THEOREMS FOR CARBON CAGES*

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Abstract

New theorems are established for cages (or polyhedra) with trivalent vertices. One theorem says that all such cages have at least three Kekulé structures (or perfect matchings). Thence, resonance generally appears as a possibility. Another theorem says that for every even vertex count ≥ 70 there is at least one cage of a "preferable" subclass, while for vertex count <70 the sole preferable cage is that of the truncated icosahedron. Thence, the unique role of the buckminsterfullerene structure for C_{60} is mathematically indicated.

1. Introduction, statement and discussion

Much scientific interest has arisen with the recent proposal [1] of a novel C_{60} species and its subsequent isolation [2]. The proposed "uniquely elegant" truncated icosahedral structure of fig. 1 thence has after a few years been verified. Not only

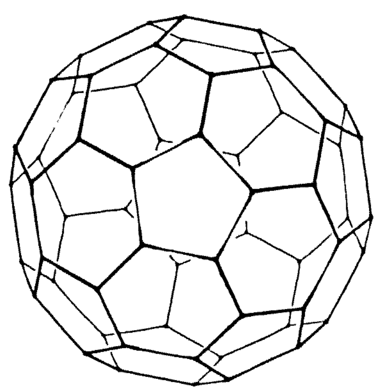

Fig. 1. The truncated icosahedron.

is there now the possibility of a new field of polyhedral structures, but also such carbon cages may be of relevance in important natural circumstances, such as (terrestrial) soot formation [3] or the occurrence [4] in dark interstellar clouds.

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Numerous theoretical questions arise as to the possibilities for suitable chemical structures and their characteristics. In attending to these questions, we have [5] focused attention on the species meeting certain criteria:

(1) threefold sigma-valency of every carbon;

(2) correspondence of structure to a polyhedron;

(3) avoidance of all rings other than those of sizes 5 and 6;

(4) minimization of the number p of abutting pairs of pentagonal rings;

(5) optimization of uniformity of Gaussian curvature; and

(6) correspondence to higher symmetry.

Criteria (2) and (3) arise from an interplay between chemical preferences and mathematical constraints. A cage satisfying criteria (1) and (2) is termed *trivalent*, and if also it satisfies (3), then it is termed *amenable*. Condition (4) arises [5] in chemistry from extended Hückel rule ideas, and is supported by calculations. If an amenable cage also satisfies (4), it is termed *preferable*. Conditions (5) and (6) are "more geometric" than the others and play little role in the present results.

Here we prove or note three results:

THEOREM A

All trivalent cages admit at least three Kekulé structures.

THEOREM B

Amenable cages occur with every even number of vertices ≥ 24, the sole amenable cage with fewer than 24 vertices being the dodecahedron.

THEOREM C

Preferable cages occur with every even number of vertices ≥ 70, the sole preferable cage with fewer than 70 vertices being the truncated icosahedron.

These theorems may be appreciated more fully, especially with regard to the comprehensiveness of B and C, if it is noted that all trivalent polyhedra have an even number of vertices. This is readily seen on using the number υ of vertices and the number e of edges to count the vertex–edge connections in two ways to give $3\upsilon = 2e$ (whence υ must be even). Also, theorem A may be viewed to imply that υ is even. Perhaps, too, it should be noted that *Kekulé structures* are often given other names: 1-factors or perfect matchings in mathematics (graph theory); dimer coverings in statistical mechanics; and perfect pairings in some recent work concerning high-temperature superconductors.

Theorem A tells us that "π-electron" resonance is conceivable for *all* such cages, the quantitative value depending on detailed electronic structure computations.

Particularly, theorem A implies that the standard (and best tested) version of "conjugated-circuits" theory is applicable.

Theorem B has previously been proved by Grünbaum and Motzkin [7], so we will not repeat the proof here. This theorem is relevant in indicating the range of possibilities addressed in our detailed cage generation scheme [6].

Theorem C identifies the buckminsterfullerene truncated icosahedron as a singular mathematico-chemical structure, in support of the enthusiasm shown by Kroto et al. [1] in describing it as "uniquely elegant". Theorem C also identifies the next largest preferable cage as being in correspondence with the next most experimentally noted [1,2] species (C_{70}), much as earlier [5] surmised. Further, it allows preferable cages of any larger even size.

2. Mathematical explanation and rigorization

There are a few mathematical points which deserve further note. First, in speaking of different polyhedra we should actually more properly be speaking of equivalence classes of polyhedra. Two polyhedra are *combinatorially equivalent* whenever the graphical connection patterns of their edges are the same. More precisely, two polyhedra $\mathcal{P}$ and $\mathcal{P}'$ are combinatorially equivalent [8] whenever there are three one-to-one mappings from the vertex, edge and face sets of $\mathcal{P}$ to the corresponding sets of $\mathcal{P}'$ such that incidence relations are conserved: a vertex, edge or face α of $\mathcal{P}$ is incident to (or touches upon) β of $\mathcal{P}$ if and only if the images of α and β are incident in $\mathcal{P}'$.

