indicates that the phase changes are quite sensitive to the strength of the microscopic interactions between the solvent molecules. It is likely that the missing phase change in $Li(ND_3)_4$ occurs so near its melting point that the transition has not been observed.

Although no phase change is observed for $Li(ND_3)_4$ at 82 K, there are significant changes in the neutron diffraction pattern for $Li(NH_3)_4$ above and below this temperature. Only 11 reflections are observed for solid-phase I above the background scattering, making an unambiguous determination of the structure impossible. The data fit reasonably well to a body-centered-cubic phase with a = 14.98 Å at 85 K. While the positions of the reflections at 85 K for solid phase I are rather similar to those of solid-phase II near 82 K, there are striking differences in the line intensities. It is suggested that the phase transition at 82 K retains the body-centered-cubic symmetry with a similar lattice parameter. However, a distortion changes the space group and therefore the line intensities.

Given that there are relatively few body-centered-cubic space groups and few ways of ordering tetrahedra in a body-centered-cubic pattern, we can make a fairly good guess at the structure of solid-phase II. The density of this phase is about 0.60 g/cm^3 [13], and with a = 14.93 Å at 60 K, the number of $Li(NH_3)_4$ molecules per unit cell must be 16. In body-centered-cubic symmetry, other possibilities are 12 and 24, both of which yield unreasonable densities, 0.44 and 0.88 g/cm^3, respectively. All of the body-centered-cubic space groups with 16 symmetry equivalent sites require a minimum symmetry of a 3-fold axis. Therefore, one NH_3 group per $Li(NH_3)_4$ molecule must be unique and on the same Wyckoff position as the lithium atoms. The other NH_3 groups can be placed on 48 general positions. In space group $I\bar{4}3d$, the 16 lithium atoms and 16 nitrogen atoms would be on Wyckoff position c and 48 nitrogens on Wyckoff position e. One possible choice for the positions of the molecules is shown in Figure 3.

The flaw in the above analysis is that it does not account for the very weak, lowest angle line observed by neutron diffraction in $Li(ND_3)_4$ at 3 K (Table I) and, at the same angle, by X-ray diffraction in $Li(NH_3)_4$ at 77 K (Table II). This line may be spurious. It did not appear in all the X-ray specimens. Also, a reexamination of some preliminary data taken on $Li(ND_3)_4$ by M.J.S. with neutron diffraction at Grenoble in 1971 showed the line recorded on one of the counters but not on the other!

That the three solid phases of $Li(NH_3)_4$ and the two phases of $Li(ND_3)_4$ are body-centered-cubic with similar lattice parameters is not unexpected. Many studies have shown that body-centered-cubic structures have the lowest electrostatic energy in the limit of low electron densities,[16] as are represented here by these "expanded-metal" compounds.

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Registry No. $Li(NH_3)_4$, 19453-81-7; $Li(ND_3)_4$, 81097-62-3.

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Contribution from the Department of Theoretical Chemistry,
University Chemical Laboratory, Cambridge CB2 1EW, England

A New Model of Structure and Bonding in the Boron Hydrides

A. J. STONE* and M. J. ALDERTON

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Tensor surface harmonic theory, recently developed by one of us, is used to describe the structure and bonding in the boron hydrides. The theory is extended to cover the *nido-* and *arachno-*boranes in a general way. The model yields the characteristic structural and electron-counting rules obeyed by *closo-*, *nido-*, and *arachno-*boranes in a direct and simple manner. *Nido-* and *arachno-*boranes are found to have pairs of high-energy occupied orbitals localized around the open (nontriangular) face. These orbitals are similar in form to those found in the cyclic planar hydrocarbons, thus explaining chemical similarities between these hydrocarbons and some nido clusters. In most nido and arachno clusters these orbitals are stabilized by the extra hydrogen atoms around the open face.

1. Introduction

The nature of bonding in the boron hydrides (or boranes) has been of interest for over 25 years. The group forms one of the largest and most coherent groups of cluster molecules, with members containing up to 15 boron–hydrogen units bonded in a closo, nido, or arachno structure.

Experience has led to the formulation of structural and electron-counting rules[1-4] for the boranes and their isoelectronic derivatives (such as the carboranes). The primary structural and electron-counting rules are summarized in Table I; they govern the boron atom skeleton of the borane. Williams[4] has formulated secondary rules dealing with hydrogen atom and heteroatom positioning; his article complements this one.

Table I. Primary Structural Rules in the Boranes

type	skeleton	formula	no. of skeletal electron pairs
closo	deltahedron	$B_pH_p{}^{2-}$	$p + 1$
nido	as closo with HCV^a missing	$[B_pH_p{}^{4-}]$ B_pH_{p+4}	$p + 2$
arachno	as nido with an adjacent HCV^a missing	$[B_pH_p{}^{6-}]$ B_pH_{p+6}	$p + 3$

^{a} HCV = highest coordination vertex.

