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GRAPH-THEORETICAL ANALYSIS OF THE BONDING TOPOLOGY IN POLYHEDRAL ORGANIC CATIONS

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Abstract—It is shown that in several cases where planar delocalisation in organic cations would result in the formation of an anti-aromatic system, polyhedral delocalisation is the form of bonding actually preferred. This explains, for instance, why organic cations in such cases adopt cage-like structures. A full graph-theoretical analysis, similar to one previously published[12] for polyhedral boranes, carboranes and metal clusters, indicates that the nido structure for $(CH)_5^+$ may readily be accounted for. Moreover, in the case of the dication $(CH)_6^{2+}$ the fact that its energy minimum also corresponds to a nido structure is explained. In fact, no closo- or arachno-type structures appear to be possible for organic cations. A number of structural predictions concerning these species are given in the conclusion.

The structures adopted by organic cations consisting only of CH groups have been the focus of much interest and speculation over the past decade. In 1972, for instance, it came as something of a surprise to organic chemists when Stohrer and Hoffmann concluded,[1] on the basis of a theoretical treatment using Extended Hückel Theory, that the energy minimum for the $(CH)_5^+$ cation does not correspond to any of the planar classical structures I to III illustrated in Fig. 1. The structure they proposed was rather a cage structure in the form of a square pyramid, namely the structure V in Fig. 1. Analogous pyramidal structures were already known or had at least been postulated within the realm of borane and carborane chemistry.[2] The surprise deepened when experimental proof was presented by Masamune *et al.*[3,4b] that the actual structure of the cation is indeed that represented by V. Further theoretical calculations using a variety of differing methods later confirmed[5] that structure V is in fact more stable than those of structures I–III. A fourth classical structure is even possible for this cation,[6] though this was not considered in any of the theoretical treatments. As a vinylic cation, however, this structure, depicted as IV in Fig. 1, is likely to have a higher energy than that for the structures I–III. Accordingly, we shall not enter into further discussion of it in this work.

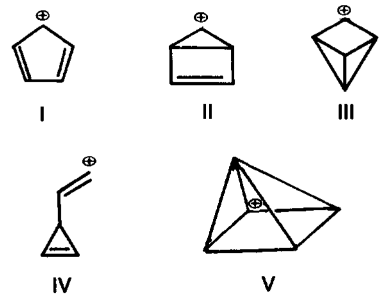


Fig. 1. Structures for $(CH)_5^+$ where each vertex represents a CH group.

A number of related pyramidal cations with bis-homo-$(CH)_5^+$ structures were subsequently prepared by Masamune *et al.*[4] and by Hart *et al.*[7,8], e.g. the cation VI in Fig. 2 having the formula $C_8HMe_8^+$. Moreover, the very interesting $(CH)_9^+$ cation, shown as VII in Fig. 2, was obtained by Coates and Fretz.[9] Evidence from the ^{13}C–^1H coupling constants indicates that the apical C atom in the carbo-cation VI has *sp*-hybridization,[8] a fact which will be seen to be highly significant in our later discussion.

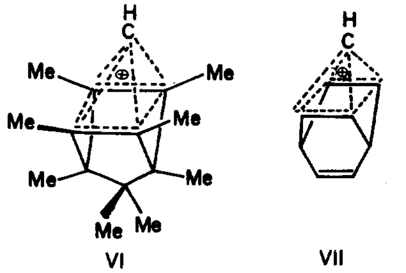


Fig. 2. Structures of the species $C_8H(CH_3)_8^+$ (VI) and $(CH)_9^+$ (VII).

