

Spectra of conic carbon radicals

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Conic carbon radicals with non-trivial automorphism groups are topologically possible when the curvature originates from 1, 3 or 5 pentagons in the otherwise hexagonal graphene sheet. By splitting determinants of quotient graphs, we determine the bonding nature of the last occupied and first unoccupied Hückel orbitals of the radicals constituting the three infinite series with the most plausible topologies. Each member of the series with three pentagons at the tip has one electron in the first anti-bonding orbital, each member of the series with one or five pentagons at the tip has one vacancy in the last bonding orbital, and none of the radicals have any un-bonding orbital. Within the limits of the Hückel model, this implies, respectively, stable conic cations and anions. The quotient graphs also give the collected Hückel energy for each of the one-dimensional irreducible representations of the point groups.

KEY WORDS: conic carbon radicals, adjacency matrix, quotient graphs, Coefficients Theorem, eigenvalue bounds

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1. Introduction

Much of current theoretical nano-science is about the electronic properties of new, and – at least from a chemist's point of view – *large* molecular structures. Further tools for extracting essential spectral information from entire classes of molecules are therefore needed. In the case of sp^2 -hybridized carbon networks, with the Hückel model [1] as a common point of departure, it is exciting to explore topologies where the methods of spectral graph theory can spare us from downright solution of the secular equation. The vast majority of results achieved along this line have been for molecules with *bipartite* graphs, i.e. graphs with

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only even circuits and consequently symmetric spectra, which tremendously simplifies the search for closed-shell topologies. The well-known *fullerenes*, on the other hand, are not bipartite, and it was a notable achievement to prove the fact that all the *leapfrog fullerenes* [2] have properly closed Hückel shells [3]. However, the fullerenes and most bipartite molecules have in common that they are *conjugated* systems; far less graph theoretical results have been achieved for radicals. Due to their symmetric spectra, bipartite radicals necessarily have at least one electron in an un-bonding Hückel orbital, and are thus of secondary chemical interest. For the remaining radicals we are not aware of any spectral predictions of comparable range to those achieved for conjugated systems. In this work, we find the number of negative and positive eigenvalues in the Hückel spectra for the three classes of conic carbon radicals that are most likely to be synthesized, but we cannot claim to offer a general method for extracting such information without solving the secular equation. This restriction is due to our application of prior knowledge particular to certain induced subgraphs of the investigated systems. However, the series of radicals with the lowest symmetry demands some ideas that may prove useful outside the context of this work.

The network and geometry of a carbon nanocone can be constructed by cutting 1–5 sectors of 60° disclination angle from a flat graphene sheet and joining the resulting dangling bonds. The new sheet will then have a curvature determined by the number of pentagons at the tip. According to Euler's rule, cones with other facial combinations than pentagons and hexagons are topologically possible, but are considered less likely to exist due to enhanced bond stress at the non-hexagonal faces. This construction should not be understood as a model of the synthesis; there is computational evidence [4] that the energy cost of curvature is negligible in comparison with the energy of the dangling bonds of a growing graphene sheet, so the current view is that the pentagons are introduced at an early stage of the nucleation process. The first observation of fullerene cones and open-ended carbon nanocones were reported in 1994 [5], and 3 years later a method for synthesizing large quantities of mesoscopic open-ended cones with all the five possible apex angles were discovered by accident [6]. The latter process [7] starts with heavy oil, and the deliberated hydrogen is directed back to the reactor vessel during the operational cycle. The cones should therefore be terminated by hydrogens, and thus amenable to the molecular orbital theory of conjugated systems.

