

# Closed-Shell Carbon Frameworks: Leapfrog Fullerenes and Decorated Spheriphane Hydrocarbons

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Received May 18, 1993\*

Two geometrical constructions generate structures with closed  $\pi$  shells from an arbitrary fullerene graph. In the first, closed-shell fullerenes are given by the leapfrog transformation. The starting fullerene is capped on every face and then dualized, producing a new cage of the same symmetry with three times as many atoms, isolated pentagons, and a guaranteed closed shell. Leapfrog fullerenes have  $n = 60 + 6k$  ( $k \neq 1$ ) atoms, and together with the cylinder series ( $70 + 30k$  and  $84 + 36k$  (all  $k$ )) they exhaust the known properly closed-shell fullerenes up to  $C_{100}$ . In the second, decoration of a fullerene skeleton replacing each vertex by a (1, 3, 5)-linked  $C_6H_3$  hexagon produces the spheriphane hydrocarbon series  $C_{2m}H_m$  where  $m$  is  $60 + 6k$  ( $k \neq 1$ ). Each molecule has a closed  $\pi$  system, a fixed HOMO–LUMO gap, and a  $\pi$  energy that is independent of the starting isomer.

## 1. INTRODUCTION

Electron counting is a favorite and fruitful activity for chemists. One of the early triumphs of qualitative molecular orbital theory was the Hückel ( $4n + 2$ ) rule for cyclic polyenes,<sup>1</sup> which provided a basis for modern treatments of aromaticity.<sup>2,3</sup> Forty years later, Wade's ( $n + 1$ ) rule for boranes<sup>4</sup> systematized a whole area of inorganic chemistry. Analogous schemes now cover the electronic structures of main-group and transition-metal clusters of many types and topologies.<sup>5</sup> Much of organometallic chemistry is concerned with applications of, and deviations from, simple counting rules. In all these areas the central theme is the link between geometric and electronic structure, and progress can often be made with very simple models.

The present paper is concerned with electron counting for two new classes of molecules, the all-carbon fullerenes and the spheriphane hydrocarbons. In the first part of the paper we review two geometric constructions by which examples of fullerenes with properly closed shells can be found and which lead to the analogues for fullerenes of the Hückel ( $4n + 2$ ) rule: the leapfrog ( $60n + 6k$ ) and the cylinder ( $70n + 30k$ ) and ( $84n + 36k$ ) rules.<sup>6,7</sup> In the second part, a new construction is described by means of which a spheriphane hydrocarbon (a closed network of 1,3,5-linked benzene rings) with a guaranteed closed  $\pi$  shell can be generated from an arbitrary fullerene or other trivalent polyhedral cage.

## 2. FULLERENES

The first observation of  $C_{60}$  and  $C_{70}$ <sup>8</sup> suggested the existence of the new class of all-carbon molecules which have become known as the fullerenes<sup>9</sup> and are now accessible in macroscopic amounts by chromatographic separation<sup>10</sup> of arc-processed soot.<sup>11</sup> Though the class is potentially infinite, only certain "magic" numbers of carbon atoms are associated with stable structures. One factor in determining stability is the electronic structure, and that is the aspect of the fullerenes to be explored in the present section.

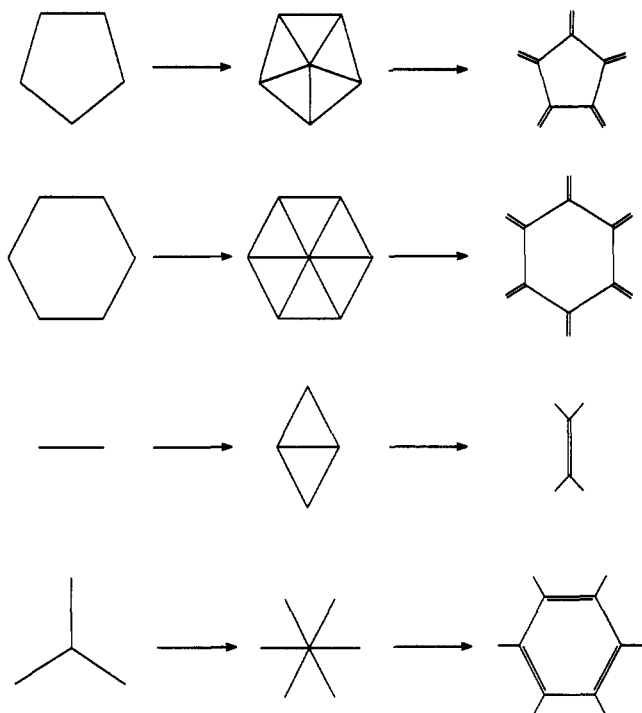
**2.1. The Model.** A fullerene  $C_n$  is defined to be a geometrically closed polyhedral framework of  $n$  carbon atoms arranged in pentagonal and hexagonal rings. Each vertex

