metal σ orbital, described in the previous paragraph, the relativistic level shifts are small and are apparently well described by the simpler quasi-relativistic calculations. This is an important point, since it helps to validate the use of these simpler calculations in other molecules with metal–metal bonds. For detailed conclusions on photoelectron intensities and angular distributions, however, it is expected that results of the type described here will be most useful.

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(16) An earlier calculation on $Re_2Cl_8^{4-}$ has been reported in which the spin–orbit interaction is added at the CI step: Hay, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 7007.

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Use of the Bireciprocal Length–Energy Relationship To Predict the Structures of Boron Hydrides and the Structural Analogy between Boron Hydrides and Other Atom Clusters

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Recently we[1] developed a new approach for the prediction of the structures of *closo*-boron hydrides $B_nH_n^{2-}$, in which each boron atom is considered to bond directly to all other boron atoms, the interaction depending only on the interatomic distance. A simple bireciprocal equation was used to relate energy u to internuclear distance d: $u = d^{-x} - d^{-y}$. The total energy is then $U = \sum u$. A good fit with experimental structures was found for low values of x and y, typical values being $x = 2$ and $y = 1$. The simplicity of this model allows the rapid assessment of a large number of complex molecular polyhedra in which the geometric parameters are free to vary in order to reach a minimum energy and to map out more clearly the potential energy surfaces needed to understand the intramolecular rearrangements of these molecules.

Housecroft and Wade[2] have criticized this approach by raising four main arguments that are now discussed in turn. Then follows a short discussion on the inadequacy of the supposed structural analogy between the boron hydrides and other atom clusters that is the basis of "Wade's rules".

(1) The first criticism is that the variation of energy U with size of the $B_nH_n^{2-}$ cluster is misleading, and it was pointed out that U/n is a linear function of n. There are a number of minor errors in Housecroft and Wade's work that should be corrected before dealing with the substance of this criticism:

(a) The U values cited[2] for $B_8H_8^{2-}$ and $B_{12}H_{12}^{2-}$ are correct, but they have been incorrectly converted to U/n values.

(b) The U values cited[2] for $B_6H_6^{2-}$ and $B_{10}H_{10}^{2-}$ are incorrect, the correct values being −3.6928 and −10.6933, respectively.[3]

(c) Housecroft and Wade have quoted the slope of the U/n vs. n line as equal to $0.133n$, which is a miscalculation or misprint; from their figures the slope is $-0.113n$. (The sign of U/n given in their equations is also incorrect.) If the correct values for U are used for all values of n from 6 to 12,[1,3] the relationship becomes

$$U/n = -0.113n + 0.058$$

(d) This linear relation between U/n and n corresponds to a quadratic relation between U and n and does not lead to "the implication that all these closo anions $B_nH_n^{2-}$ use their skeletal electron pairs with precisely the same efficiency".[2]

However the important point is that we believe that it is a gross misuse of our approach to compare bonding energies for differently sized clusters. In spite of categorical statements in Housecroft and Wade's paper, we did not advocate this application. The simple bireciprocal energy expression $u = d^{-2} - d^{-1}$ is normalized neither with respect to energy units nor with respect to length units, and it was clearly stated[1] that both u and d are in arbitrary units. Normalization procedures, for example using the expression $u = a(d^{-2} - cd^{-1})$, lead to different values of the constants a (which normalizes with respect to energy) and c (which normalizes with respect to distance) for every cluster (see below).

(2) The second criticism is that the double-reciprocal potential does not lead to the correct size of the cluster. This comment arises from a misunderstanding of the properties of a bireciprocal expression and from a misreading of the original work. A simple bireciprocal potential $u = d^{-x} - d^{-y}$ cannot be used to predict the *size* of a molecule but can be used to predict its *shape*, the shape being defined either by the ratios of the bond lengths or by the angular coordinates plus the ratios of the radial coordinates. All distances are therefore in arbitrary units as clearly stated in the original work,[1] but these have been consistently misread as angstroms by Housecroft and Wade.

If desired, the calculated size of the cluster can be varied by modifying the potential to $u = d^{-2} - cd^{-1}$. The effect of decreasing c is to expand the u vs. d plot uniformly along the distance axis, leading to an increase in calculated size of the cluster but without change in shape. The known sizes of *closo*-$B_nH_n^{2-}$, where n = 6, 8, 9, 10, and 12, obtained from experimental crystal structures leads to

$$c \sim 1.30 - 0.033n$$

where the distances are now in angstroms.

(3) The third comment is the rather obvious observation that the relative number of cross-polyhedral terms increases as the number of atoms in the cluster increases.

In our approach it is the cross-polyhedral interactions that tend to make the cluster more spherical whereas the surface-polyhedral interactions tend to make the edge lengths of the polyhedron more equal. The experimental structures of $B_nH_n^{2-}$ molecules, with the exception of $B_6H_6^{2-}$ (see below), represent the balance between these two types of interaction and are best modeled by the particular bireciprocal potential we have chosen. The $B_6H_6^{2-}$ cluster is different from the other clusters as the octahedron is a regular polyhedron with all vertices equidistant from the polyhedron center and all edge lengths identical. There is therefore no conflict between the cross-polyhedral and surface-polyhedral interactions, and a regular octahedral structure is predicted for all values of x and y in the bireciprocal energy expression.