Our interest in the associated radicals stems from the fact that they can appear as neutral molecules with the same topological symmetry as conjugated cones with the same apex angles, although the geometrical symmetry will be broken by the Jahn–Teller effect if the last occupied orbital is degenerate. This preservation of symmetry is possible only for conic graphene sheets where the curvature originates from 1, 3, or 5 pentagons, and is thus a distinguished feature of the nanocones. Carbon nanotubes, the more renowned relatives, are either open-ended or capped with a hemisphere containing six pentagons, and

the radical tubes must therefore be charged if the rotational symmetry shall be preserved. The conic radicals may be stabilized by adding or removing electrons, provided the resulting anions or cations are closed-shell systems. These associated anions or cations may play a role in the extraordinary hydrogen storage capacity observed for crude samples of this material [8]. In addition, the size span of the cones make the radicals potentially interesting as spin probes in biomedical applications (see the recent review [9] on carbon nanocones for more details and emerging technological applications).

2. Hückel levels and molecular graphs

The σ -bonds connecting the n carbon atoms in a sp^2 -hybridized network defines a graph G , and the corresponding adjacency matrix $A(G)$ commutes with the Hückel matrix; the bonds between carbons and terminating hydrogens are not relevant to the Hückel theory of the π -orbitals. It is customary to index the eigenvalues of the adjacency matrix in non-increasing order

$$\theta_1(A(G)) \geq \theta_2(A(G)) \cdots \geq \theta_n(A(G)) \quad (1)$$

such that the Hückel energy of the i th π -orbital,

$$E_i(G) = \alpha + \beta \cdot \theta_i(A(G)), \quad (2)$$

is bonding, anti-bonding or un-bonding if $\theta_i(A(G))$, is respectively, larger, smaller than or equal to zero, as α and β are both negative constants [10]. Also for the curved graphene surfaces of fullerenes and tubes has this highly simplified model of the π -orbitals been found to work remarkably well in that essential part of the spectrum where the energies change sign [11–13]. Figure 1 shows the molecular graphs of the first three members of the radical series with a single pentagon at the tip. Three graphs are sufficient to deduce that a radical with r stacked carbon rings, including the central pentagon, has the chemical formula $C_{5r^2}H_{5r}$, where the

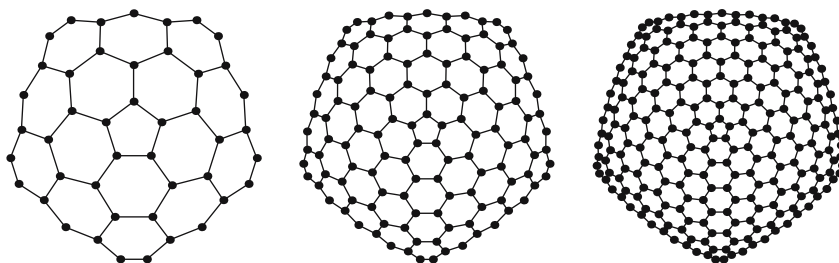


Figure 1. The molecular graphs of the first three members of the infinite series of conic carbon radicals with a single pentagon at the tip.

number of terminating hydrogens equals the number of 2-valent vertices along the edge of the graph.

For radicals with three or five pentagons at the tip, one can imagine many possible tip topologies. However, in a previous work [14] we proved that all conjugated carbon cones with the pentagons configured as in a Fries Kekulé structure and with each edge of the molecular graph in a hexagon, satisfy

$$\theta_{n/2}(A(G)) > 0 > \theta_{n/2+1}(A(G)), \quad (3)$$

the condition for properly closed Hückel shells. If the pentagons of the otherwise hexagonal network are placed as close as possible without being adjacent, the configuration is consistent with a Fries Kekulé structure, the tightest one. The local cusps that would result from a larger separation of the pentagons are mechanically unfavorable, and, on the other hand, breaking the so-called *isolated pentagon rule* [15] is theoretically unfavorable from several points of view [16–21]. So, there is abundant support for the tightest possible non-adjacent configuration of the pentagons at the cone tips. The nucleation puzzle is largely in the dark [6,22,23], but we expect the radicals to grow from the same seeds as the conjugated cones. If this assumption is wrong, the radicals can be still produced by etching carbon rings off the cones. Therefore, between the topologically possible radicals with three or five pentagons at the tips, we choose those with the tightest non-adjacent configurations of the pentagons.