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Many theories have been advanced to explain the bonding in the boron hydrides.[5–9] None account for the primary structural rules in a general manner, nor has a satisfactory model for the orbital structure of these clusters emerged. King and Rouvray[9] have used graph theory to derive some of the electron-counting rules; however, their approach gives no information on the orbitals and does not explain the primary structural rules.

One of us has recently published[10] a theory of bonding for all approximately spherical clusters, called tensor surface harmonic theory (TSH theory). This theory correctly predicts the deltahedral structures and the electron counts of the *closo*-boranes and gives a vivid and detailed model of the bonding and orbital structure. In this paper we shall extend TSH theory to describe the *nido*- and *arachno*-boranes, thus covering almost all of the boron hydrides.

2. Application of TSH Theory to the Boranes

2.1. TSH Theory. This subsection briefly summarizes the parts of TSH theory necessary for this application. The development, terminology, and application to *closo*-boranes are covered in detail in the two earlier papers.[10]

TSH theory[10] assumes that a cluster has its v atoms distributed over the surface of a sphere with the position of each atom i described by angular coordinates (θ_i, ϕ_i). Each atom has three orbitals available for cluster bonding: one inward-pointing (radial) hybrid orbital, h_i, and two p orbitals tangential to the cluster sphere, defined in the directions of increasing θ and ϕ, called p_i^θ and p_i^ϕ.

A set of v independent L_m^σ cluster orbitals is formed by using the scalar surface harmonics $C_{lm}(\theta,\phi)$ to supply the coefficients for the LCAO:

$$L_m^\sigma = \sum_{i=1}^{v} (C_{lm}(\theta_i,\phi_i))h_i \qquad (1)$$

(In this notation, L represents one of the symbols S, P, D, ... according as $l = 0, 1, 2, ...$ by analogy with atomic structure notation.) The v independent L^σ cluster orbitals span the same representations of the molecular symmetry group as the v radial atomic orbitals h_i, as group theory requires.

The L_m^π and $\bar{L}_m^\pi$ cluster orbitals are formed in a similar way from the tangential atomic orbitals, with the vector surface harmonics $\mathbf{V}_{lm}$ and $\bar{\mathbf{V}}_{lm}$:

$$L_m^\pi = \sum_i [(V_{lm}^\theta(\theta_i,\phi_i))p_i^\theta + (V_{lm}^\phi(\theta_i,\phi_i))p_i^\phi] \qquad (2)$$

$$\bar{L}_m^\pi = \sum_i [(\bar{V}_{lm}^\theta(\theta_i,\phi_i))p_i^\theta + (\bar{V}_{lm}^\phi(\theta_i,\phi_i))p_i^\phi] \qquad (3)$$

The vector surface harmonics are vector fields that obey the same equations as the more familiar scalar surface harmonics.[10]

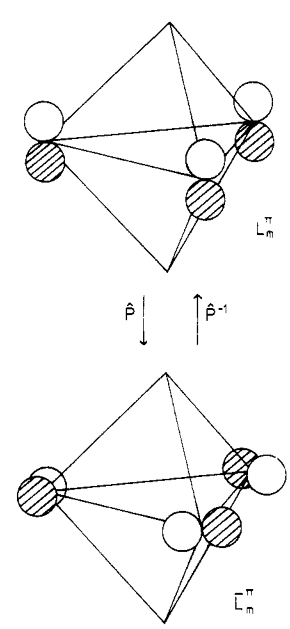

Figure 1. L_m^π and $\bar{L}_m^\pi$ orbitals of the same l and m, illustrating the parity transformation P.

There are v independent L_m^π orbitals and v independent $\bar{L}_m^\pi$ orbitals in a cluster of v atoms. Together they span the same representations in the molecular symmetry group as the $2v$ tangential atomic orbitals from which they are derived. The $\bar{L}_m^\pi$ orbitals are very closely related to the L_m^π orbitals, although they are of opposite parity (symmetry under inversion). The following relationships hold:

$$\bar{V}_{lm}^\theta = -V_{lm}^\phi \qquad (4)$$

$$\bar{V}_{lm}^\phi = V_{lm}^\theta \qquad (5)$$

These equations imply that if each atomic p orbital in an L_m^π orbital is rotated through 90° about a radial axis through the atom, the $\bar{L}_m^\pi$ orbital is produced (see Figure 1). Repetition of the process, which we shall call the parity transformation P, recovers the original L_m^π orbital, except for a change in sign. Thus we have a one-to-one correspondence between the L_m^π orbitals and the $\bar{L}_m^\pi$ orbitals in any cluster, of any symmetry. The parity transformation does not alter the ϕ dependence of the cluster orbital.