Investigations carried out on the $(CH)_6^{2+}$ dication also produced some surprises. Hogeveen and Kwant pointed out[10] that a description of its structure must involve certain non-classical features. Their preparative work[11] resulted in the synthesis of the $(CMe)_6^{2+}$ dication, and a subsequent structural determination based on ^1H-NMR and ^{13}C-NMR spectral data revealed that it adopts the non-planar, non-classical structure VIII (Fig. 3), a structure which is again pyramidal. In this instance the bonding topology involves a hexa-coordinated C atom, a

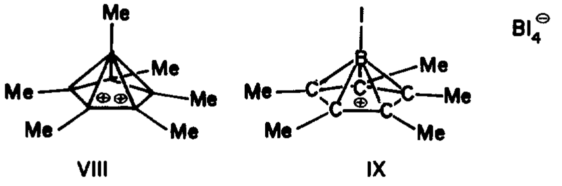


Fig. 3. Structures of $(CCH_3)_6^{2+}$ (VIII) and of an analogous isoelectronic salt (IX).

feature normally encountered only within the field of organometallic chemistry. This latter observation leads us directly into the subject matter of this paper.

The basic analogy. It is our considered opinion that the analogy suggested here between the bonding situation in organometallic species and the carboranes on the one hand, and that in organic cations on the other may be profitably exploited. In fact, we believe that the analogy can be developed so far as to provide a rationalisation of the bonding topology in those organic cations possessed of a polyhedral structure. Our argumentation will make use of a wide-ranging, general theory,[12] first put forward to account for and characterise the bonding toplogy in borane, carborane, and metal cluster species. The basic mathematical tool employed in this approach was algebraic graph theory.[19] The considerable success of this theory in explaining and rationalising a large number of differing structural types suggested to us that an extension to the purely organic sphere of carbo-cations may well pay dividends. In this first attempt to do this, we start by giving an outline of the principal features of the new theory, then go on to indicate how it may be applied in the specific area of organic cations, and conclude by making several novel predictions concerning the structures adopted in such species.

Graph-theoretical preliminaries. As the theory we shall be using rests essentially upon a graph-theoretical interpretation of the bonding topology in the relevant chemical species, we provide first a summary of the pertinent parts of the mathematical discipline of graph theory. This discipline involves primarily the study of *topological graphs*, so designated here to distinguish them from the more frequently encountered Cartesian variety, with which they have nothing in common. A topological graph consists rather of a set of points, known as *vertices*, and a set of lines, known as *edges*, which connect pairs of the points together. Graphs may be conveniently used to depict either molecules (where vertices symbolise atoms and edges the covalent chemical bonds) or complex reactions (where vertices symbolise chemical species and edges the elementary reactions which may interconvert the species into one another). In recent years graphs have also been employed for a variety of other purposes; the reader interested in the details of this aspect of graph theory is referred to several reviews on the subject.[13–15]

The former type of graph representing a molecule is referred to variously as a structural, constitutional, or molecular graph whereas the latter type is usually called a reaction graph. In the present context where we shall be using only structural graphs, two particular types of graph are relevant for our subsequent discussion. These are the so-called cyclic graph (diagram X) and the complete graph (diagram XI). Both of them are illustrated in Fig. 4 for the case when there are $n = 6$ vertices. A cyclic graph, designated as a C_n-graph, is a graph having all n of its vertices connected by means of n edges such that a single cycle results. A complete graph, designated as K_n, is a graph having every pair of its n vertices connected by an edge. Further mathematical description of these graphs is to be found in two monographs treating this topic.[16,17]

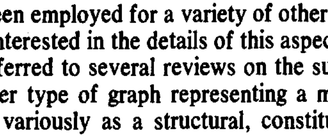


Fig. 4. The cyclic graph C_6 (X) and the complete graph K_6 (XI).

King-Rouvray theory. The essential, underlying idea behind the theory put forward[12] by King and Rouvray is that whereas C_n-type graphs are appropriate for the representation of planar, polygonal systems such as benzene, K_n-type graphs have to be employed for the characterisation of three-dimensional, closed polyhedral systems such as the boranes and carboranes. After making due allowance for this important difference, however, both 2- and 3-dimensional systems may thereafter be analyzed in graph-theoretical terms in a completely analogous way. As our present interest is centred primarily on the analysis of polyhedral structures, we shall indicate hereinafter how the theory may be applied to rationalise the bonding topology in such systems. As our starting point we shall suppose that the skeletal framework consists of n atoms arranged in a polyhedral configuration and that the system may be represented by means of a K_n graph. The significance of the edges of this graph, which represent the bonds existing between the atoms, is now explored in some detail.