The first three members of the chosen infinite series of radicals with three pentagons at the tip are shown in figure 2. A member of this series has the chemical formula $C_{3(r^2+2r-1)}H_{3(r+1)}$, where r is the number of stacked carbon rings, including the central hexagon. The radicals with the tightest non-adjacent configuration of five pentagons at the tips, represented in figure 3, cannot entirely be decomposed into rings, so in their chemical formula, $C_{(\bar{r}^2+20\bar{r}+40)}H_{(\bar{r}+10)}$, \bar{r} refers to the number of concentric rings around the conjugated “core tip”, obtained by removing the outer ring of the first member of this series. Also for the other two series, the chemical formulas hold for the conjugated cones resulting from

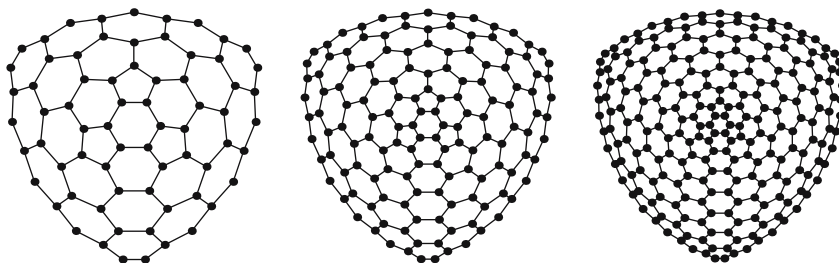


Figure 2. The molecular graphs of the first three members of the infinite series of conic carbon radicals with three pentagons at the tips.

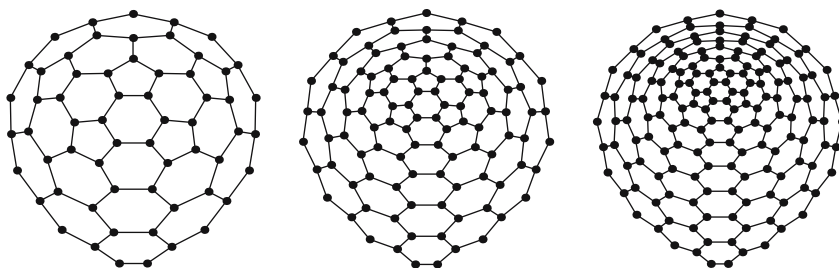


Figure 3. The molecular graphs of the first three members of the infinite series of conic carbon radicals with five pentagons at the tips.

removal of the outer carbon rings, a fact that will be applied at several occasions in the following.

3. Spectral information from determinants

To establish a preliminary bound on the numbers of negative and positive eigenvalues of the radicals, we apply the *Interlacing Theorem* (see, e.g. [24–26]):

Theorem 1. Let A be a real symmetric $n \times n$ matrix and let B be a principal submatrix of A with order $m \times m$. Then, for $i = 1, \dots, m$,

$$\theta_i(A) \geq \theta_i(B) \geq \theta_{i+n-m}(A).$$

Notice that at the outer ring of each radical graph G there is one 2-valent vertex lying in each of the reflection planes. If one of these vertices are deleted, we are left with a molecular graph satisfying (3), according to our previous work. Theorem 1 then gives for the radicals

$$\theta_{(n-1)/2}(A(G)) > 0 > \theta_{(n+3)/2}(A(G)), \quad (4)$$

which means that a radical belonging to one of the three series has an adjacency matrix with at most $(n+1)/2$ positive or negative eigenvalues. From elementary matrix theory we have

$$\det A(G) = \prod_{i=1}^n \theta_i(A(G)), \quad (5)$$

which, in conjunction with (3), (4) and the chemical formulas from the last paragraph of the previous section, implies

- (a) For all three series of radicals, $\theta_{(n+1)/2}(A(G)) \geq 0$ iff $\det A(G) \geq 0$.
- (b) Removal of the outer ring of carbon atoms from a radical with one or five pentagons at the tip gives a conjugated cone with positive determinant, while the same operation gives a conjugated cone with negative determinant for a radical with three pentagons at the tip.