Next, unique labels for (combinatorial equivalence classes) of polyhedra are found in their *Schlegel* graphs, such a graph being that with vertices and edges corresponding to those of the polyhedron. With the standard convention that polyhedra are homeomorphic to the sphere, the corresponding Schlegel graph can be embedded on the surface of a sphere. Punching a small hole through this surface so that no components of the graph are touched, then topologically deforming the remnant surface to a disc, one then recognizes the Schlegel graph to be *planar*. This process is reversible and the planar embedding is topologically unique [9] up to the choice of which face through which the hole is punched.

Finally, we wish to speak synomonously of cages and polyhedra. By a *cage*, we think of the (sigma-bonded) chemical network of a type such that it corresponds to a (molecular) chemical graph which is 3-connected and planar. (A graph is 3-connected if at least three edges must be cut in order to break it into two pieces.) Now in our present nomenclature, Steinitz's theorem [8] says: a graph is a Schlegel graph if and only if it is a cage graph. Thence, our co-identification of cages and (combinatorial equivalence classes of) polyhedra is justified.

3. Proof of theorem A

Theorem A may be established by way of the famous four-color theorem [10]. We assume this latter result in a special form:

For any trivalent polyhedron there exists at least one coloring of the faces with but four colors such that no two adjacent faces are of the same color.

For the sake of discussion, let the four colors be red, yellow, green and blue, denoted by R, Y, G and B. Then, granted a coloring asserted by the theorem, there is exactly one color missing at each vertex. If the missing color at a vertex i is G or B, then let the edge between the incident R- and Y-colored faces be chosen to be double. However, if the missing color at a vertex i is R or Y, then let the edge between the incident G- or B-colored faces be chosen to be double. Thence, one has exactly one double bond into each vertex. This Kekulé structure clearly is uniquely associated to the partitioning of the colors into sets $\{R, Y\}$ and $\{G, B\}$. The two further partitionings $\{R, G\} \oplus \{Y, B\}$ and $\{R, B\} \oplus \{Y, G\}$ yield two further Kekulé structures so that theorem A is proved.

Actually, somewhat more general conclusions apply. The four-color theorem applies in somewhat more general circumstances: to trivalent 2-connected planar graphs. Also, one sees from the proof we have presented that no edge of a cage is always single or always double. Finally, the idea of the proof we have presented is implicit in an old work by Tait [11].

4. Proof of theorem C

The main idea of approach to this proof is to identify several different "cap" structures with the same boundaries and join them together by some number of "strands" or "belts", as indicated in fig. 2. Each strand will turn out to add 12 vertices, so if requisite caps can be identified, whole infinite sequences of cages for all larger vertex counts will be obtained. The approach is reminiscent of that taken

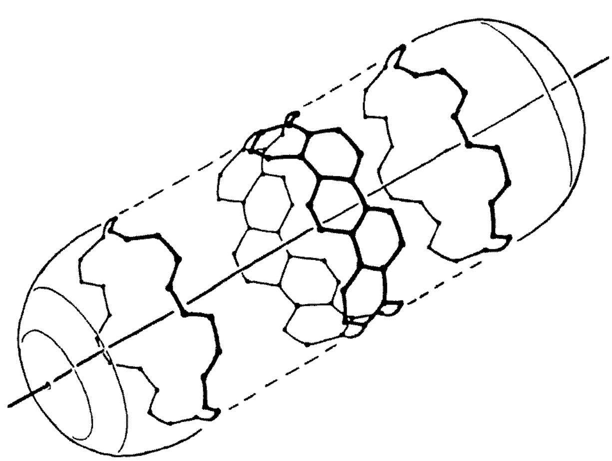

Fig. 2. The general idea for the construction of (modulo-12) sequences of preferable cages.

by Grünbaum and Motzkin [7] in proving theorem B. Also, it can be mentioned that theorems B and C are examples of a general class described [11] as of "Eberhard type".