(atom) is connected to three others, so the structure has  $3n/2$  edges (carbon–carbon contacts) and  $(n/2 + 2)$  faces (rings). The faces can be irregular and even nonplanar. If we restrict attention to cages with *only* pentagonal and hexagonal faces, then there are exactly 12 pentagons and  $(n/2 - 10)$  hexagons and the formula for the number of vertices is  $n = 20 + 2k$ , where  $k$  is the number of hexagons which may be zero (in the  $C_{20}$  pentagonal dodecahedron) or any integer greater than 1 (e.g. in  $C_{60}$   $k = 20$ ), but cannot be equal to 1 itself (the implied  $C_{22}$  cage with a single hexagon cannot be realized).<sup>12</sup> All clusters are roughly spherical or cylindrical in shape if reasonable bond lengths and angles are assumed. For fullerenes beyond  $C_{26}$ , at least two different distributions of the 12 pentagons and  $k$  hexagons can be postulated, the number of isomers growing very rapidly with  $n$ .<sup>13</sup>

In the Hückel model of a fullerene, each carbon atom retains its  $1s^2$  core, donates three electrons to an electron-precise network of  $\sigma$  bonds spanning the  $3n/2$  cage edges, and has one electron and one "radial" orbital left to contribute to the formation of a delocalized surface  $\pi$  system. On the simplest assumption that all vertices have a single  $\alpha$  parameter and all edges a single  $\beta$  parameter, the  $\pi$  orbitals and their energies are determined entirely by the eigenvectors and eigenvalues of the vertex adjacency matrix of the molecular graph in much the same way as for planar hydrocarbons. The fullerene is predicted to have an open, closed, or pseudoclosed shell according to the Aufbau filling of the energy levels by the  $n$   $\pi$  electrons. (A pseudoclosed shell<sup>14</sup> has two electrons in every occupied orbital but a bonding LUMO and therefore presumably a propensity for second-order Jahn–Teller distortion; a properly closed shell has a bonding HOMO and an antibonding or nonbonding LUMO.) Only a small proportion of isomers have properly closed shells; no fullerene below  $C_{60}$  has one; for  $C_{60}$  itself only 1 of the 1812 distinct isomers<sup>15</sup> is properly closed.

Once the molecular graph is specified, the maximal point-group symmetry, spectroscopic signature, and even the approximate Cartesian coordinates of the atoms can be deduced from the adjacency matrix, in addition to the more obvious approximate information about electronic structure.<sup>13</sup> Several algorithms have been devised for the solution of the isomer problem, i.e. for the enumeration of all distinct fullerene graphs for a given atom count. The ring-spiral algorithm

\* Abstract published in *Advance ACS Abstracts*, February 15, 1994.

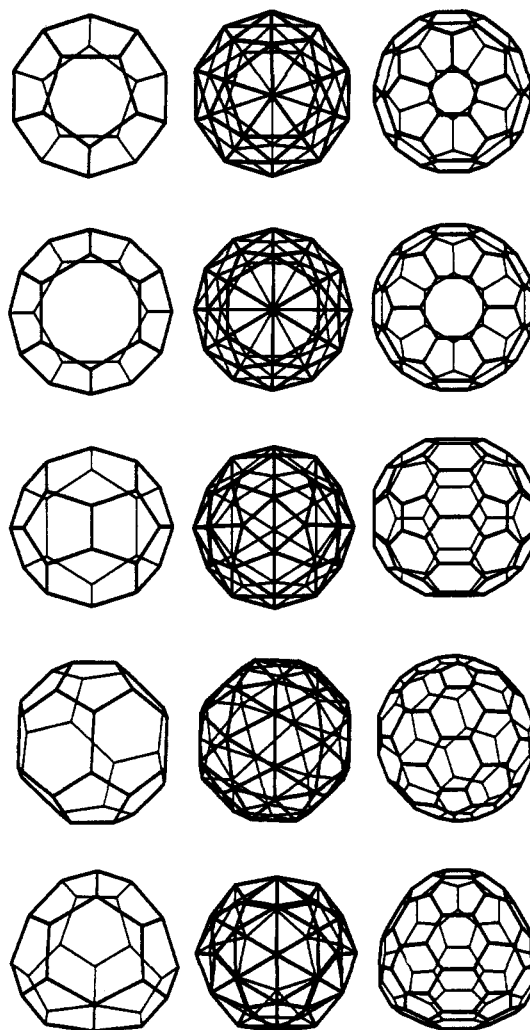


**Figure 1.** Transformation of fullerene faces, edges, and vertices under the leapfrog operation of omnicaapping and taking the dual. The double and single bonds marked on the entries in the final column refer to the special Kekulé structure mentioned in the text.

developed in Nottingham<sup>16</sup> is straightforward to implement and has been used to count isomers to  $C_{100}$  and beyond.<sup>13,17</sup> It is known to be incomplete for very large  $n$ , but as the first known counterexample to the spiral conjecture is for  $n = 380$ ,<sup>18</sup> where the total isomer count must be of the order of millions, this does not seem to pose a serious practical problem. A formally complete enumeration could be obtained by extending the Coxeter construction for icosahedra<sup>19</sup> down to all 28<sup>20</sup> possible fullerene symmetries; fullerenes belonging to the groups  $I_h$ ,  $I$ ,  $T_h$ ,  $T_d$ ,  $T$ ,  $D_{6h}$ ,  $D_{6d}$ ,  $D_6$ ,  $D_{5h}$ , and  $D_5$  have already been counted in this way,<sup>14</sup> and it was from the listing of tetrahedral isomers that the  $C_{380}$  counterexample was identified. The cataloguing of possible isomers by these or various other methods can be considered a solved problem for the range of  $n$  that is of practical interest ( $C_{20}$ – $C_{120}$ , for example).