The transition to determinants relates the critical questions to the *simple* eigenvalues of the adjacency matrices, as the degenerate eigenvalues of the fivefold and threefold symmetric radicals with, respectively, one or three pentagons at the tips do not contribute to the sign of the determinants. In addition, $\theta_{(n+1)/2}(A(G))$ must be a simple eigenvalue if it equals zero, according to (4). From the graph G of each three- or fivefold symmetric cone or radical we can extract a quotient graph, which spectrum consists of the simple eigenvalues of $A(G)$. In the next sections, we will show how these graphs look, and how to take advantage of point (b) above. The radicals with five pentagons at the tip demand some additional ideas, and will therefore be treated separately.

4. Equitable partitions and quotient graphs

At this point it will be necessary to distinguish between the edges of *undirected* graphs and the *arcs* of *directed* graphs. All molecular graphs of the type shown in figures 1–3 are examples of undirected graphs; their edges have no directions. If each edge of an undirected graph is replaced by two arcs (directed edges) pointing in opposite directions, we obtain a directed graph with the same adjacency matrix as the undirected graph. Unless a graph is referred to as a *digraph*, it is by consensus an undirected graph.

A graph G has an *equitable partition* X of its n vertices into m cells if each vertex in cell j has the same numbers of arcs to a vertex in cell k for $j, k = 1, 2, \dots, m$. This is also called a *D-feasible m-coloration* of the vertices, and the orbits of any automorphism of G clearly forms an equitable partition X . Any partition can be represented by a $n \times m$ matrix P , where each column is a characteristic vector projecting on the vertices filling the corresponding cell. If X is equitable, it follows that (see, e.g., [26])

$$A(G)P = PA(G/X), \quad (6)$$

where $A(G/X)$ is the adjacency matrix of the *quotient graph* G/X representing the arcs between the m cells of X . If $A(G/X)v = \theta(A(G/X))v$, then (6) implies that $\theta(A(G/X))$ is an eigenvalue of $A(G)$, with corresponding eigenvector $u = Pv$. Since (6) further implies that the column space of P is $A(G)$ -invariant, u is constant on vertices belonging to the same cell of X . By orthogonality, any eigenvector of $A(G)$, which is not constant on the cells of X , must then sum to zero on each cell of X . There is an apparent relationship between this approach and

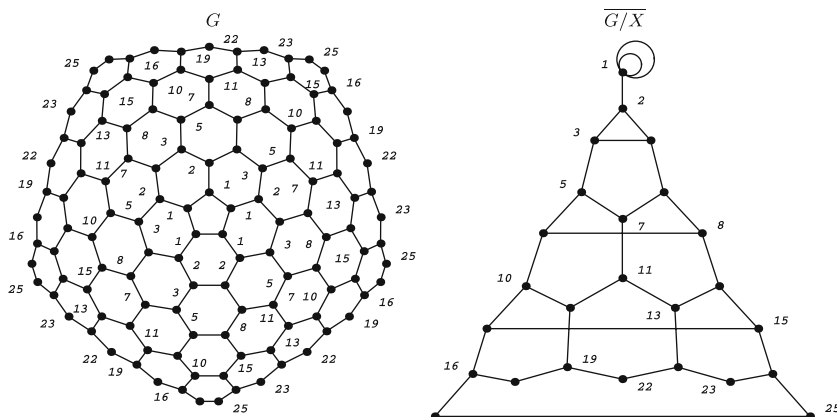


Figure 4. The undirected graph $\overline{G/X}$, which is co-spectral to the quotient graph G/X , where the cells of X are the orbits of the C_5 operation on G . A major fraction of the orbits in G and the corresponding vertices in $\overline{G/X}$ are labeled in order to clarify the relationship.

the block-diagonalization of $A(G)$ into irreducible representations of the (point) group of automorphisms. The features we shall benefit from in this work, however, would be completely masked in a matrix representation.

