

A GRAPH-THEORETICAL INTERPRETATION OF THE BONDING TOPOLOGY IN POLYHEDRAL BORANES, METAL CLUSTERS AND ORGANIC CATIONS

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Introduction

The structures adopted and the bonding present in a wide range of cage and cluster species, including the boranes, the carboranes, metal clusters and certain organic cations, have been the focus of considerable attention over the past two decades. We report here continuing work (1) which has revealed how the structure and stability of these species may be analysed and interpreted in terms of their bonding topology. Many boron cage molecules exhibit an unusually high chemical stability coupled with a rather low chemical reactivity. Examples would include the dianions (2, 3)  $B_nH_n^{2-}$ , where  $6 \leq n \leq 12$ , and also the carboranes (4)  $C_2B_{n-2}H_n$ , where  $5 \leq n \leq 12$ . Moreover, it has been demonstrated (5) that close analogies exist between the skeletal bonding in boron cage compounds and that found in metal clusters, especially those of high nuclearity (6). More recently, it has been shown that the general treatment outlined here may be applied to certain organic cations (7), such as the  $(CH)_5^+$  cation and the  $(CH)_6^{2+}$  dication.

All of the species referred to above may be visualised as being constructed from triangulated, polyhedral systems, which for convenience we shall term deltahedral systems. For systems having a total of  $n$  vertex atoms, LCAO-MO calculations by the Extended Hückel method have led to results consistent with the presence of  $n + 1$  skeletal bonding orbitals(8). Upon filling these orbitals the system acquires a total of  $2n + 2$  skeletal bonding electrons. In our treatment of such systems we demonstrate how the  $n + 1$  bonding orbitals may be generated directly from the bonding topology. We also extend our analysis to systems having other than triangular faces. It is our belief that this approach may well prove to be of value in the further understanding of the species discussed and possibly also in the development of polymers of high thermal stability and catalysts of novel reactivity based on these species.

#### Algebraic Graph Theory

The basic tool which we shall employ in our analysis is algebraic graph theory (9). It is well-known that the topology of a chemical species may be formally represented by a graph, and that from the adjacency matrix of this graph one may determine the orbital energy scheme for the species within the simple Hückel one-electron framework (10). In many semi-empirical theories a satisfactory treatment of electronic structure is possible from a purely topological analysis of the system, for the integrals not directly determinable from the topology remain as parameters in the equations. It has been shown by Ruedenberg (11) how the topological effects may be separated out from the usual secular equation

$$|H - ES| = 0 . \quad (1)$$

The energy and overlap matrices are first resolved as follows:

$$H = \alpha I + \beta A \quad (2)$$

and

$$S = I + SA , \quad (3)$$

where  $I$  is the unit matrix,  $\alpha$  and  $\beta$  are the Hückel Coulomb and resonance integrals respectively, and  $A$  is the adjacency matrix of the graph representing the species in question. Substitution of equations (2) and (3) into equation (1) then leads to the result

$$|A - \lambda I| = 0 , \quad (4)$$

where  $\lambda$  corresponds to the energy eigenvalues via the relationship

$$E = \frac{\alpha + \lambda\beta}{1 + \lambda S} .$$

The eigenvalues of the adjacency matrix thus yield the Hückel energy levels of the species.

#### Polygonal and Polyhedral Species

In both the polygonal  $C_nH_n$  systems, such as benzene, and the polyhedral boranes and carboranes on  $n$  vertices, the four valence orbitals associated with each vertex atom may be classified into one external orbital, two equivalent twin internal orbitals, and one unique internal orbital. The external orbitals are used in each case to form one  $\sigma$  bond from the vertex atom to an external atom or group. The twin internal orbitals mutually overlap to produce either a polygonal or polyhedral framework of vertex atoms, this interaction leading to the splitting of the  $2n$  orbitals into  $n$  bonding and  $n$  anti-bonding orbitals. Global mutual overlap of the  $n$  unique internal orbitals generates additional bonding and anti-bonding orbitals, with relative ener-

gies which may be determined from the eigenvalues of the matrix A.

In order that facility be gained in the application of our approach, we start with the familiar example of the benzene molecule. Benzene may be viewed as the two-dimensional analogue of the three-dimensional deltahedral species. In benzene the external and twin internal orbitals are  $sp^2$  hybrids whereas the unique external orbital is of p type. As illustrated in Figure 1, the twelve twin internal orbitals interact pairwise to form six bonding and six anti-bonding orbitals, corresponding to the  $\sigma$  bonding and the  $\sigma^*$  anti-bonding orbitals of the six carbon-carbon bonds in the usual MO treatment (12). The six unique internal p orbitals interact to give the familiar eigenvalue spectrum of the planar  $C_6$  hexagon, producing three  $\sigma$  bonding orbitals and three  $\sigma^*$  anti-bonding orbitals.