**2.2. The Leapfrog Construction.** Given any fullerene isomer  $C_n$ , it is possible to find an isomer of the larger  $C_{3n}$  fullerene by the two-stage leapfrog construction.<sup>6,14,21</sup> This is done by first omnicaapping and then taking the dual. In the process we go from one fullerene to another, jumping over an intervening deltahedron, hence the name leapfrog. Figure 1 shows how the different components of a fullerene framework transform under leapfrogging. Each  $p$ -gonal face of the parent appears in the leapfrog but rotated through  $\pi/p$  and surrounded by new hexagonal faces; each edge of the parent appears in the leapfrog but rotated through  $\pi/2$  and surrounded by four new edges; each vertex of the parent gives rise to a triplet of vertices in the leapfrog, and its site becomes the center of a new hexagonal face. Figure 2 shows the first five leapfrog fullerenes:  $C_{60}$  (from  $C_{20}$ ),  $C_{72}$  (from  $C_{24}$ ),  $C_{78}$  (from  $C_{26}$ ), and the leapfrog isomers of  $C_{84}$  obtained from the two isomers of  $C_{28}$ .

As the atom count for an arbitrary fullerene is  $20 + 2k$  ( $k \neq 1$ ), the leapfrog series has  $n = 60 + 6k$  ( $k \neq 1$ ), with one leapfrog isomer of  $C_{3n}$  for every isomer of  $C_n$ . Symmetry elements are preserved under leapfrogging, so parent and leapfrog cage share the same maximal point group (in the



**Figure 2.** Five smallest leapfrog fullerenes. The first column shows the five smallest fullerenes ( $C_{20}$ ,  $C_{24}$ ,  $C_{26}$ ,  $C_{28}(D_2)$  and  $C_{28}(T_d)$ ), the second the product of omnicaapping, and the third the leapfrogs themselves.

sense used in ref 13). The symmetries spanned by faces, edges, and vertices of the leapfrog are all predictable from those of the parent.<sup>22</sup> An alternative description of the leapfrog procedure as omnitruncation (truncation at every vertex) of the dual of the parent fullerene may be useful for some purposes.<sup>23</sup>

By construction, the pentagonal rings of the leapfrog are isolated, though not all fullerenes with isolated pentagons are leapfrogs. Icosahedral  $C_{60}$ , the smallest leapfrog, is also the first fullerene with isolated pentagons. Leapfrogging can be repeated *ad infinitum*  $C_n \rightarrow C_{3n} \rightarrow C_{9n} \rightarrow \dots$ , with the pentagons of the original (which may have been in contact or not) moving further and further apart. Because it has a predictable effect on the connectivity, leapfrogging can be carried out at the level of the adjacency matrix, so the Hückel eigenvalues and other properties of the first, second, etc. transformed fullerene can be calculated from the parent adjacency matrix without explicit construction of any of the polyhedra.

Leapfrogging is just one of a number of ways of expanding a fullerene skeleton,<sup>15</sup> but, unlike the others, it has a chemical as well as a mathematical significance. The leapfrog fullerene is always found to have a properly closed  $\pi$  shell in Hückel theory. This regularity was first noted for the icosahedral fullerenes,<sup>22</sup> where a cage has either  $60m + 20$  atoms and an open-shell ( $G^2$ ) configuration or  $60m$  atoms and a closed-

shell ( $H^{10}$ ) configuration (where  $3m$  is an integer of the form  $i^2 + ij + j^2$ ,  $i \geq j \geq 0$ ). Systematic Hückel calculations then showed that this was part of a more general pattern. The closed-shell result holds in fact for all leapfrogs, irrespective of the symmetry, state of aggregation of the pentagons, or ground-state  $\pi$  configuration of the parent.

Several rationalizations of the leapfrog principle were published<sup>6,22,24</sup> before a fully satisfactory proof was obtained.<sup>25</sup> Two schemes depend on assigning a special role to the  $(3n/2)$  edges of the parent, all of which survive but are isolated from each other in the leapfrog. In the first, which is an MO scheme, the  $3n$   $\pi$  atomic orbitals of the leapfrog are paired up as localized bonding and antibonding combinations along the special edges. This exhausts the basis. It is then argued that interaction among these localized orbitals should not change the number and symmetry of the bonding combinations. The prediction is therefore that the bonding orbitals of the leapfrog should span the same symmetry as the *edges* of the parent polyhedron. This prediction of the electronic configuration has been verified for small leapfrogs, though it may break down at large  $n$ , when symmetry-allowed delocalization within the benzenoid hexagons may introduce competing totally symmetric Kekulé structures.