Closo deltahedral systems. In electron-deficient polyhedral molecules, i.e. in those having less electrons than bonding orbitals, a global delocalisation occurs which results in a triangulated polyhedral or *deltahedral* structure. In the simplest case when all of the faces of the polyhedron are triangular, i.e. when we consider a *closo* system, and when *d* orbital involvement (which normally occurs only in metal clusters) is neglected, every atom having a valency greater than one is assumed to adopt an *sp*-type hybridisation. This assumption is in accordance with the relevant experimental data on VI cited above.[8] Each atom may then use one of its two *sp* orbitals, a so-called *external* orbital, to form a normal, covalent, localised bond with a univalent atom or group such as hydrogen. The other *sp* orbital, referred to as a *unique internal* orbital or *radial* orbital,[18] is directed towards the centre of the polyhedron, where it participates in global delocalisation as described below.

Overlap of the two remaining, non-hybridised *p* orbitals, known as the *twin internal* orbitals, gives rise to the deltahedral structure. Both of the *p* orbitals are used in the formation of bonds to two adjacent atoms within the skeletal framework. As a result of these overlaps several Hamiltonian circuits, i.e. closed paths passing only once through each vertex, may be traced out on the surface of the deltahedron. Such circuits are to be considered as representing the limiting bonding structures formed from the mutual overlaps of the twin internal orbitals. The actual enumeration of these circuits for a given polyhedron is an interesting, only partially solved mathematical problem.[19]

The interaction at the centre of the deltahedron of the *n* unique internal orbitals from the *n* skeletal atoms constituting the deltahedral framework means that all of these atoms are directly connected through the core bonding. Now a bonding situation of this type, which implies a global delocalisation of electrons within the deltahedron, may be conveniently represented by means of a K_n-type graph. It is well-known[20] that the eigenvalue spectrum of any K_n graph has exactly one positive eigenvalue equal to $n-1$ and a total of $n-1$ degenerate, negative eigenvalues equal to -1. This eigenvalue pattern is used here to represent the electronic energy levels available to the system when interaction of the twin internal orbitals and that among the unique internal orbitals takes place. It is readily seen that the resulting system must have a total of $n+1$ bonding orbitals (consisting of the above-mentioned single positive eigenvalue and one from each of the n twin internal orbitals[12]). Application of the Aufbau Principle now leads directly to the conclusion that the number n_c of electrons required to form a closed shell (corresponding to the most favoured energetic situation in a closo system) will be given by the expression

$$n_c = 2n + 2. \qquad (1)$$

Nido and arachno systems. Less electron-deficient systems, frequently referred to as electron-rich systems,[12,21] are amenable to similar treatment. Such systems are based on polyhedral frameworks having one or more holes. In the present context a hole is defined as any face which has more than three edges.[22] Using as our reference starting point the relation (1), it may be seen that when a single extra pair of electrons is available, i.e. when the system contains $2n+4$ skeletal bonding electrons in all, one bond in the skeletal framework becomes effectively deleted. This is because the extra pair of electrons must go into an antibonding orbital and so cancel out one bonding orbital. For this reason, the process of deletion is referred to as *polyhedral puncture.*[12] As this process may be repeatedly performed, we may conclude that in general, whenever h extra pairs of electrons are available, h bonds in the polyhedral framework will be deleted and h holes will be formed. For the special case with $h = 1$, the system will have only one hole and is termed a *nido* system. If $h = 2$, there will be two holes present and the system is then known as an *arachno* system. It should be mentioned, though, that in some instances instead of two square holes one larger bent hole may be formed.