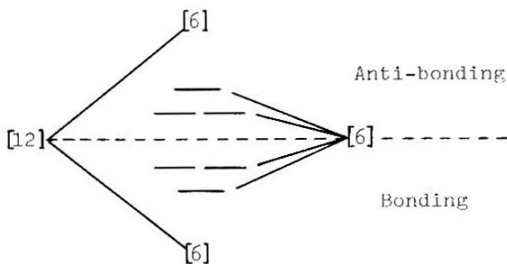


Figure 1. The energy level pattern in the planar  $C_6$  hexagon, i.e. in benzene.

An entirely analogous treatment may be applied to the deltahedral boranes and carboranes. The external and unique internal orbitals may now be considered as  $sp$  hybrids and the twin internal orbitals as p orbitals. Pairwise interaction between the  $2n$  twin internal orbitals, which is responsible for the surface bonding in

the polyhedron, leads similarly to  $n$  bonding and  $n$  anti-bonding orbitals. Such pairwise interaction is possible whenever the polyhedron contains at least one Hamiltonian circuit (13); all of the deltahedra known in polyhedral borane and carborane chemistry may be readily shown to contain more than one Hamiltonian circuit. The unique internal orbitals are directed inward and interact at the centre of the deltahedron. As a reasonable first approximation we assume that this interaction at the core may be represented by the complete graph  $K_n$  (13).

#### Energy Level Patterns

It is known (9) for all  $K_n$  graphs that the eigenvalue spectrum has one positive eigenvalue equal to  $n - 1$  and that the remaining  $n - 1$  are all negative and equal to  $-1$ . From this eigenvalue pattern we may now suppose that the interaction of the unique internal orbitals at the core will yield one new bonding orbital and  $n - 1$  new anti-bonding orbitals. Upon summing all the bonding and anti-bonding orbitals in a deltahedral species, we arrive at the following table:

Description of Bonding Type	B.O.	A.B.O.
Surface: $2n$ twin internal orbitals	$n$	$n$
Core: $n$ unique internal orbitals	$1$	$n - 1$
Total:	$n + 1$	$2n - 1$

Our table reveals clearly that the  $n$  bonding orbitals arising from the surface bonding and the single bonding orbital originating from the core interaction together give a total of  $n + 1$  bonding orbitals for any chemically feasible deltahedron. Upon fill-

ing these orbitals with electrons, one obtains in all  $2n + 2$  bonding electrons, a result in accord with quantum chemical calculations (8).

The analogy existing between the two-dimensional polygonal systems and the three-dimensional polyhedral systems is now apparent. Both may be analysed using algebraic graph theory, and the only significant difference between the two lies in the type of graph used to represent the interaction of the unique internal orbitals of the vertex atoms. Whereas for polygonal species cyclic graphs  $C_n$  have to be used, in the case of deltahedral systems complete graphs  $K_n$  are appropriate. This seemingly minor difference is responsible for a major difference in the energy level patterns which are produced. By a liberal extension of classical terminology and on the basis of our analysis, we propose that polygonal systems be regarded as two-dimensional aromatic systems and that polyhedral systems be interpreted as three-dimensional aromatic systems. In passing it should also be mentioned that as the cyclic  $C_n$  graphs and the complete  $K_n$  graphs are the only types of graph which are regular for any number of vertices, it follows that no other bonding topology of the unique internal orbitals of a type fundamentally different from those considered is possible.

#### Polyhedral Clusters

In addition to the deltahedral systems examined above, we may also consider the bonding topology in electron-rich polyhedral clusters, which contain more than  $2n + 2$  skeletal electrons, and in electron-poor polyhedral clusters, which contain less than  $2n + 2$  skeletal electrons. The electron-rich systems have been discussed in the literature, especially in the case of boron hydride derivatives (14). In fact, there are well-established families of nido and of

arachno compounds containing respectively  $2n + 4$  and  $2n + 6$  skeletal electrons. In contrast to the deltahedra considered thus far, nido systems will contain one hole, i.e. one non-triangular face, and arachno systems will contain two holes or one large bent hole. Each successive addition of electron pairs to a  $2n + 2$  deltahedron thus results in a puncture of the deltahedral surface. The process by which this occurs we shall refer to as polyhedral puncture. An alternative way of viewing this process is to envisage the excision of one or more of the vertices along with all of the edges leading from them; such a process we will designate as polyhedral excision.