Since the fivefold symmetric radicals with a single pentagon at the tip have the simplest topology, we start by extracting from one of these the quotient graph G/X , which spectrum consists of the simple eigenvalues of the molecular graph G . The cells of X must hence be the orbits of the subgroup C_5 , since only the eigenvectors of $A(G)$ that transform in accordance with the one-dimensional irreducible representations of the full automorphism group can be constant on these cells. It has no consequence that the graph has a larger group (D_{5h}) than the molecule it represents (C_{5v}), since reflections through the paper plane do not effect additional equitable partitions. When it comes to assigning symmetry labels to eigenvalues, we will therefore use the irreducible representations of the molecular point group. When only the spectra are of interest, the quotient graphs can frequently be replaced simpler, co-spectral graphs, and in figure 4, we have exploited the facts that the direction of a loop has no meaning, and, as mentioned, two arcs in opposite directions are equivalent to an undirected edge. The shown graph $\overline{G/X}$ is co-spectral with the G/X , where the cells of X are the orbits of the C_5 operation on the molecular graph G of a radical with 125 carbons. Notice that the number of horizontal edges in $\overline{G/X}$ equals $r-1$, the number of concentric rings around the central pentagon in G .

5. The coefficients theorem

Recapitulating section 3, we now have that $\theta_{(n+1)/2}(A(G)) \geq 0$ iff $\det A(\overline{G/X}) \geq 0$, and in the following we will use invariant properties of $\overline{G/X}$ to show

that $\text{sgn det } A(\overline{G/X})$ is the same for all members of the series of radicals with a single pentagon at the tip. For this purpose we make use of what is called the *Coefficients Theorem* [27–30] for the characteristic polynomial

$$\Phi(\theta) = \det(\theta I - A) = \theta^m + a_1\theta^{m-1} + \dots + a_m \quad (7)$$

for a (di)graph on $m > 1$ vertices with adjacency matrix A . This important theorem gives expressions for each of the coefficients a_1, a_2, \dots, a_m and was originally formulated for digraphs. For a full treatment including the history of the theorem, see [24]. Here we only quote the results we need. When the characteristic polynomial is written in the present form, $\det A = (-1)^m a_m$, and the coefficients theorem gives for an undirected graph:

$$a_m = \sum_{U \in \mathcal{U}} (-1)^{p(U)} \cdot 2^{c(U)}, \quad (8)$$

where \mathcal{U} is the set of all spanning “basic figures” of the graph; each figure $U \in \mathcal{U}$ is composed of $p(U)$ “elementary figures” in the graph, namely disjoint edges and circuits, and $c(U)$ is the number of circuits, including loops, in U . The determinant of any odd-numbered circuit except the loop thus equals 2.

If we now try to decompose $\overline{G/X}$ of figure 4 in accordance with this scheme, we see that its longest horizontal edge *must be contained in every spanning basic figure*. This inverse analogy to the problem of the bridges of Königsberg originates from the mapping of the concentric odd-numbered circuits of G to stacked odd-numbered circuits in $\overline{G/X}$; if this particular edge in the mapping of the outermost circuit is removed, there is no disjoint set of elementary figures containing all vertices of $\overline{G/X}$. We can now apply (8) and split the determinant;

$$\det A(\overline{G/X}) = 2 \det A(\overline{G'/X'}) - \det A(\overline{G''/X''}), \quad (9)$$

where $\overline{G'/X'}$ and $\overline{G''/X''}$ are pointed out with arrows in figure 5, and the somewhat awkward notation will be justified in a moment.