The L^π orbitals are usually bonding and the $\bar{L}^\pi$ orbitals antibonding owing to the forms of the vector functions $\mathbf{V}_{lm}$ and $\bar{\mathbf{V}}_{lm}$. Generally speaking, strongly bonding L^π orbitals are associated with strongly antibonding $\bar{L}^\pi$ orbitals and weakly bonding L^π orbitals with weakly antibonding $\bar{L}^\pi$ ones. Thus the parity transformation reverses the bonding or antibonding characteristics of a tangential cluster orbital, as Figure 1 illustrates.

We define the limiting geometry of a cluster type as the geometry of that type of cluster in the limit of high v. TSH theory assumes that the cluster orbitals of a finite cluster have approximately the symmetry characteristics of the tensor surface harmonics in the limiting geometry. The limiting geometry of closo clusters is a sphere, symmetry group R_{3h}; in effect, we are assuming that all closo clusters look like spheres—that is, much the same from any direction. A result of this assumption is that the cluster orbitals of a finite closo cluster do not mix much with other cluster orbitals of different l or m and the L^σ and L^π orbitals do not mix much with the $\bar{L}^\pi$ orbitals.

TSH theory shows[10] that a closo cluster of v atoms will have $v + 1$ bonding cluster orbitals, which are all the L^π orbitals and the S^σ orbital. (There may be substantial interaction between the L^σ and L^π orbitals, but the essential picture is not affected.) All other cluster orbitals are antibonding. Simple energy considerations[10] show that a deltahedral structure will be preferred in such a case, since it maximizes the number of nearest-neighbor interactions.

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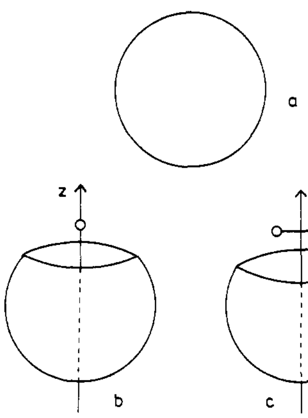

Figure 2. Limiting geometries of (a) *closo*-boranes, (b) *nido*-boranes, and (c) *arachno*-boranes.

Table II. Cluster Orbitals in Various Symmetries

cluster orbital	R_{3h}	$D_{\infty h}$	$C_{\infty v}$
S^σ	S_g	Σ_g^+	Σ^+
P^σ	P_u	$\Sigma_u^+ + E_{1u}$	$\Sigma^+ + E_1$
D^σ	D_g	$\Sigma_g^+ + E_{1g} + E_{2g}$	$\Sigma^+ + E_1 + E_2$
P^π	P_u	$\Sigma_u^+ + E_{1u}$	$\Sigma^+ + E_1$
D^π	D_g	$\Sigma_g^+ + E_{1g} + E_{2g}$	$\Sigma^+ + E_1 + E_2$
$\bar{D}^\pi$	D_u	$\Sigma_u^- + E_{1u} + E_{2u}$	$\Sigma^- + E_1 + E_2$
$\bar{P}^\pi$	P_g	$\Sigma_g^- + E_{1g}$	$\Sigma^- + E_1$

2.2. Nido Clusters. Nido clusters do not look much the same from all directions; there is a unique axis down which they look very different. The limiting geometry of these clusters is a truncated sphere, of symmetry $C_{\infty v}$; see Figure 2. As a result of this lower symmetry, the cluster orbitals are not separated into groups by symmetry to the same extent as in the closo clusters.

Table II gives the symmetries of some of the cluster orbitals in R_{3h}, $D_{\infty h}$, and $C_{\infty v}$; we can see that in $C_{\infty v}$ the L_m^π and $\bar{L}_m^\pi$ orbitals are often of the same symmetry and able to interact. There is no reason to assume that this interaction will be small.

$D_{\infty h}$ is a useful group for describing a closo cluster in the following procedure. We have used E_1, E_2, E_3, ... in place of the more usual Π, Δ, Φ, ...; an E_m symmetry pair of orbitals (E_m pair for short) has cos $(m\phi)$ or sin $(m\phi)$ dependence on ϕ.

The parity transformation will link each E_1 pair in the independent L^π orbitals with a corresponding E_1 pair in the independent $\bar{L}^\pi$ orbitals. Suppose that there are n E_1 pairs in the independent L^π orbitals of a closo cluster; then there will be n E_1 pairs in the independent $\bar{L}^\pi$ orbitals also. Since in a closo cluster the L^π and $\bar{L}^\pi$ orbitals are of different symmetry, this gives $2n$ E_1 pairs in the independent tangential cluster orbitals in our closo cluster.