In the second,<sup>22</sup> which is a valence bond (VB) version of the same argument, it is noted that a particular Kekulé structure can be drawn for a leapfrog fullerene by placing a double bond on every one of the  $n/2$  special edges, leaving the other  $n$  edges as single bonds (Figure 1). This Kekulé structure is totally symmetric within the point group and has the significant feature that it maximizes the number of benzenoid hexagons on the surface of the leapfrog polyhedron; all pentagons are composed entirely of single-bond edges and have five *exo* double bonds radiating from them;  $n/3$  of the  $n/2 - 10$  hexagons are benzenoid (i.e. have alternating formal single and double bonds along their edges). On the stability model proposed by Taylor,<sup>26</sup> the (electronic) stability of a fullerene is determined by counting the number of benzenoid hexagons; on this criterion the leapfrogs are therefore all maximally stable.<sup>22</sup> In MO theory their stability comes from the bonding HOMO and large band gap. In practice, electronic factors are in fine balance with steric factors, and the latter may favor other, pseudoclosed fullerene isomers.<sup>13</sup>

Both rationalizations are useful in that they make contact with chemical intuition about stability and make qualitatively reliable predictions about the symmetries of the occupied orbitals and the relative lengths of carbon-carbon bonds in the leapfrog cage, but neither constitutes a rigorous proof. More detailed graph-theoretical considerations<sup>25</sup> yield the required proof and show the action of the leapfrog transformation outside the fullerene series. Any trivalent polyhedron can be leapfrogged and considered as a base for a 3D  $\pi$  system. A proof using the Rayleigh inequalities<sup>27</sup> shows that *all* trivalent leapfrog clusters have antibonding LUMOs, and all trivalent leapfrog clusters containing at least one ring with  $p \neq 3r$  atoms have bonding HOMOs. *Any* trivalent leapfrog has either a bonding or nonbonding HOMO. Within the definition of a closed shell used earlier, therefore, all fullerene leapfrogs have closed shells.

The main class of exceptions to the bonding HOMO-antibonding LUMO rule are the (non-fullerene) clusters with 4 triangular and  $n/2 - 2$  hexagonal faces, which generalize the tetrahedral Goldberg polyhedra<sup>28</sup> in the same way that the fullerenes generalize the icosahedra. In particular, carbon frameworks based on the tetrahedron and its leapfrogs would all have (degenerate) nonbonding HOMOs. An analogy can

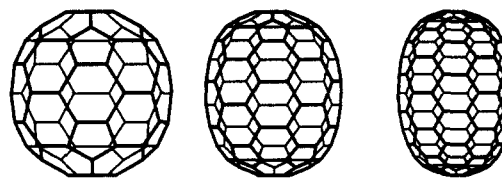


Figure 3. First members of the carbon-cylinder series of 5-fold symmetric closed-shell fullerenes:  $C_{70}$ ,  $C_{100}$ , and  $C_{130}$ .

be drawn between the breaking of the normal leapfrog pattern by the tetrahedron and its role as an exception to Wade's ( $n + 1$ ) rule for a *closo*-borane.<sup>25</sup>

Perhaps more directly relevant to carbon chemistry is the observation that "fulleroid" structures with heptagonal, hexagonal, and pentagonal rings obey the normal leapfrog pattern, so closed shells with reasonable band gaps and high resonance energies are possible. A series of cylindrical cages incorporating heptagons at the poles and a total of 14 pentagons per cage has been studied.<sup>29</sup>

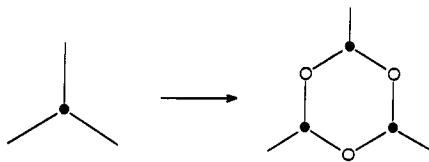
**2.3. Carbon Cylinders.** Although the  $(60 + 6k)$  rule generates many (nearly all) closed shells, there are some closed-shell fullerenes outside the leapfrog series. The most conspicuous nonleapfrog is  $C_{70}$ , which in the simple Hückel picture has 35 doubly occupied bonding  $\pi$  orbitals lying below an exactly nonbonding LUMO.  $C_{70}$  is the prototype for a second series with  $n = 70 + 30k$ , where  $k$  may take any nonnegative integer value.<sup>7</sup> The cages (Figure 3) can be envisaged as expansions of  $C_{60}$  along a 5-fold rotational axis. Belts of hexagons are inserted at the equator between the two halves of  $C_{60}$  and with the addition of every third layer of hexagons a cluster with a closed-shell configuration is produced. The nonbonding LUMO is explained by considering the standing-wave patterns for a particle moving freely on the surface of a cylinder.<sup>7</sup> The  $D_{5h}$  cylinders can be dissected into five vertical strips, and insertion of a sixth strip does not disturb the wave pattern, so that the  $D_{6h}$  series also has sporadic closed shells at  $C_{84}$ ,  $C_{120}$ ,  $C_{156}$ , .... The general rule is therefore that the nonleapfrog closed shells occur at  $n = 2p(7 + 3k)$ , where  $p = 5$  or  $6$  is the size of the polar ring,  $k$  is  $0, 1, 2, \dots$ , and there is just *one* isomer of this kind at each magic value of  $n$ . More details of the construction and its symmetry aspects are given in ref 7, but we can note here that, like the leapfrog construction, it ensures isolation of pentagons.