In applying our analysis to nido systems, it is observed that the vertex atoms of the nido polyhedron may be divided into two sets. These are the border atoms which form the border of a hole and the interior atoms which form only triangular faces. In the square pyramid, for instance, the four basal vertices form the border vertices since they border on the square hole, whilst the apical vertex is the only interior vertex. Experimental results (15) suggest that the external and twin internal orbitals of the border vertex atoms should be taken to be  $sp^2$  hybrids; the unique internal orbitals will thus be p orbitals. For the interior vertex atoms we shall associate  $sp$  hybrids with the external and unique internal orbitals, and p orbitals with the twin internal orbitals. We now suppose that of the total of  $n$  vertices  $v$  will be interior vertices for a given nido structure. There are actually three differing types of interaction among the internal orbitals, which generate bonding and anti-bonding orbitals as indicated in the table overleaf. The results are also presented pictorially in Figure 2.

Description of Bonding Type	B.O.	A.B.O.
$2(n - v)$ border and $2v$ interior twin internal orbitals in surface	$n$	$n$
$v$ unique internal orbitals of interior atoms at core	$1$	$v - 1$
$n - v$ unique internal orbitals of border atoms over surface of hole	$1$	$n - v - 1$
Total	$n + 2$	$2n - 2$

The first two types of interaction are the same as those occurring in deltahedral systems, whereas the third type can clearly occur only in systems having at least one hole. It is of interest to note here that the second and third interactions always produce exactly one new bonding orbital each, irrespective of the values assumed by  $v$  and  $n - v$  (provided, of course, that they are both greater than one). This is because any complete graph  $K_n$  can have only one positive eigenvalue for all  $n$ , as pointed out earlier. As a direct consequence, it may be seen that the total number of bonding orbitals for all nido systems is always  $n + 2$ . The number of skeletal bonding electrons will accordingly be  $2n + 4$ , in agreement with experimental observation.

Upon continuing the process of polyhedral puncture, deltahedral fragments containing two or more holes are produced. In our analysis the treatment for each new hole is, however, exactly the same as that described for the nido structures. In fact, every time a new hole is formed there will be a new splitting of the core interaction of the unique internal orbitals into an interaction across the hole and a core interaction of the remaining interior atoms. Each new hole will



thus necessitate the introduction of one new complete graph, which in turn will be responsible for the addition of one new bonding orbital to the overall energy level pattern. In other words, each new hole will effectively contribute two new electrons to the total number of skeletal electrons. Arachno systems having two holes, for instance, will accordingly have a total of  $2n + 6$  skeletal electrons. An actual example of polyhedral puncture is provided by the addition of two electrons to the closed icosahedral carborane  $\alpha\text{-C}_2\text{B}_{10}\text{H}_{12}$  to give the nido dianion  $\text{C}_2\text{B}_{10}\text{H}_{12}^{2-}$  containing a hexagonal hole (16). It is not surprising that the reagent for effecting this chemical transformation is sodium metal in the presence of naphthalene, an excellent source of electrons.

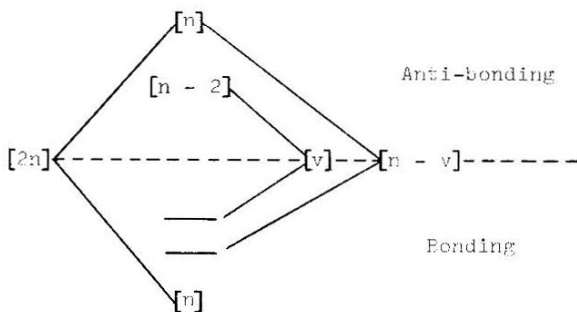


Figure 2. The energy level pattern for a nido polyhedral cluster having  $n$  vertices,  $v$  of which are interior vertices.

#### Capped Deltahedra

The properties of electron-poor polyhedral clusters containing less than  $2n + 2$  skeletal electrons have not been as thoroughly investigated as those of their electron-rich counterparts. This is apparently be-

cause representatives of this class of compound are much rarer. To understand these systems we note first that for deltahedra containing 7, 8, 10 and 11 vertices two alternative closed deltahedral structures are possible. In each case one of the structures is actually found in deltahedral boranes whilst the other is not. The unfavored structure on  $n$  vertices may be partitioned into a tetrahedron and a smaller deltahedron having  $n - 1$  vertices, such that the tetrahedron and the deltahedron have one face in common. Thus, the bicapped octahedron on 8 vertices may be partitioned into a tetrahedron and a capped octahedron on 7 vertices. The latter may in turn be further partitioned into a tetrahedron and an octahedron on 6 vertices. Yet further partitioning is, however, not possible. The deltahedra which can be partitioned may be visualized as having one or more capped triangular faces. Deltahedra for which capping is not possible contain no vertices of degree three; all of their vertices are of degree four or higher.