In specifying the bonding topology of nido and arachno systems, one considers separately the two groups of atoms having a valency higher than one. These are the atoms forming the border of a hole (represented as the *border vertices* of the graph, e.g. the four vertices of the base of the pyramid in III), and the remaining atoms (represented as *interior vertices* of the graph, e.g. the apex of the pyramid in III). The latter atoms behave exactly as those discussed above in closo systems. In the case of the border atoms, however, two kinds of hybridisation have to be considered. These are (i) sp^2 hybridisation, as indicated in the previous paper,[12] where the external and twin internal orbitals are taken to be sp^2 hybrids, thereby leaving the non-hybridised p orbital as the unique internal orbital, and (ii) non-hybridised orbitals, with the external orbital as an *s* orbital, and the two twin internal orbitals and the unique internal orbital as unhybridised *p* orbitals. The latter possibility seems rather more likely on purely geometrical considerations, as square holes, for instance, could then much more readily assume their valence angle of 90°.

At the present time there are no experimental data available on the hybridisation adopted by border atoms, although data are to be found on the apical atoms.[8] It is of interest to note that both of the possibilities (i) and (ii) will give rise to the same closed shell structure in nido systems when there is a total of

$$n_c = 2n + 4 \qquad (2)$$

skeletal electrons in the internal orbitals. This conclusion may be reached by a separate consideration of the two complete graphs formed respectively by the border vertices and by the interior vertices, and subsequent combination of their eigenvalue spectra.[12] Analogously, for arachno systems the closed shell must contain

$$n_c = 2n + 6 \qquad (3)$$

skeletal electrons.[12] By combining the eqns (1)–(3), we obtain a single formula for the skeletal electrons in closo, nido and arachno systems as follows:

$$n_c = 2n + 2h + 2, \qquad (4)$$

where h is the number of holes.

Polyhedral organic cations. By applying the conclusions of the graph-theoretical treatment for delocalised polyhedral systems outlined above, we may make several deductions concerning the structures adopted by certain organic cations. We shall now present a simple topological rationalisation of the structures of the $(CH)_5^+$ and $(CH)_6^{2+}$ cations, and at the same time explore a number of other similar cases. This will result in our making predictions for organic cations of undetermined structure.

A nido structure with one square hole and five vertices implies the presence of one interior vertex and four border vertices. By making use of formula (2), which is equivalent to formula (4) with $h = 1$, it may be seen that for a closed shell there is a total of $2 \times 5 + 4 = 14$ skeletal electrons. This is indeed the number of skeletal electrons in V, since each CH group in $(CH)_5$ contributes three electrons to the three interior orbitals, whilst one electron is removed to form the cation $(CH)_5^+$. We may thus conclude that $(CH)_5^+$ fits well within the framework of polyhedral delocalised structures as a nido-type system. Relative to the classical localised structures II–IV, the nido structure attains additional stability by virtue of its closed shell of bonding electrons. The planar, delocalised, classical structure I will clearly be energetically unfavourable because it is anti-aromatic.

In order to determine whether other organic cations can fit into this same general scheme, we now go on to develop a universal equation. The latter may be derived by equating the number of skeletal electrons as given in eqn (4) to the number of electrons obtained from an appropriate count of the atoms and charges present in each species. We then arrive at the general balance

$$2n + 2h + 2 = 3n - c, \qquad (5)$$

where n is the number of carbon atoms involved in polyhedral delocalisation and c is the number of positive charges in the organic cation $(CH)_n^{c+}$. As each of the (CH) groups may be assumed to contribute three electrons to the total number of skeletal electrons, eqn (5) may be seen to represent simply the electron balance for a closed electron shell in a generalised organic cation with a cage structure.