**2.4. Completeness.** Two rules have been given for fullerene closed shells. The indications from explicit (and complete) searches in the range  $C_{20}$  to  $C_{100}$  are that these rules exhaust the possibilities at least in that range of  $n$ . An apparently different series involving  $D_2$  expansions of  $C_{60}$  has been reported,<sup>30</sup> for example, but the closed-shell members (with  $n = 76 + 4m$ ,  $m = 2 + 3k$ ) form a subset of the leapfrogs belonging to that point group. (See Note Added in Proof.)

### 3. SPHERIPHANE HYDROCARBONS

Many variations on the fullerene theme can be imagined, and some have already been realized in the laboratory. The bare carbon vertices of the polyhedron can be functionalized by addition of hydrogen<sup>31</sup> or halogen atoms,<sup>32</sup> substituted by B or N heteroatoms,<sup>33</sup> and at least in imagination replaced by tetrahedral<sup>34</sup> or other larger trivalent units.<sup>35</sup> In a sense, the fullerenes existed before the advent of  $C_{60}$  in the shape of clathrate and water clusters or "decorated fullerenes" (see e.g. the discussion and references in ref 36).

Leapfrogging is a mode of decoration of a fullerene (or other trivalent polyhedron) in which vertices are replaced by hexagons lying athwart the old edges of the parent graph. An



**Figure 4.** Hexagonal decoration of trivalent vertices to produce a spheriphane. Each original vertex gives rise to three trivalent and three divalent vertices, denoted by filled and empty circles, respectively.

alternative is to place the hexagon with vertices one-third along each the parent edge (Figure 4). If this is repeated at every vertex, the result is a transformation from a graph with  $n$  trivalent vertices to one with  $3n$  trivalent and  $3n$  divalent vertices. Saturation of the divalent vertices by hydrogen atoms gives the hypothetical hydrocarbon  $C_{6n}H_{3n}$ , consisting of a framework of (1,3,5)-linked benzene rings retaining the overall topology of the fullerene or other starting polyhedron. Some examples of this spheriphane decoration of fullerene frameworks are shown in Figure 5.

The resulting graphs are of interest, partly because of their curious mathematical properties, some of which will be described below, and partly because frameworks of this type are starting to make an appearance in chemistry.

It is suggested, for example, that tetrahedral  $C_{28}$  may encapsulate a uranium atom under laser ablation conditions;<sup>37</sup> the tetravalence of  $C_{28}$  can be rationalized<sup>38</sup> by considering the graph obtained when the four apical atoms are deleted from the  $\pi$  system (either by physical excision or saturation by electrons from external or internal ligating atoms). This fragment has a closed-shell  $\pi$  system and is the spheriphane decoration of the tetrahedron. A similar deletion of 12 vertices from the  $C_{60}$  graph gives the spheriphane decoration of a cube as an alternant with an "aromatic" closed shell; the stability of this arrangement of conjugated bonds may be a driving force in  $C_{60}$  addition chemistry.<sup>39</sup>

The term "spheriphane" was coined by Vögtle *et al.*<sup>40</sup> to describe their new  $C_{36}H_{36}$  hydrocarbon which is thought to contain a tetrahedral array of four benzene rings linked 1,3,5 by methylene bridges. The same molecular graph describes a plausible candidate for the structure of  $C_{60}H_{36}$  in which the 24 remaining vertices of the  $\pi$  system are grouped in four benzene rings in an arrangement of overall  $T$  symmetry.<sup>41</sup>

From the point of view of qualitative electronic structure theory, the spheriphanes with methylene bridges are expected to be simple "localized" systems: they can be pictured as clusters of weakly interacting benzene rings well insulated one from another by saturated chains. When the hexagons are joined by only a single carbon-carbon link, as envisaged in the construction of Figure 4, there is more scope for interesting "delocalized" behaviour.

