H_6^{2-}$, and clearly the energy of the D^π orbitals is determined only by $F_{(\sigma)}$-type interactions. The reason why the truncated equation works is due to the validity of Stone's $F_{(\pi)}^\pi = F_\pi^\pi$ identity and the correlation of b_2 and b_3.

Unfortunately, but inevitably, the π orbitals of the carboranes are less clearly organised. There is no doubt that the $(n - 3)$ occupied π orbitals are the same as those of the borane anions but the reduction in symmetry removes the symmetry assignment criterion and enhances the mixing of orbitals in a number of molecules. As a result, the spread of π molecular orbital energies is much greater and unlike the P^σ case there is no clear separation into two distinct groups. The D^π orbitals have lobes in many directions and the carbon atomic orbitals tend to be involved to some extent in all π orbitals. A qualitative division of the orbitals is possible. The two D^π orbitals of 1,5-$C_2B_3H_5$ are strongly localised on carbon, similarly two of the three orbitals of 1,6-$C_2B_4H_6$, whilst the third is localised on boron atoms. In fact, in most molecules there are one or two boron localised D^π orbitals and these present a correlation very similar to that of the D^π orbitals of the borane anions. The other D^π orbitals have varying amounts of carbon 2*p* composition and these do not correlate very predictably. There is little value to be gained from a detailed analysis of these orbitals. It can be assumed that the energies of the high energy boron localised orbitals can be approximately reproduced from the borane energy equation by the subtraction of 13.5 eV (the effect of the 2− charge); the energy of the lowest energy orbital is lower than this by 3 eV for $C_2B_3H_5$ and 1.5 eV for $C_2B_{10}H_{12}$. The reduction in the energy spread reflects the reduction of carbon atom localisation in the low energy orbitals as the ratio of carbon to boron atoms reduces. One unusual effect occurs due to this localisation on carbon or boron atoms. In 1,10-$C_2B_8H_{10}$ and 1,12-$C_2B_{10}H_{12}$, F^π orbitals (localised on carbon) are found at lower energy than D^π orbitals (localised on boron), an energy order that does not occur in the borane anions.

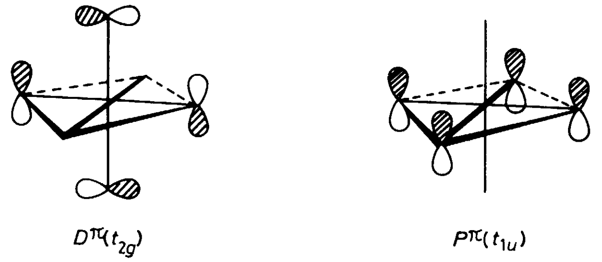

Figure 5. Examples of a D^π and a P^π molecular orbital of $B_6H_6^2$ illustrating the different π interactions involved

(*iii*) *The* BH *Bonding Orbitals*.—These orbitals, directed radially outwards from Stone's hypothetical spherical molecule, may be expected to have very similar properties to the orbitals directed radially inwards that produce the σ cluster molecular orbitals of section (*i*). Thus one may expect *exo* molecular orbitals of S^x, P^x, D^x, *etc.* type, with energies increasing in that order and obeying the energy equation (4).

$$W_l^x = \alpha^x + (2e/n)P_l(\cos\omega)\beta^x \qquad (4)$$

Assignment of the BH bonding orbitals of the borane anions shows definitely that these types of orbitals exist, from S^x, $3P^x$, and $2D^x$ in $B_5H_5^{2-}$ to S^x, $3P^x$, $5D^x$, and $3F^x$ in $B_{12}H_{12}^{2-}$, but with energies in the order $D^x < S^x < F^x < P^x$. A further complexity arises when W_l^x is plotted against $(2\,e/n)P_l(\cos\omega)$, for whilst each of S^x, P^x, and D^x correlate well with their individual ω function, the three lines obtained apparently have no relationship one to the other.