If we remove the outermost concentric ring of G and partition the vertices into the orbits of C_5 , the quotient graph will be co-spectral to $\overline{G'/X'}$.

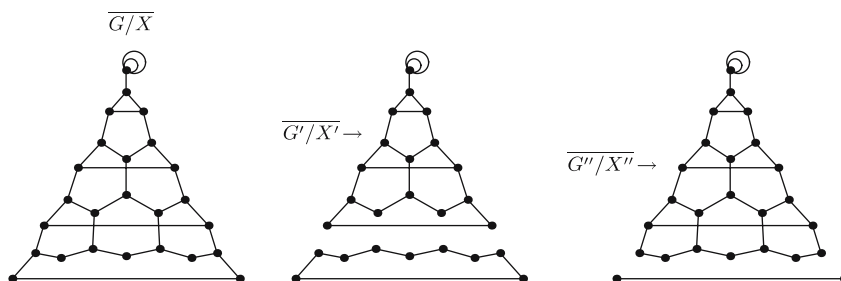


Figure 5. Decomposition of $\overline{G/X}$ from figure 4 in terms of spanning basic figures.

Thus $\det A(\overline{G'/X'})$ has the same sign as the determinant of a conjugated fivefold symmetric cone which, according to point (b) in section 3 is positive. The challenge is $\overline{G''/X''}$, which is co-spectral to the quotient graph of a new fivefold symmetric radical with molecular graph G'' . Both $\overline{G/X}$ and $\overline{G''/X''}$ have a σ_v -plane normal to the horizontal edges and the paper, and their determinants can be factorized into eigenvalues of A1 and A2 eigenvectors of G and G'' ;

$$\det A(\overline{G/X}) = \det A(G/X_{A1}) \cdot \prod_j \theta_{j(A2)}(A(G)) \tag{10}$$

and

$$\det A(\overline{G''/X''}) = \det A(G''/X''_{A1}) \cdot \prod_j \theta_{j(A2)}(A(G'')), \tag{11}$$

where $\theta_{j(A2)}$ refers to an eigenvalue with corresponding A2 eigenvector, and only the A1 eigenvectors of G and G'' are constant on the cells of X_{A1} and X''_{A1} . As shown in figure 6, the quotient graphs G/X_{A1} and G''/X''_{A1} can also be obtained by partitioning the vertices of $\overline{G/X}$ and $\overline{G''/X''}$ into the orbits of their only non-trivial automorphism, which is reflection through the σ_v -plane. Due to graphical limitations, figure 6 must be read with the following filter: each pair of oppositely directed arcs in G/X_{A1} is represented by a simple undirected edge, and the drawn double edges indicate presence of an additional unpaired arc.

Now we need the *digraph version* of the Coefficients Theorem, which states that the last coefficient of (7) is given by

$$a_m = \sum_{L \in \mathcal{L}} (-1)^{p(L)}, \tag{12}$$

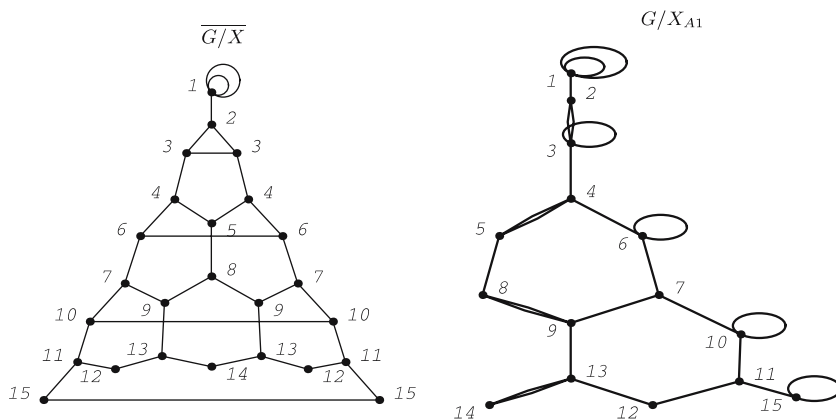


Figure 6. G/X_{A1} as quotient graph of $\overline{G/X}$. The labeled orbits of the σ_v reflection are the vertices of G/X_{A1} .