We can form the nido cluster by removing one vertex (situated at (0, 0)) from the closo cluster. When we remove one vertex, we remove three atomic orbitals; hence, there will be three fewer independent cluster orbitals. The radial atomic orbital removed has symmetry Σ^+ in $C_{\infty v}$; thus one of the high-energy unoccupied L^σ orbitals of this symmetry is lost. The two tangential orbitals removed span E_1 in $C_{\infty v}$; this leaves us with $2n - 1$ E_1 pairs in the independent L^π and $\bar{L}^\pi$ orbitals of the nido cluster.

The parity transformation still requires that each E_1 pair in the L^π orbitals be matched by an E_1 pair in the $\bar{L}^\pi$ orbitals. Since there is an odd number of E_1 pairs in total, an odd number of E_1 pairs must belong to both L^π and $\bar{L}^\pi$. (We shall see later that "an odd number" is in fact 1, since the LCAO description of an E_1 pair belonging to both L^π and $\bar{L}^\pi$ is very restricted.) Since the parity transformation associates strongly bonding L^π orbitals with strongly antibonding $\bar{L}^\pi$ ones and weakly bonding L^π orbitals with weakly antibonding $\bar{L}^\pi$ ones, the $L^\pi/\bar{L}^\pi$ pair, which is associated with itself, must lie somewhere in the frontier region between bonding and antibonding.

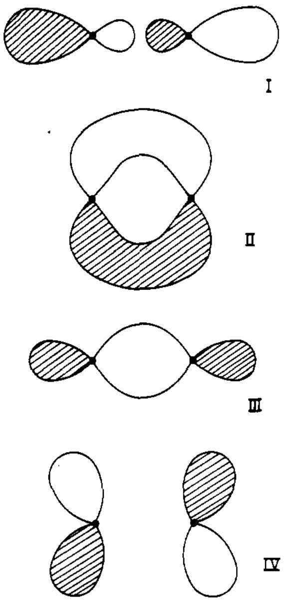

Figure 3. C_{2v} symmetry combinations of the tangential atomic orbitals on the arachno-cluster dimer unit. See Table III for details of the orbitals.

In a nido cluster of p atoms, this gives $p - 1$ bonding L^π orbitals, one bonding S^σ orbital, and the pair of $L^\pi/\bar{L}^\pi$ orbitals. If all of these are occupied, we have $p + 2$ occupied cluster orbitals, in agreement with empirical electron-counting rules (Table I). We can only be sure that the frontier pair are occupied if there is some method of stabilizing them. One way in which this can occur is by adding extra hydrogen atoms to the system. Four extra hydrogen atoms around the open face of a nido cluster will give four atomic orbitals with large overlaps with the frontier pair (we shall show in the next section that the two frontier orbitals are located around the open face). From the frontier pair and these extra hydrogen atoms, a bonding pair of orbitals can be constructed; occupying this pair gives the same electron count as above, but now all the occupied orbitals are definitely bonding. The number of extra hydrogen atoms need not be four; the frontier pair is stabilized by as few as two (as in the stable $B_{11}H_{13}^{2-}$ nido cluster[11]). Another way of stabilizing the frontier orbitals is to add a transition-metal atom above the open face.

This type of stabilization is not always necessary; the $C_2B_9H_{11}^{2-}$ ion has no extra hydrogen atoms yet occurs as a discrete ion in solution[12] as well as forming many transition-metal complexes.

2.3. Arachno Clusters. The limiting geometry of arachno clusters is a $C_{\infty v}$ symmetry cup, derived from the closo cluster by loss of a two-atom dimer unit. This suggests we can use the same approach as that used for the nido clusters. However, the dimer unit, unlike a single atom, has low symmetry (C_{2v}), so it is necessary to approximate the orbitals on this unit to $C_{\infty v}$ symmetry.

We work from the independent closo-cluster orbitals. Two radial atomic orbitals are lost, so two of the high-energy unoccupied L^σ orbitals vanish on orthogonalization, but the low-energy S^σ orbital is retained. Four tangential p orbitals

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Table III. Symmetries of Tangential Orbitals on the Arachno Dimer Unit

dimer orbital	C_{2v}	$C_{\infty v}$	Cartesian form
I: $p_x{}^A + p_x{}^B$	B_1	E_1	x
II: $p_y{}^A + p_y{}^B$	B_2		y
III: $p_x{}^A - p_x{}^B$	A_1	E_2	$x^2 - y^2$
IV: $p_y{}^A - p_y{}^B$	A_2		xy

are also lost; we shall take them as p_x and p_y orbitals on the two atoms of the dimer with the dimer axis taken in the x direction. (We are assuming for convenience that the dimer is small compared with the cluster sphere, so these tangential p orbitals are coplanar. The analysis is the same if they are not, but they are no longer p_x and p_y orbitals.) The symmetry combinations of these orbitals are shown in Figure 3. Table III gives the C_{2v} symmetries of these orbitals and the symmetries in $C_{\infty v}$ when they are approximated to orbitals on a single center.