The boron atomic orbital involved in BH bonding is a 2*sp* hybrid orbital and hence β^x is not independent of ω, due to its 2*p* component; the dependence on ω for pure 2*p* orbitals is[3] given by equation (5), where β_π^x is the *exo* orbital interaction

$$\beta^x(\omega) = \cos^2(\omega/2)\beta_\pi^x - \sin^2(\omega/2)\beta_\sigma^x \qquad (5)$$

perpendicular to the chord joining adjacent boron atoms, and β_σ^x is that along the chord. Clearly the orbital components of β_σ^x are directed away from each other in all molecules and hence this parameter makes a very small contribution to W_l^x. Plotting W_l^x against $(2e/n)P_l(\cos\omega)\cos^2(\omega/2)$ produces a single correlation line for the S^x and P^x orbitals (correlation coefficient 0.97, $\alpha^x = -1.871$ eV, $\beta_\pi^x = -2.22 \pm 0.09$ eV) clearly demonstrating the 2*p* orbital nature of the atomic orbitals involved in the interaction. Using the same ω function for the D^x orbitals produces a curve and is clearly a disimprovement on the $(2\,e/n)P_l(\cos\omega)$ correlation. Hence the atomic orbitals involved in D^x molecular orbitals are boron 2*s*, as were those involved in S^σ and P^σ, this is also clear from the composition of the orbitals. The linear correlation of the D^x orbital energies with this simpler function gives a correlation coefficient of 0.857 with $\alpha^x = -15.99$ eV and $\beta^x = -4.36 \pm 0.50$ eV.

The reason for the separation of boron 2*s* atomic orbitals contributing to D^x and F^x and 2*p* to S^x and P^x is simple. The *S*, *P*, *D*, and *F* molecular orbitals can be formed from both 2*s* and radical 2*p* atomic orbitals separately, with energies increasing in that order. The *S* and *P* contributions from 2*s* are involved in σ-*endo* cluster bonding, the *D* and *F* combinations in σ-*exo* bonding, lower in energy than the *S* and *P* combinations from radial 2*p* which makes up the necessary *n* σ-*exo* molecular orbitals.

Discussion

The MNDO calculated molecular orbital energies show that Stone's description of *closo*-borane anions is very accurate, and readily extended to *closo*-carboranes. All the approximations and assumptions, the approximate spherical symmetry, the σ/π separation, the nature of the orbital interactions, used by Stone are supported by this study. Additionally the description is equally valid for the *exo*-BH bonding orbitals. We feel that Stone's description is an extremely powerful one, showing that borane bonding is not as complex as it has often appeared to be. In fact it is now capable of being put on an equivalent level of understanding as, for example, π bonding in organic molecules is through Hückel theory. The only point of disagreement between Stone and ourselves is in the nature of the $(2n + 1)$ occupied orbitals of *closo* systems; we determine it to be $S^{\sigma} < P^{\sigma} < n$, σ-*exo* $< (n - 3)\,\pi$, whilst Stone proposed $S^{x} < n$, σ-*exo* $< n\,\pi$.*

The equations tested above allow prediction of the σ-*endo* (S^{σ} and P^{σ}), σ-*exo* (S^{x}, P^{x}, *etc.*), and π-*endo* (D^{π} and F^{π}) molecular orbitals from a small set of parameters. In fact as all the energy equations turn out to be single variable linear relationships the Hückel approach can be used directly, simply varying the parameter values for the different types of molecular orbital. Diagonalising the secular determinant gives the occupied orbital energies. As the different types of orbitals can be considered as each composed of one type of atomic orbital ($2s$-S^{σ}, P^{σ}, D^{x}, F^{x}; radial $2p$-S^{x}, P^{x}; tangential $2p$-D^{π}, F^{π}), the composition of the molecular orbitals can be determined, straightforwardly for σ-*endo* and σ-*exo* and with some care for π-*endo*. It is interesting to note that Stone's description accounts equally well for the *exo* B–H bonds, which are clearly two-electron bonds, as it does for the cluster bonding, usually described as electron deficient. In fact there is nothing in his description that corresponds to the concept of electron deficiency, except perhaps that two-centre bonding is not a fundamental concept in it.