where \mathcal{L} is the set of all spanning *linear directed subgraphs* L of the digraph, and $p(L)$ is the number of components in L . In a linear directed graph, each vertex has one in-degree and one out-degree, so each $L \in \mathcal{L}$ is a decomposition of the digraph into a disjoint set of cycles, loops, and vertex pairs connected by two oppositely directed arcs. We then see from figure 6 that

$$\det A(G/X_{A1}) = \det A(G''/X''_{A1}) \quad (13)$$

since the particular edge that had to be included in every spanning basic figure of $\overline{G/X}$ is transformed into a loop on the last vertex of G/X_{A1} : deleting this vertex, which, together with its loop, must be a component of any spanning basic figure of G/X_{A1} , gives G''/X''_{A1} , and the claim (13) follows. This necessity, originating from the fact that the bounding circuit of the molecular graph contains an odd number of vertices, is thus a property shared by all radicals in this series.

6. Class \mathcal{A} bipartite subgraphs

The eigenvectors that sum to zero on the orbits of reflection through the σ_v -planes of $\overline{G/X}$ and $\overline{G''/X''}$, have eigenvalues belonging to the $A2$ vectors of G and G'' . These eigenvalues are thus contained in the spectra of the graphs \tilde{H} and \tilde{H}'' , obtained by deleting the vertices lying in the σ_v -planes, since each of these vertices constitutes an orbit of the reflection, on which the corresponding eigenvectors of $\overline{G/X}$ and $\overline{G''/X''}$ must sum to zero. As shown in figure 7, \tilde{H} and \tilde{H}'' are isomorphic to the bipartite plane graphs H and H'' , which are identified as induced subgraphs of G and G'' . Moreover, H and H'' belong to the class \mathcal{A} graphs [31], defined by Cvetković et al., as all connected bipartite plane graphs in which every face-boundary is a circuit of length $4s+2$, where s is any positive integer. (Relations between this class of graphs and Hückel's $4n+2$ rule are not relevant to the present problem.) To realize that this holds for all radicals of this series, notice that the outer faces, i.e. the boundaries, of H and H'' will always have the same length, since the two extra vertices of H will always be connected by the lowest horizontal edge in the lowest hexagon. Apart from the upper and lowest horizontal edge, which are the only edges of the outer faces that are cut by the σ_v -plane, the outer faces of H and H'' have $2 \cdot 8$ edges for the present radical, and the corresponding bipartite graphs derived from other radicals in this series are obtained by symmetric expansion of the hexagonal lattice. Each new hexagon adds four and subtracts two edges from the outer faces, so the number of boundary edges that are not cut by the σ_v -plane will always be two times an even number, and the $4s+2$ length of the outer face is preserved.

A *1-factor* of a graph, often called just a *factor*, is a regular spanning subgraph in which each vertex has degree 1, and for a class \mathcal{A} graph there is a special relation between the number of factors and the determinant of the adjacency matrix. It is seen that a factor is the same as a *perfect matching*. The vertices of