In $C_{\infty v}$ the four tangential atomic orbitals lost are of symmetries E_1 and E_2. By the same reasoning as we have used for nido clusters, we can conclude that an arachno cluster will have two frontier orbital pairs, one of E_1 symmetry, one of E_2 symmetry. In an arachno cluster of p atoms this gives $p - 2$ bonding L^π orbitals, one bonding S^σ orbital, and two pairs of $L^\pi/\bar{L}^\pi$ orbitals. Occupying all these orbitals gives $p + 3$ skeletal electron pairs, in agreement with electron-counting rules. As with nido clusters, the frontier pairs can be stabilized by extra hydrogen atoms (four to six atoms) around the open face.

A further comment is needed on low-symmetry clusters. Many nido clusters and all arachno clusters have low symmetry (C_{2v} or less). The analysis above applies precisely to the nido clusters of symmetry C_{nv}, where n is larger than 2; degenerate $L^\pi/\bar{L}^\pi$ pairs are obtained. In lower symmetries, degenerate E_1 and E_2 pairs are not possible, but pairs of orbitals that approximate to the degenerate pairs appear. Thus the arachno cluster $B_{10}H_{14}{}^{2-}$, of C_{2v} symmetry, will have four high-energy occupied orbitals, two of symmetries B_1 and B_2 (corresponding to E_1) and two of symmetries A_1 and A_2 (corresponding to E_2), all localized around the open face.

3. Frontier Orbital Pairs

The frontier orbital pairs are the highest energy occupied orbitals in both nido and arachno clusters and so are of great chemical interest. We shall ignore the contributions to these orbitals from the extra hydrogen atoms for the moment, since their main effect is to stabilize the frontier orbitals.

The frontier E_1 orbitals in a nido or arachno cluster belong to both L^π and $\bar{L}^\pi$ and are degenerate. The parity transformation maps one of the pair onto the other. When the missing vertex (or vertices) is centered at (0, 0), these conditions give E_1 orbitals of the form

$$\psi_{1c} = \sum_i (f(\theta_i))[(\cos\theta_i)p_i{}^\theta + (\sin\phi_i)p_i{}^\phi] \qquad (6)$$

$$\psi_{1s} = \sum_i (f(\theta_i))[-(\sin\phi_i)p_i{}^\theta + (\cos\phi_i)p_i{}^\phi] \qquad (7)$$

Similarly the frontier E_2 orbitals have the form

$$\psi_{2c} = \sum_i (g(\theta_i))[(\cos 2\phi_i)p_i{}^\theta + (\sin 2\phi_i)p_i{}^\phi] \qquad (8)$$

$$\psi_{2s} = \sum_i (g(\theta_i))[-(\sin 2\phi_i)p_i{}^\theta + (\cos 2\phi_i)p_i{}^\phi] \qquad (9)$$

The functions $f(\theta)$ and $g(\theta)$ describe the θ dependence of these orbitals. If we add the missing vertex (or vertices) to the cluster, the frontier orbitals must interact with the orbitals on this vertex (or vertices) strongly enough to produce the closo-cluster orbitals that are definitely bonding or antibonding. For this to occur, the $L^\pi/\bar{L}^\pi$ orbital pairs must have most of their electron density around the open face (the cluster ring), on atoms adjacent to the missing vertex (or vertices). Thus $f(\theta)$ and $g(\theta)$ must be large at the ring atoms and small elsewhere. The ring atoms usually occur in a small range of θ.

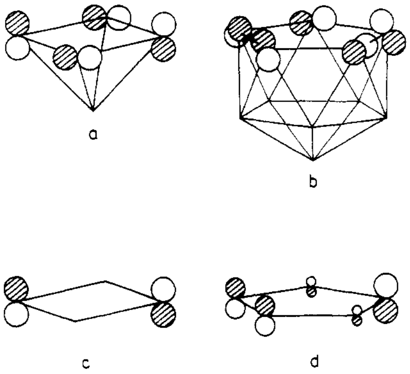

Figure 4. (a) E_1 $L^\pi/\bar{L}^\pi$ orbital in $B_5H_5{}^{4-}$. (b) E_1 $L^\pi/\bar{L}^\pi$ orbital in $B_{11}H_{11}{}^{4-}$ (open-face atom contributions only). (c) E_1 π orbital in $C_4H_4{}^{2-}$. (d) E_1 π orbital in $C_5H_5{}^-$.