(4) The fourth comment concerns the partitioning of the total energy of $B_8H_8^{2-}$, $B_9H_9^{2-}$, and $B_{10}H_{10}^{2-}$ into the energy associated with the individual boron atoms. They find that the atoms with the highest coordination number are associated with the highest energy. Unfortunately the figures used to reach this conclusion are seriously in error. For example, they calculated that the five-coordinate atoms in $B_8H_8^{2-}$ are 36.6% more strongly bonding than the four-coordinate atoms, al-

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though the correct figure is only 2.1%. The corresponding figures for $B_9H_9^{2-}$ are 3.4% (Housecroft and Wade) and 2.1% (correct) and for $B_{10}H_{10}^{2-}$ are 3.2% (Housecroft and Wade) and 2.4% (correct). It should also be noted that because of the large range of boron–boron distances in these molecules the definition of coordination number becomes rather arbitrary. Thus each of the "five-coordinate" boron atoms in $B_8H_8^{2-}$, $B_9H_9^{2-}$, and $B_{10}H_{10}^{2-}$ has two of the boron atoms approximately 10% further away than the other three. However, since this "coordination number" only measures the number of polyhedral edge interactions and not the cross-polyhedral interactions, the correlation between "coordination number" and bonding energy is not very significant for our model. A more direct correlation is that the boron atoms closest to the center of the cluster will be the most strongly bonded to the cluster. It is inevitable from simple geometric arguments that these most strongly bonded atoms with the smallest radial coordinates will have the highest "coordination number".

Discussion

The results obtained by using the bireciprocal length–energy relation may, to quote Housecroft and Wade, "have considerable value for exploring the relative energies of different hypothetical structures for specific compounds and for considering the energetics of rearrangements". They then continue: "However, some features that appear to have been overlooked make their approach inappropriate for some of the other applications advocated for it." We advocated no other applications for this approach in our original paper![1] However, we have since shown that our approach can be extended to other *closo*-$B_nH_n^{2-}$ clusters[3] and to nido clusters $B_nH_n^{4-}$, arachno clusters $B_nH_n^{6-}$, planar aromatic molecules, and some hypho clusters $B_nH_n^{8-}$.[4] The calculated stereochemistries compare reasonably favorably with those obtained from quantum-mechanical MNDO calculations[5] and PRDDO calculations,[6] but we would not claim that our method is the ultimate answer to the theoretical problems concerning these compounds. A real advantage of the present approach is its utility. Molecular shape can be rapidly calculated completely free of symmetry constraints and qualitative information obtained about the barriers to intramolecular rearrangement and possible transition states.

The polyhedral structures observed for some clusters of other p-block elements have a superficial resemblance to the structures of the boron hydrides, particularly the closo compounds. This relationship is the basis of the electron-counting system known as "Wade's rules".[7] However, modeling these structures using a bireciprocal length–energy relationship reveals significant differences between these clusters. For example, clusters of the heavier p-block elements Sn_5^{2-},[8] Pb_5^{2-},[8] $TlSn_8^{3-}$,[9] and $TlSn_9^{3-}$ [9] have the electron count appropriate for closo compounds if it is assumed that one nonbonding pair of electrons is attached to each metal atom but have structures with more equal atom–atom distances around the surface of the cluster, corresponding to a somewhat "harder" potential: $x \sim 4, y \sim 1$ or $x \sim 3, y \sim 1.5$.

Extension of these calculations demonstrates that the structural analogy between boron hydrides and transition-metal complexes[7] is very tenuous. For example, the metal–metal distances in multinuclear transition-metal carbonyls are approximately equal, in sharp constrast to the atom–atom distances in clusters of the p-block elements. The larger transtion-metal clusters are accordingly much less "spherical" than the boron hydride clusters and in many cases correspond to a close-packed arrangement of metal atoms. For example, all nine metal–metal bond lengths in $[Os_5(CO)_{16}]$[10] are similar, and the structure should be considered as two Os_4 tetrahedra sharing a common face rather than as an analogue of the trigonal-bipyramidal $B_5H_5^{2-}$. The structure of $[Os_5(CO)_{16}]$ can be modeled by using the bireciprocal length–energy relationship with $x \sim 10, y \sim 4$. Similarly, the structure of $Cs_3[Rh_9(CO)_{19}]$[11] can be modeled with $x \sim 10, y \sim 4$ and should be considered as two Rh_6 octahedra sharing a face rather than as an analogue of the tricapped trigonal-prismatic $B_9H_9^{2-}$. Only in the case of octahedral clusters is there a good structural correspondence between boron hydride clusters and transition-metal clusters as only in octahedral clusters is the structure independent of the values chosen for x and y.

The structural analogy between boron hydrides and transition-metal clusters becomes even less useful for nido and arachno compounds.

Finally, we regret that we were unaware of the work by Housecroft, Snaith, and Wade,[12] who proposed that the energy of a boron–boron bond is given by a fourth-power relation, $u \propto d^{-4}$, and by Housecroft, O'Neill, Wade, and Smith,[13] who proposed $u \propto d^{-4.6}$ for metal–metal bonds in transition-metal carbonyls.

Registry No. Boron hydride, 11129-13-8.

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