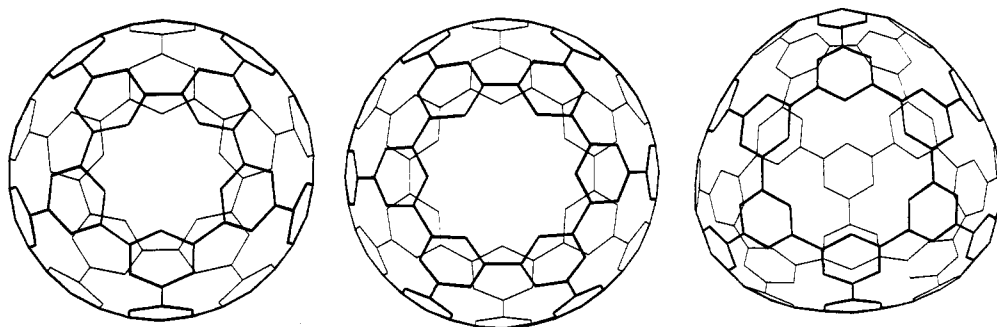
**3.1. Electronic Structure.** Spheriphane decoration of a trivalent carbon polyhedron is expected to produce a  $\pi$  system with a properly closed shell, and this expectation is borne out by explicit Hückel calculations using an algorithm that "decorates" the adjacency matrix directly, without constructing the new polyhedron. Two rationalizations suggest themselves, based, as with the leapfrog "proofs", on MO or VB ideas.

The MO version runs as follows. In the decoration step each vertex of the original graph is replaced by one triplet of divalent and one of trivalent vertices (Figure 6a). Symmetry elements are preserved under this procedure so that the same point group describes both graphs. Within that point group the symmetry spanned by the Hückel basis of radial orbitals on the parent framework is  $\Gamma_\sigma$ , the (reducible) permutation representation for the  $n$  points at the vertices. On the decorated framework the  $3n$  basis functions on the divalent vertices span  $\Gamma_\sigma \times \Gamma_{xyz} = \Gamma_\sigma + \Gamma_\pi$ , where  $\Gamma_{xyz}$  is the dipole representation and  $\sigma$  and  $\pi$  describe the three independent (one "radial" plus two "tangential") combinations of three basis functions  $f_i$  (Figure 6b). Similarly the  $3n$  functions on the trivalent vertices must also span  $\Gamma_\sigma + \Gamma_\pi$ .

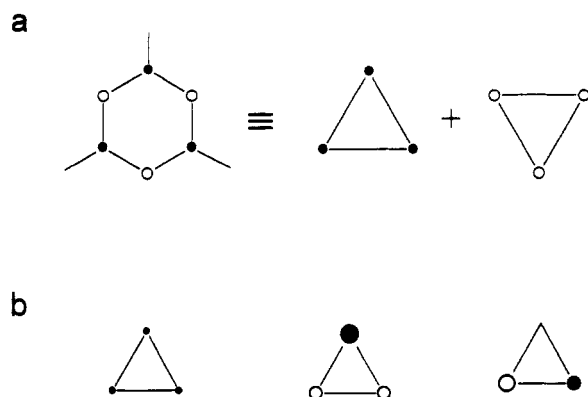
This doubling of all symmetries present in the basis suggests that when the molecular orbital combinations are formed, the interactions will produce equisymmetric bonding and antibonding manifolds, each of dimension  $3n$ , and hence a closed shell for the neutral  $6n$  electron  $\pi$  system. If the original framework was an alternant, then the energies of the decorated cluster will have exact mirror symmetry about the nonbonding line, since the alternant property is preserved under decoration (see e.g. Figure 7a). The doubling argument suggests that nonbonding orbitals (NBOs), if they occur at all for spheriphane decorations, whether alternant or non-alternant, must occur in pairs. In fact, NBOs can be ruled out by using the usual trick of summation of coefficients around a vertex; summation around first the trivalent and then the divalent vertices shows that all coefficients would vanish and hence that no NBO exists.

A VB-based picture starts with the  $n$  hexagonal rings of the decorated framework. If all  $3n/2$  links between hexagons were cut and dangling bonds saturated, then the  $\pi$  system could be represented by a Kekulé structure with three formal double and three formal single bonds in each ring. Reinstating the links should stabilize the system but not change the basic picture, so a bonding capacity of  $6n$  electrons is predicted. The set of  $3n$  localized double bonds or combinations of the three local bonding orbitals of each benzene ring would span the representation  $\Gamma_\sigma + \Gamma_\pi$  as in the MO argument.

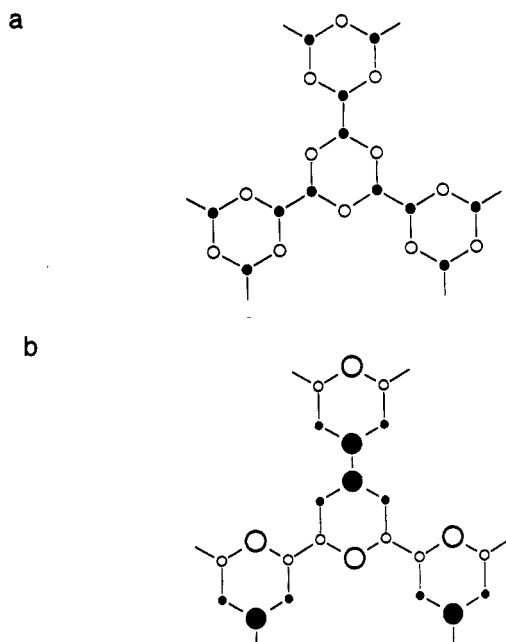
Figure 8 compares the eigenvalue spectra of the tetrahedral  $C_{28}$  fullerene, its leapfrog  $C_{84}$ , and its spheriphane decoration  $C_{168}H_{84}$ . Several features common to all spheriphane decorations are illustrated by the figure. They include (i) a fixed