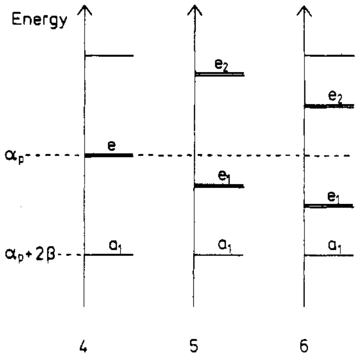

Figure 5. Hückel energies of four-, five-, and six-carbon-atom cyclic planar hydrocarbons.

Figure 4 shows $L^\pi/\bar{L}^\pi$ E_1 orbitals in $B_5H_5{}^{4-}$ and $B_{11}H_{11}{}^{4-}$. (In the latter case only the orbital contributions on the open face are shown.) It also shows the E_1 π orbitals in the planar hydrocarbon systems $C_4H_4{}^{2-}$ and $C_5H_5{}^-$; these orbitals are similar in form to the boron cluster frontier E_1 orbitals. The low-energy $p_0{}^\pi$ orbital in the boron clusters is similar to the A_1 symmetry π orbital in the cyclic hydrocarbons, completing the analogy.

The Hückel equations for the boron cluster open faces and the cyclic planar hydrocarbons have similar forms and solutions; Figure 5 shows the Hückel energies of four-, five-, and six-membered rings. We see that (i) the E_1 pair is always of lower energy than the E_2 pair and (ii) both E_1 and E_2 orbital energies decrease as ring size increases. These results are due to the nodal structure of the E_1 and E_2 orbitals and so apply even when the open face is nonplanar and the resemblance to the cyclic planar hydrocarbons is less marked.

4. Discussion of the TSH Model

We have already seen (previous papers[10] and above) that the TSH models of *closo*-, *nido*-, and *arachno*-boranes account for the deltahedral structures and electron-counting rules observed in these clusters, in a simple and easily visualized way.

Empirical rules show that the nido cluster is formed from the closo cluster by removing the highest coordination vertex (HCV). The arachno cluster is formed from the nido cluster by removing one of the vertices on the open face (adjacent to the first missing vertex), almost always the HCV on this face. These rules are explained by the discussion of the frontier orbital pairs above. The energy of these pairs decreases as the ring size increases, so in general the largest possible open face is energetically the most favorable. The rules involving the HCV give the largest possible open face.

The discussion so far has centered on the boron atoms of the boranes. In a cluster B_pH_q, p of the hydrogen atoms are outside the cluster, each attached to one boron atom by a conventional two-center bond. These exo hydrogen atoms can be ignored for cluster bonding purposes.[13] The other hydrogen atoms are found in the cluster surface. Wade[1] showed that it is necessary to include the electrons used in the bonds to these atoms in the total of cluster bonding electrons.

We can incorporate these extra hydrogen atoms by adding protons to the nido and arachno clusters $B_pH_p^{4-}$ and $B_pH_p^{6-}$. Williams[4] showed that some of the secondary rules of borane and carborane structure could be explained by assuming that the hydrogen atoms were found at the most "electron-available" sites. Applying this idea, we expect the extra protons to be found at the high electron density around the open face, parallel to and within the cluster sphere surface. This is precisely what is observed; extra hydrogen atoms are never found above the triangular faces of nido and arachno clusters, as occasionally happens in closo clusters.[14]

We saw above that the 1s orbitals on these hydrogen atoms stabilize the frontier orbitals, without altering the electron count. They do alter the electronic structure at the open face; thus only nido clusters without extra hydrogen atoms show a strong resemblance to the cyclic planar hydrocarbons.

The number of extra hydrogen atoms in a nido or arachno cluster can vary widely; for example, nido species with 11 vertices can have from zero to four extra hydrogen atoms on the open face. The number of extra hydrogen atoms is usually the number required to give a cluster with a total charge of 0, 1−, or 2−. Higher charged species are not stable. Positively charged species occasionally occur;[15] however, the reaction between a neutral hydride and a (solvated) proton is not usually favorable, and the extra hydrogen atom causes extra crowding around the open face. Protonation of negatively charged species is easier, since the electrostatic energy is reduced in the process.