Applying the universal equation. Upon rearrangement of eqn (5) we obtain the simplified version

$$n = 2h + c + 2. \qquad (6)$$

This equation implies that the formula of any polyhedral organic cation may be written as $(CH)^{c+}_{2h+c+2}$. In the case of nido monocations with $c = 1$ and $h = 1$ it follows immediately that n = 5, a result which merely confirms what has already been established in the preceding paragraph on $(CH)_5^+$. Arachno monocations (c = 1, h = 2) might not be expected to fit into this general scheme as $(CH)_7^+$ is the planar aromatic tropylium cation predicted originally by Hückel. This particular cation was first identified by Doering and Knox,[23] though it had actually been obtained much earlier in 1891 by Merling.[24] Likewise, among the dications, arachno systems (c = 2, h = 2) should not be expected to exist in the form of deltahedra but rather as planar aromatic species, e.g. the planar cyclooctatetraene dication $(CH)_8^{2+}$ reported by Olah *et al.*[25,26] The same conclusion also applies to the $(CH)^{c+}_{c+2}$ closo systems. The monocation $(CH)_3^+$ is the aromatic cyclopropenylium cation, whose derivatives were first obtained by Breslow,[24,27] and the dication $(CMe)_4^{2+}$ is the planar aromatic cyclobutadiene dication.[26]

In contrast to the foregoing, we now predict on the basis of the present treatment using *only* algebraic graph theory (as opposed to highly sophisticated quantum mechanical calculations) that the nido dication VIII of Fig. 3 (with c = 2, h = 1, and formula $(CH)_6^{2+}$) will adopt a polyhedral structure. Experimental data presented by Hogeveen and Kwant[10,11] for $(CMe)_6^{2+}$ convincingly demonstrate that this species does indeed have the predicted structure. Moreover, a derivative of the isoelectronic carborane monocation $C_5BH_6^+$ was recently reported[28] to possess the analogous structure of a pentagonal pyramid, i.e. the structure IX shown in Fig. 3.

It is striking that all three of the monocations and dications V, VII and VIII, i.e. the species $(CH)_5^+$, $(CH)_9^+$ and $(CH)_6^{2+}$, should be anti-aromatic according to Hückel MO theory because they each possess 4 m electrons, where m = 1 or 2. The theory is based upon the assumption that these systems exist in the form of planar C_n structures, whereas we know that the systems actually adopt polyhedral structures. We thus reach the general conclusion that tridimensional delocalisation to non-classical polyhedral systems appears to be an acceptable alternative for organic monocations and dications which according to Hückel MO theory should be anti-aromatic. In the predictions which are given below it is tacitly assumed that tridimensional delocalisation is the preferred alternative structure for such systems.

In purely algebraic terms, we may expect an organic cation $(CH)^{c+}_{2h+c+2}$ to be planar and aromatic whenever its number of delocalised electrons satisfies the Hückel 4 m + 2 rule. In this case we can set

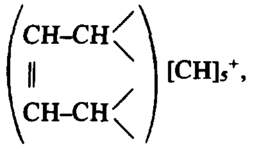
$$(2h+c+2)-c=4m+2, \qquad (7)$$

which leads directly to the result h = 2 m. This thus applies to closo systems (where m = 0, and hence h = 0) and to arachno systems (where m = 1, and hence h = 2). On the other hand, an organic cation $(CH)^{c+}_{2h+c+2}$ is predicted by the Hückel 4 m rule to be anti-aromatic whenever the equation

$$(2h+c+2)-c=4m, \qquad (8)$$

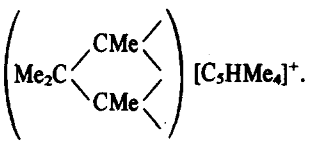
is satisfied, leading to the result h = 2 m − 1. This would apply to nido systems (where m = 1, and hence h = 1) and possibly also systems having m = 2, i.e. to systems having h = 3 holes. The derivatives $(CH)_5^+$ and $(CH)_6^{2+}$ are known to adopt the preferred polyhedral delocalisation, though there are at present no experimental analogues of systems having h = 3.