We come now to the structure of the tetrahedron itself, which is unusual in that it has twelve skeletal electrons. In deltahedra where the bonding is delocalised we have indicated that there will be a total of  $2n + 2$  skeletal electrons. In such systems where the bonding is localised, however, there must be a total of  $2k$  skeletal electrons, where  $k$  is the number of edges, as each edge is now associated with one electron pair bond. As localised systems have simple two-electron bonds directed along the edges whereas delocalised systems have global delocalisation, it is evident that in general  $2k \neq 2n + 2$ . In fact, the number of skeletal electrons may be used as an indicator of the type of bonding present in deltahedral systems. Because the tetrahedron has

2k, i.e. twelve, skeletal electrons, the bonding in it must be localised. This conclusion goes a long way in accounting for the special stability of this particular structure.

For the deltahedral systems having capped faces we make the reasonable assumption that the bonding in the tetrahedral chamber constituting the cap will be localised. In the polyhedral boranes and carboranes the vertex atoms have only four valence orbitals, one of which is used in the bonding to the external substituent. This leaves just three orbitals to participate in the delocalisation in the deltahedron. If now one face of the deltahedron is capped, four orbitals are required from each of the vertex atoms forming the capped face for the cluster bonding: three for the delocalised bonding in the deltahedron and one for the localised bond to the cap. In the case of boron and carbon atoms not all of the four bonding orbitals can be so oriented without introducing considerable strain into the system. As a general rule therefore such vertex atoms are not found at the vertices of capped faces. Certain capped deltahedra, such as the bicapped octahedron, for which the capped structure appears to be stable, represent exceptions to this general rule.

#### Transition Metal Clusters

Unlike boron and carbon atoms, transition metal atoms which form clusters have up to nine bonding orbitals available, for they can make use of d orbitals in addition to the s and p orbitals. Transition metal atoms can thus appear at the vertices of capped triangular faces in deltahedra. Two examples of capped transition metal clusters are the osmium carbonyl  $\text{Os}_6(\text{CO})_{18}$  based on a bicapped tetrahedron (17) and the rhodium carbonyl anion  $\text{Rh}_7(\text{CO})_{16}^{3-}$  based on a

capped octahedron (18). Both of these clusters exhibit considerable bonding flexibility depending upon whether the vertex metal electron pairs are involved in the cluster bonding or appear rather as lone pairs. In summary, it is evident that the analogy existing between transition metal atoms and boron or carbon atoms as vertex atoms in polyhedral clusters breaks down when capped deltahedra are considered. Such polyhedra require some vertex atoms which contribute four or more internal orbitals to the skeletal bonding.

Detailed examination of the two cited capped transition metal clusters reveals that their bonding may be understood if the cap is assumed to contribute the same number of electrons to the central polyhedron as if it were a vertex of that polyhedron. However, since the cap participates only in localised bonding and is located above the surface of the central polyhedron, it cannot contribute any new internal orbitals to affect the delocalisation of the central polyhedron. Capping would thus appear to be a suitable mechanism to contribute electrons to a central polyhedron without contributing any new bonding orbitals. It thus seems to be a good remedy for electron poverty. In fact, both  $\text{Os}_6(\text{CO})_{18}$  and  $\text{Rh}_7(\text{CO})_{16}^{3-}$  are electron-poor clusters containing  $2n$  rather than  $2n + 2$  skeletal electrons. An even simpler example of this behaviour is provided by the trigonal bipyramid, which may be considered as a capped tetrahedron. Both the tetrahedron and the trigonal bipyramid require 12 skeletal electrons for stability. This is consistent with the notion that the cap in the trigonal bipyramid contributes the usual number of skeletal electrons but no new bonding orbitals. The bonding topology in many other more exotic metalloboranes

and metallocarboranes may be similarly interpreted by means of the general principles outlined here (1).

#### Some Organic Cations

The structures adopted by organic cations consisting only of CH groups have been at the centre of much controversy over the past decade. It came as a surprise in 1972 when theoretical calculations predicted a square pyramidal structure for the  $(\text{CH})_5^+$  cation rather than a planar structure. Subsequent experimental work confirmed that these calculations were correct (19). Investigations on the  $(\text{CH})_6^{2+}$  dication further demonstrated that a description in terms of two-electron three-centre bonds would be inadequate. Preparative work again established that this species adopts a non-planar, non-classical structure which is also pyramidal (20). In this latter instance the bonding topology involves a hexa-coordinated carbon atom, a feature normally encountered only in the domain of organometallic chemistry. It is our opinion that such observations can be understood in terms of the theory we have expounded above. Work in this area is at present underway (7).

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