The open face of $C_2B_9H_{11}^{2-}$ (the carbollide ion) is predicted to resemble the π system of the cyclopentadienyl anion $C_5H_5^-$ by the discussion above. This similarity was first suggested by Lipscomb[16] and demonstrated by the synthesis of carbollide complexes of transition-metal ions that resembled the metallocenes.[17,18] Many metallocarboranes[19,20] are now known; most can be regarded as complexes of nido or arachno clusters.[20] Experimental work[21] has shown that the carbollide and cyclopentadienyl anions bind in similar ways in these complexes; however, the discussion above suggests that the carbollide ion orbitals that bond to the metal ion are not perpendicular to the ring plane (as they are in the cyclopentadienyl ion) but inclined inward (see Figure 4b). Ab initio calculations[22] agree with this.

The $C_2B_7H_9^{2-}$ ion (the carbazapide ion) is a nido cluster with a nonplanar open face; nevertheless it forms a similar series of complexes with transition-metal ions,[18] showing a similar electronic structure. This suggests that our model of the electronic structure holds for clusters with both planar and nonplanar open faces.

There is some evidence[23-25] for a fourth series of boranes, called the hypho series and characterized by $p + 4$ pairs of skeletal electrons in a cluster of p boron atoms. Most of these clusters do not have rigid structures. They can no longer be treated plausibly as a small perturbation of an essentially spherical cluster, so the present approach is unlikely to give a useful account of them. No *hypho*-borane with more than six cluster atoms is known, so the series is not yet well established.

The compound B_8H_{12} is a peculiarity. It has a nido-cluster electron count but an arachno-cluster structure.[26] In this case the E_2 frontier orbitals of the arachno structure are not degenerate, so a closed-shell molecule with one of these orbitals unfilled can occur. Williams[4] suggests that the nido structure of B_8H_{12} is unstable because the bridging hydrogen atoms are in energetically unfavorable positions; thus $C_2B_6H_{10}$, with two fewer bridging hydrogen atoms, might adopt the nido structure. In the arachno geometry, the B_8H_{12} molecule does have a comparatively low-energy LUMO of the expected symmetry[27] and readily accepts another pair of electrons (for example, it is stabilized in ether solution[28]), in keeping with the expected arachno-cluster orbital structure.

5. Conclusions

Tensor surface harmonic theory used in the way described above explains the primary structural and electronic features of the closo-, nido-, and arachno-cluster series found in the boranes and carboranes. The electron-counting rules observed in these clusters arise automatically from the theory.

The method gives an orbital model of the electronic structure of the cluster in which all the cluster orbitals can be readily derived. These orbitals should be close approximations to the correct molecular orbitals.[10] The orbitals take similar forms in all the clusters and are readily visualized. The orbital energies can be calculated with any suitable approximation for the overlap integrals; previous papers[10] show how general expressions for the Hückel energies and information on bonding and antibonding character can rapidly be derived.

The theory also gives useful expressions for the highest occupied molecular orbitals in nido and arachno clusters. From these we find that a nido cluster without bridging hydrogen atoms (such as $C_2B_9H_{11}^{2-}$) has an electronic configuration on the open face similar to that of the π system of a cyclic planar hydrocarbon such as $C_5H_5^-$, a similarity demonstrated in the chemistry of these ions. The high electron density on the open faces of nido and arachno clusters explains the positioning of the bridge and endo hydrogen atoms of these clusters; these extra hydrogen atoms stabilize the highest occupied molecular orbitals and hence the whole cluster.

Further work in this field is necessary to assess the usefulness of this model for the boron hydride clusters. The predictions on orbital structure are precise enough to be tested by either SCF calculations or pertinent physical data (where these are available). At this stage only qualitative agreement with these

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reference data can be expected, although the model has potential for considerable refinement, for example, by the use of expressions for the energy integrals better than the simple Hückel approximations. Some of our preliminary work suggests that the agreement with SCF results is good for the closo clusters.

TSH theory is not limited to the boranes or even to the first-row elements. It is of particular value in dealing with transition-metal clusters, since it greatly reduces the number of orbitals to be considered at one time. It should be possible to use the theory to model many different types of metal cluster in the same sort of way as we have used it here to model the main types of borane cluster.