Use of descriptive formulae. In deriving the eqns (1)–(6) we have always assumed that all n of the atoms considered belong to the polyhedral system. As may be seen from the compounds VI and VII illustrated in Fig. 2, however, a number of the atoms may not form part of the polyhedral cation. Provided that the distance between two pairs of atoms is not greatly distorted, the direct bonds between such pairs may be replaced by a "homo-type" bonding. In order to distinguish the pyramidal part of the system from the remainder of the molecule, we now introduce the notion of the descriptive formula in which the pyramidal part of a species is enclosed within square brackets. Thus, in the case of the system $(CH)_9^+$, represented as species VII, the descriptive formula would be written as



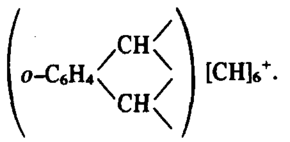
$$\left(\begin{array}{l}CH{-}CH\langle\\ \|\\ CH{-}CH\langle\end{array}\right)[CH]_5^+,$$

whilst that for the $C_8HMe_8^+$ system, represented as species VI, assumes the form



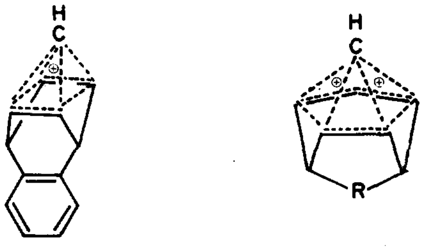
$$\left(Me_2C\begin{array}{l}\diagup CMe\langle\\ \diagdown CMe\langle\end{array}\right)[C_5HMe_4]^+.$$

A benzo-derivative of the system VII is conceivable where the vinylene group in VII is replaced by an *ortho*-phenylene group. Such a system is illustrated as the species XII in Fig. 5; in our descriptive formula notation it may be written as



$$\left(o\text{-}C_6H_4\begin{array}{l}\diagup CH\langle\\ \diagdown CH\langle\end{array}\right)[CH]_6^+.$$

Furthermore, our analysis indicates that bis-homo-dications, which could result from an appropriate combination of the features of systems VI and VII with those of system VIII, may also assume the form of polyhedral organic cations. These dications may possibly exhibit fluxional character; as indicated by the structure XIII in Fig. 5, R may be a CR_2, RC=CR, or an o–C_6H_4 group.



XII XIII

Fig. 5. Predicted polyhedral structures for the monocation XII and for the dication XIII.

CONCLUSION

We have restricted the present discussion almost exclusively to the mono- and di-cation species, that is to those cases where c is either 1 or 2. This is because to date no stable analogous structures with more than two positive charges have been prepared. If either $(CH)_7^{3+}$ or some of its derivatives could be synthesized, we would on the above reasoning expect them to adopt polyhedral delocalised structures rather than a planar anti-aromatic structure or any sort of classical localised structure.

Several authors have emphasized the fundamental similarity existing between the geometrical (or molecular orbital) structures of the polyhedral boranes and carboranes and the corresponding structures of the polyhedral organic cations. As examples one might cite here the Nobel Prize address of Lipscomb[29] and Schleyer's comments on Brown's book concerning the non-classical ion problem.[30] A theoretical treatment of polyhedral delocalisation and its basic similarity to planar aromatic delocalisation has recently been presented by Aihara.[31] Elian and Hoffmann[32] have pointed out the similarity between isolobal groups of the type BH, CH^+ and $Fe(CO)_3$, which contribute one pair of electrons and two vacant orbitals to a molecule. This similarity was used by Schleyer *et al.*[33] to draw analogies between known organometallic complexes on the one hand and polyhedral boranes, carboranes and organic cations on the other. By combining such isolobal groups a host of feasible polyhedral structures could result, all of which would fit into our graph-theoretical treatment of polyhedral delocalisation outlined above. Such an approach is obviously much more straightforward than one involving elaborate theoretical calculations[5,34] on these species and accordingly it might be hoped that the ideas presented herein may be appropriately developed in subsequent work.

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