**Figure 5.** Spheriphanes derived from small fullerenes ( $C_{20}$ ,  $C_{24}$ , and  $C_{28}(T_d)$ ).

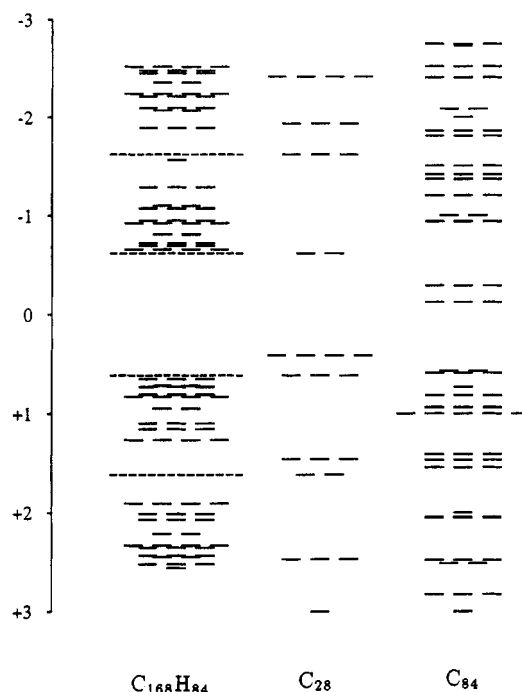


**Figure 6.** (a) Decomposition of the decorating hexagon into inequivalent triplets. (b) Independent radial and tangential combinations of equivalent basis functions  $\{f_i\}$  on a triplet of vertices. From right to left, the diagrams represent  $F_1 = 1/\sqrt{3}(f_1 + f_2 + f_3)$ ,  $F_2 = 1/\sqrt{6}(2f_1 - f_2 - f_3)$ , and  $F_3 = 1/\sqrt{2}(f_2 - f_3)$ .



**Figure 7.** Local structure of molecular orbitals common to all spheriphanes. (a) The molecular orbital of lowest energy. All trivalent vertices (black) have a common coefficient  $c_3$ , and all divalent vertices (white) have a single coefficient  $c_2$  with  $c_2 = (2/x)c_3$ , where the energy is  $\alpha + x\beta$ . When  $c_2$  and  $c_3$  are of the same sign,  $x = 1/2(1 + \sqrt{17}) \approx 2.56155$  and this is the maximally bonding orbital in all spheriphane decorations; in the antibonding combination  $x = 1/2(1 - \sqrt{17}) \approx -1.56155$ . (b) Highly degenerate orbitals with energies  $\alpha \pm \phi\beta$  and  $\alpha \pm \phi^{-1}\beta$ . Tangential functions on the two triplets within a hexagon can be arranged to be bonding or antibonding within the decorating hexagon and bonding or antibonding between hexagons. Global combinations of these local patterns, allowing for the two choices of local tangential function (see Figure 6b) and the requirements of phase-matching (or antimatching) account for the multiple degeneracies at these energies noted in the text.

energy of the maximally bonding orbital ( $\alpha + 1/2(\sqrt{17} + 1)\beta$ ) (see Figure 8a); (ii) a fixed HOMO energy ( $\alpha + \phi^{-1}\beta$ ), where  $\phi$  is the golden ratio  $(1/2)(\sqrt{5} + 1)$ ; (iii) a fixed LUMO energy ( $\alpha - \phi^{-1}\beta$ ), and hence a fixed band gap of  $2\phi^{-1}$ ; and (iv) systematic multiple "accidental" degeneracies. A spheriphane decoration of an  $n$ -vertex trivalent polyhedron has an  $n/2$ -fold degeneracy at  $\alpha + \phi\beta$  and  $\alpha - \phi^{-1}\beta$  and an  $n/2 + 1$  fold degeneracy at  $\alpha + \phi^{-1}\beta$  and  $\alpha - \phi\beta$  if the original structure is non-alternant, but  $n/2 + 1$ -fold degeneracies for all four energy levels if it is an alternant. Figure 7b shows the way that the orbitals of the multiply degenerate levels are



**Figure 8.** Hückel eigenvalues of the fullerene  $C_{28}(T_d)$  and its derivative forms. The fullerene spectrum is given in the center, that of its leapfrog on the right, and that of the derived spheriphane on the left. The vertical axis represents the orbital energy  $(\epsilon - \alpha)/\beta$  where  $\alpha$  and  $\beta$  are the usual Hückel Coulomb and resonance integrals.

built up from local components. An analogy can be drawn between the tangential combinations  $F_2$  and  $F_3$  (Figure 6b) and the p orbitals of a single super-atom at the triangle center. The combinations with energies  $\alpha \pm \phi\beta$ ,  $\alpha \pm \phi^{-1}\beta$  can be mapped on to the  $\pi$  and  $\bar{\pi}$  vector harmonic orbitals of Stone's tensor surface harmonic theory of bonding in clusters.<sup>42</sup>