The four "caps" we utlize are shown in fig. 3, while the strand, two or more copies of which are to intervene between the two caps, is shown in fig. 4. Note that any number $n \geq 2$ of strands may be fused together before fusion to the two caps

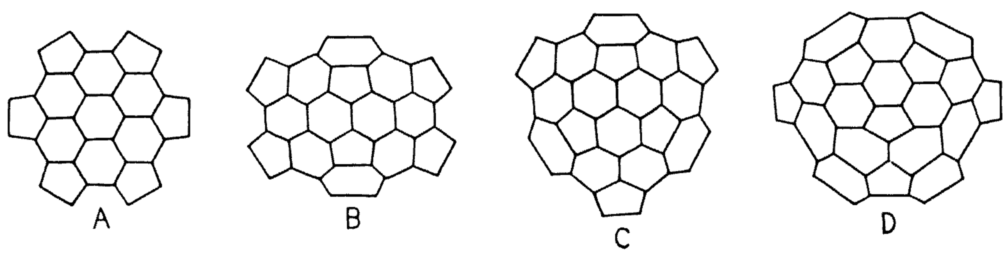

Fig. 3. The four types of caps used in the construction of the (modulo-12) sequences of preferable cages. They have, respectively, 36, 42, 46 and 50 vertices.

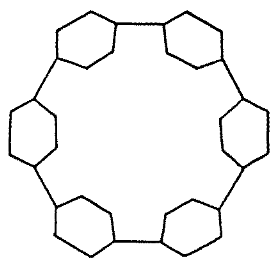

Fig. 4. The Schlegel-graph representation of the strands to be fused between two caps. Note that the belt of fig. 2 entails two such mutually fused strands. (Also note that in the fusion process, one needs to avoid countng some vertices twice.)

to yield a preferable polyhedron. Each strand added after the first two adds 12 more vertices. Thus, the total number of vertices in such a polyhedron is the sum of the numbers in each of the two caps and $12(n-1)$. Each pair of caps of fig. 3 then gives rise to a modulo-12 class of polyhedra. A set of such pairs for such disjoint classes together with their vertex counts are:

AA: $v = 72 + 12(n-2)$,

AD: $v = 86 + 12(n-2)$,

BC: $v = 88 + 12(n-2)$,

AB: $v = 78 + 12(n-2)$,

CC: $v = 92 + 12(n-2)$,

AC: $v = 82 + 12(n-2)$.

The vertex counts here have modulo-12 values of 0, 2, 4, 6, 8, and 10, respectively. Thence we have specified examples for all vertex counts of theorem C except $\upsilon = 80, 76, 74, 70$ and 60. Examples for 80, 70 and 60 may be obtained via a similar construction with two caps as in fig. 5(a) along with 3, 2 or 1 strands as in fig. 5(b)

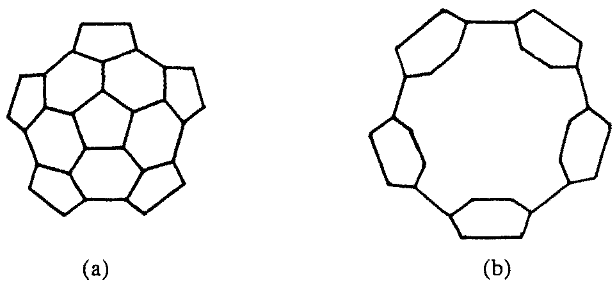

Fig. 5. A "fivefold" cap and associated strand that may be used to construct preferable cages.

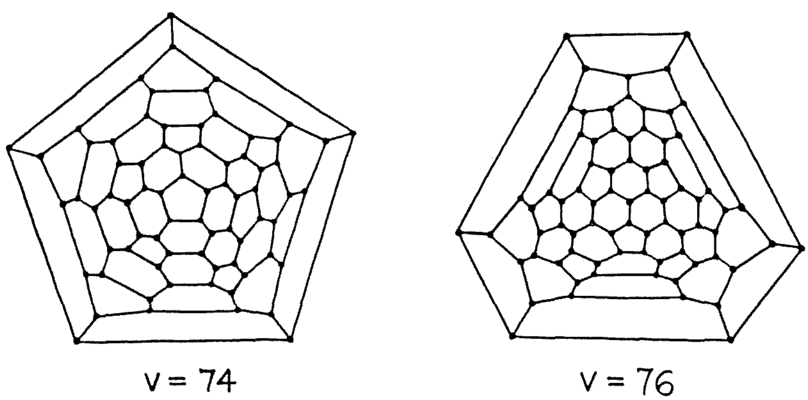

Fig. 6. Preferable cages of 76 and 74 vertices.

fused between. Examples of cages with $\upsilon = 76$ and 74 obtained via the program of our earlier paper [6] are shown in fig. 6. The sole $\upsilon = 70$ preferable cage has been mentioned several times previously, as in ref. [5], and $\upsilon = 60$ is of course the truncated icosahedron. That this last is the only preferable polyhedron with $\upsilon \leq 60$ was proved in ref. [5]. The absence of preferable cages with $\upsilon = 62, 64, 66$ and 68 was established via the program of our earlier paper [6] (the requisite manipulations having also been done by hand for $\upsilon = 62$, 64 and 66).

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