It is valuable to try to extrapolate from the results of this analysis of Stone's theory to *closo*-metal clusters. Many metal clusters have geometries related to those of boranes, and of those related to *closo*-boranes, $[Fe_6C(CO)_6]^{2-}$ and $[Co_6(CO)_{16}]$ can be taken as examples of two distinct types. One type involves a first-row atom in the centre of the *closo* geometry and the other does not. Examples of both types can be found for many sizes of clusters, and other clusters involving *exo* hydride ligands, for example $[Os_6H_2(CO)_{18}]$ and $[Ru_6H_2(CO)_{18}]$ can be considered as examples of the second type with the protons acting as charge compensating ligands. Assuming the validity of Hoffman and Mingos' metalloborane relationship it is necessary that the metallo-groups combine to produce an orbital energy of $S^{\sigma} < P < (n - 3)\pi$ (there is no criterion for judging the extent of P^{σ}–P^{π} mixing in these compounds, so we do not specify which type of P orbital is occupied) in order to mimic the borane geometry. The energy order of the metal valence atomic orbitals $3d > 4s > 4p$ means that for the individual metallo-group the π-type atomic orbitals will be of similar energy or possibly even lower energy than that of the axial orbital as this orbital has significant $4s$ and $4p$ composition. Even so it is possible to provide an explanation as to why the required order of molecular orbitals is achieved. The two-centre interaction equivalent to β^{σ} above now involves orbitals that are strongly directionally polarised towards one another which must enhance the effectiveness of this interaction. The π-type orbitals of the metallo-group are not perpendicular to the metal–ligand axis and although this means that the $F_{\sigma}{}^{\pi}$ contribution of $F_{(\sigma)}{}^{\pi}$ is enhanced this is only at the loss of the $F_{\pi}{}^{\pi}$ contribution, and $F_{(\sigma)}{}^{\pi}$ is certainly a less effective interaction added to which the π interaction of diffuse $3d$ orbitals is always fairly inefficient. It is reasonable to expect that the S^{σ}, and possibly P orbitals, will therefore be lower in energy than the π molecular orbitals, although not by as large an amount as in the boranes. This is presumably the situation in $[Co_6(CO)_{16}]$.

The introduction of the central main group atom provides a method of approaching the borane orbital arrangement more closely. Clearly the S^{σ} and P molecular orbitals of the metal cluster will have the same symmetries as the C $2s$ and $2p$ atomic orbitals respectively. Interaction between these should produce a low energy set of orbitals predominantly on the central atom which become the S^{σ} and P orbitals of the cluster whilst displacing the predominantly metal concentrated orbitals above the π orbitals. One warning here is that whilst this is certainly possible for the S^{σ}–$2s$ interaction it may be less effective for the P–$2p$ interactions, the metal group σ atomic orbitals actually overlapping and cancelling throughout the region of the carbon atom, and any P^{π} component will not interact efficiently. Either way the result will be a much greater separation between σ- and π-type molecular orbitals, much closer to the borane order.

Clearly any chemical interaction that interferes with the *exo* ligands sufficiently to disturb the energy order of the metal group atomic orbitals will have far more effect on the σ molecular orbitals of the $[Co_6(CO)_{16}]$ type of cluster than on those of the $[Fe_6C(CO)_{16}]^{2-}$ type. Disturbing this energy order can produce loss of the required molecular orbital energy order which would lead to break up of the cluster. This correlates with the observed stabilities of these two clusters, $[Fe_6C(CO)_{16}]^{2-}$ is extremely stable whereas $[Co_6(CO)_{16}]$ is decidedly not.

Conclusions

The statistical analysis of Stone's energy equations with MNDO calculated molecular orbital energies shows that these energies for *closo*-borane anions and carboranes with non-adjacent carbon atoms can be accurately reproduced by linear equations $W_i = \alpha + f_i(\omega)\beta$. The α and β parameters have been determined for each of the types of molecular orbital, σ-*endo*, σ-*exo*, and π-*endo*, and the $f_i(\omega)$ functions depend only on the geometry of the individual molecules. The linearity of the equation for the π-*endo* orbitals is an oversimplification of the physical interactions but is valid.

Probably the major result is that Stone's theory is not only correct and a useful description of the bonding in these compounds but is also a remarkably accurate one. Extension to the *nido*- and *arachno*-boranes will certainly be valuable but probably of more general utility would be extension to the geometrically related metal carbonyl clusters.

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* Dr. Stone comments that P^{σ}–P^{π} mixing is probable in the symmetries of the molecules and the question is which, if either, of the individual symbols provides an accurate description of the resultant molecular orbital, and that his preference is for P^{π}. Certainly MNDO calculates the orbitals to be almost pure P^{σ}, with the exception of $B_5H_5{}^{2-}$ where some mixing is evident, and this is shown by the excellent correlation of Figure 2.

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