If the discussion is restricted to those spheriphanes that arise from decoration of fullerene frameworks, an additional quite startling regularity is observed. The total  $\pi$  energy for the neutral system is equal for all spheriphanes with a given number of hexagons, regardless of the fullerene isomer from which they are derived. The two fullerene isomers of  $C_{28}$ , for example, yield spheriphanes with  $E_\pi(28) = 168\alpha + 240.02445\beta$ , and all forty fullerene isomers of  $C_{40}$  yield spheriphanes with  $E_\pi(40) = 240\alpha + 324.89208\beta$ . The spheriphanes derived from isomeric fullerenes are not isomorphic, and their spectra are different, but the bonding half of the spectrum sums to a constant, depending only on  $n$ . Decoration of a non-fullerene trivalent polyhedron does not necessarily produce this magic  $\pi$  energy; starting from a prism with two eicosagonal faces yields a cluster with a different value of  $E_\pi(40)$ , for example.

A related observation concerns the moments of the eigenvalue spectrum. As is well-known, the  $r$ th moment

$$\mu_r = \sum_i (x_i)^r$$

of the Hückel spectrum is determined by the number of closed walks of length  $r$  on the graph so it can be used to count structural motifs. Isomeric fullerenes share common values for the first eight spectral moments  $\mu_0, \dots, \mu_7$ . A general fullerene  $C_n$  has  $\mu_0 = n$ ,  $\mu_1 = 0$ ,  $\mu_2 = 3n$ ,  $\mu_3 = 0$ ,  $\mu_4 = 15n$ ,  $\mu_5 = 120$ ,  $\mu_6 = 93n - 120$ , and  $\mu_7 = 1680$ . Terms beyond  $\mu_7$  depend on the detailed arrangement of pentagons, because a pentagon adjacency introduces an 8-circuit. Isolated-pentagon fullerenes, including leapfrogs, have common expressions for  $\mu_0 - \mu_{11}$ .<sup>37</sup> When the fullerene is decorated to give a spheriphane,

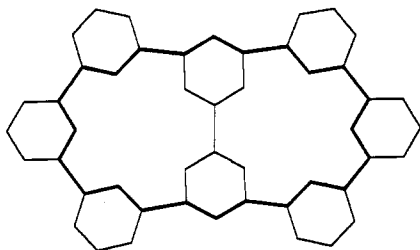


Figure 9. Decoration of a pair of adjacent pentagons introduces a 24-circuit in the spheriphanes graph.

riphane, the expansion of the structure produces 15- and 18-circuits from the pentagons and hexagons of the original graph. The first moment affected by a pentagon adjacency in the original fullerene is therefore  $\mu_{24}$  (see Figure 9), and spheriphanes derived from isomeric fullerenes share moments  $\mu_0$ – $\mu_{23}$ . Spheriphanes derived from isomeric isolated-pentagon isomers share moments up to and including  $\mu_{35}$ . For the spheriphanes with a general fullerene parent  $C_n$  the moment series is  $\mu_0 = 6n$ ,  $\mu_1 = 0$ ,  $\mu_2 = 15n$ ,  $\mu_3 = 0$ ,  $\mu_4 = 63n$ ,  $\mu_5 = 0$ ,  $\mu_6 = 315n$ ,  $\mu_7 = 0$ ,  $\mu_8 = 1695n$ ,  $\mu_9 = 0$ ,  $\mu_{10} = 9495n$ ,  $\mu_{11} = 0$ ,  $\mu_{12} = 54543n$ ,  $\mu_{13} = 0$ ,  $\mu_{14} = 318711n$ ,  $\mu_{15} = 360$ ,  $\mu_{16} = 1885503n$ ,  $\mu_{17} = 12240$ ,  $\mu_{18} = 11260521n - 360$ ,  $\mu_{19} = 237120$ ,  $\mu_{20} = 67756383n - 14400$ ,  $\mu_{21} = 3452400$ ,  $\mu_{22} = 410219583n - 322080$ , and  $\mu_{23} = 42095520$ .

Finally, we note that the spheriphanes are geometrically closed analogues of the planar hydrocarbons produced by leapfrogging planar benzenoid systems. In two dimensions the analogue of the fullerene leapfrog operation is defined by Dias<sup>43</sup> to be capping of all hexagonal faces followed by construction of the *inner dual*. The leapfrog of phenalenyl (a fused triple of hexagons) is triphenylene (a hexagon with one hexagon fused to each alternate edge), and repetition of the operation gives 1,3,5-triphenylbenzene. The latter molecule can be regarded as a planar net which folds up to make the smallest spheriphanes—the decoration of the tetrahedron and the 24-carbon core of tetrahedral  $C_{28}$ .<sup>38</sup>

**Note Added in Proof:** Some closed shell fullerenes that are neither leapfrogs nor carbon cylinders have now been found at  $C_{112}$  and above. See ref 17 for details.

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