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Contribution from the Istituto Chimica Generale, Università di Pisa, 56100 Pisa, Italy, CAMEN, 56010 S. Piero a Grado, Pisa, Italy, and the Departments of Chemistry, University of British Columbia, Vancouver, B.C., Canada V6T 1Y6, and Royal Roads Military College and University of Victoria, Victoria, B.C., Canada V8W 2Y2

Synthesis and Mössbauer Spectroscopic Studies of Carbonyl Derivatives of (Phthalocyaninato)iron(II)

FAUSTO CALDERAZZO,*[1a] SERGIO FREDIANI,[1b] BRIAN R. JAMES,[1c] GUIDO PAMPALONI,[1a] KENNETH J. REIMER,*[1d] JOHN R. SAMS,*[1c] ANNA MARIA SERRA,[1b] and DARIO VITALI[1a]

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The monocarbonyl complexes of (phthalocyaninato)iron(II), FePc(CO)L, where L = *N,N*-diethylacetamide, pyridine, piperidine, hexamethylphosphoramide, and triphenylphosphine oxide, have been prepared and characterized, as has the dicarbonyl compound $FePc(CO)_2$, which was isolated after exposing FePc in a hydrocarbon solvent to a high pressure of CO. The Mössbauer spectroscopic parameters, ΔE_Q and δ, both decrease upon replacement of an axial ligand of the bisadducts, $FePcL_2$, by CO to give FePc(CO)L. These changes are consistent with a decrease in mean axial bond distances upon carbonylation and a concomitant increase in s-electron density along the *z* axis. The electronic basis of these structural modifications requires consideration of both cis and trans effects.

Introduction

(Phthalocyaninato)iron(II), FePc,[2] has been studied extensively as a model for the heme group.[3] Complexes containing the FePc moiety, unlike ferrous porphyrins, do not undergo reversible 1:1 O_2 binding;[4] however, both classes bind CO reversibly. Solution studies have considered the reaction of FePc with CO in Me_2SO,[5] in concentrated sulfuric acid,[6] and in the presence of nitrogen Lewis bases.[7] Our groups have reported independently the isolation of the carbonyl complexes FePc(CO)L, where L = nitrogen-,[8] oxygen-, and sulfur-donor[9,10] ligands, and the solid-state structure of the dimethylformamide adduct FePc(CO)DMF[10] has been determined. This paper describes the synthesis and properties of several additional monocarbonyl complexes, together with the new dicarbonyl derivative, $FePc(CO)_2$, and then discusses the bonding in these compounds as investigated by Mössbauer spectroscopy.

The Mössbauer technique provides a useful probe for the electronic structure of the central metal, and several reports have attempted to correlate Mössbauer parameters with the σ- and π-bonding characteristics of metalloporphyrin complexes.[11] The large decrease in both isomer shift δ and quadrupole splitting ΔE_Q, observed upon replacement by CO of an amine ligand in the diamine complexes $FePL_2$ (P = dianion of a porphyrin or phthalocyanine ligand), to give the monocarbonyl derivatives FeP(CO)L, has attracted considerable attention.[10-14]

The preliminary reports on the Mössbauer spectra of FeP(CO)L complexes[10,13] attributed the changes in δ and ΔE_Q to two different causes: (1) a substantial cis effect, whereby carbonylation causes pronounced changes in the Fe–P bonding,[13] and (2) a significant trans effect relating changes in the Mössbauer spectroscopic parameters to the nature of the ligand trans to CO.[10] In this paper we will use the expanded data base of the phthalocyaninato complexes to consider these arguments in more detail.

Experimental Section

Syntheses. Unless otherwise stated, all operations were carried out under an atmosphere of prepurified argon or nitrogen. Solvents were purified by conventional methods prior to use.

The syntheses of FePc[9,10] and some of the carbonyl adducts FePc(CO)L[8,10] were carried out as reported earlier. Only the preparations of the new complexes are described here. Occlusion of solvent in the crystals of these materials is a characteristic that has been noted previously.[10]

Preparation of FePc(CO)DEA. FePc (1.24 g, 2.2 mmol) suspended in DEA (20 mL) was stirred under an atmosphere of CO for about 10 h. The violet microcrystalline solid was filtered from the blue solution and dried in vacuo (1.34 g, 74% yield). Anal. Calcd for FePc(CO)DEA·DEA: C, 65.4; H, 5.1; N, 17.0. Found: C, 65.5; H, 5.0; N, 17.3.

The solid compound is stable in air, soluble in DEA with a deep blue color, and slightly soluble in acetone, dichloromethane, and

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(1) (a) Universtiy of Pisa. (b) CAMEN. (c) University of British Columbia. (d) Royal Roads Military College and the University of Victoria.

(2) Abbreviations: Pc, TPP, OEP = the dianions of phthalocyanine, tetraphenylporphyrin, and octaethylporphyrin, respectively; DEA, *N,N*-diethylacetamide; DMF, *N,N*-dimethylformamide; Me_2SO, dimethyl sulfoxide; HMPT, hexamethylphosphoramide; *n*-$PrNH_2$, *n*-propylamine; pip, piperidine; py, pyridine; THF, tetrahydrofuran; THT, tetrahydrothiophene.

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