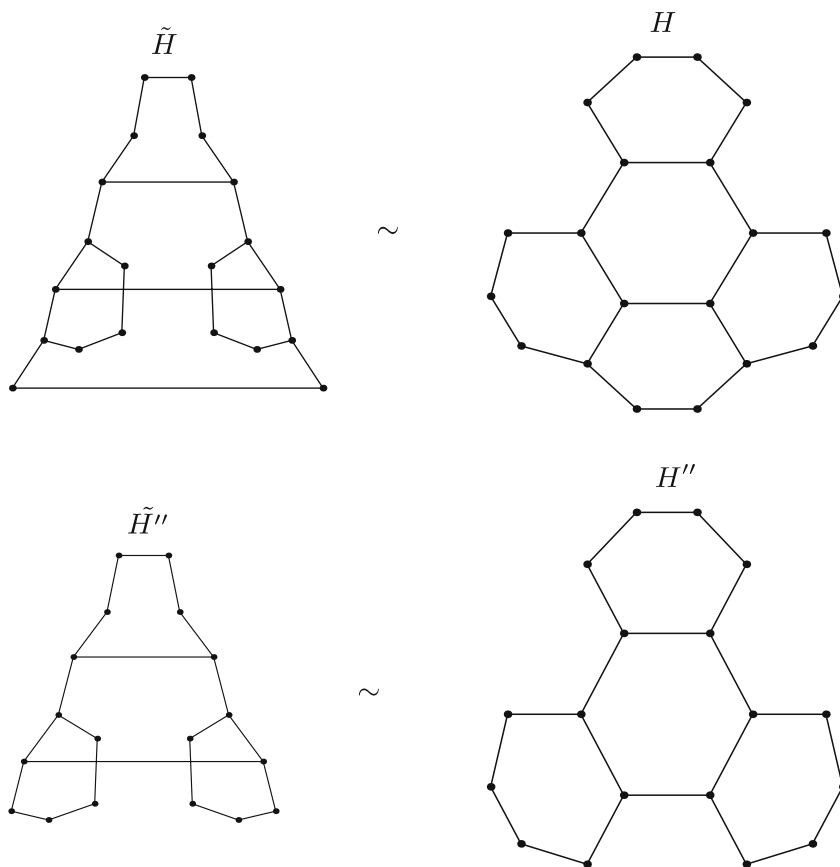


Figure 7. The subgraphs \tilde{H} and \tilde{H}'' of $\overline{G/X}$ and $\overline{G''/X''}$ shown together with their isomorphic class \mathcal{A} graphs H and H'' .

an even-numbered bipartite graph can be separated into two color sets of ν vertices, such that each edge of the graph connects two vertices of different color. If the graph additionally belongs to class \mathcal{A} , and has k different perfect matchings, we have the following theorem:

Theorem 2. Let H be a bipartite graph with $\nu + \nu$ vertices and adjacency matrix A , belonging to class \mathcal{A} . Then

$$\det A = (-1)^\nu \cdot k^2. \tag{14}$$

The full version of this theorem, given in [24], contains two additional statements outside the current context. For each perfect matching of H'' , there is a corresponding perfect matching of H , where the two extra vertices are matched by the edge between them. Thus, according to theorem 2,

$$|\det A(H)| \geq |\det A(H'')|, \quad (15)$$

where the equality sign probably does not apply for any of the radicals in the series.

It is possible to label the vertices of a bipartite graph such that the adjacency matrix takes the form

$$A = \begin{pmatrix} O & B \\ B^T & O \end{pmatrix}, \quad (16)$$

where O is a zero matrix and B is the "incidence matrix" between the two color sets (see, e.g., [24,26,32]). If $f^T = (u^T v^T)$ is an eigenvector of A with eigenvalue θ , and u and v are the projections of f on the two color sets, then $f^T = (u^T - v^T)$ is also an eigenvector of A , but with eigenvalue $-\theta$. An eigenvector of $A(H)$ or $A(H'')$ that sums to zero on each of the orbits of reflection through the σ_v -plane have opposite signs on the two color sets, and therefore,

$$\left| \prod_j \theta_{j(A_2)}(A(G)) \right| = \sqrt{|\det A(H)|} \quad (17)$$

and

$$\left| \prod_j \theta_{j(A_2)}(A(G'')) \right| = \sqrt{|\det A(H'')|}. \quad (18)$$

On insertion of (17) and (18) into (15), we obtain

$$\left| \prod_j \theta_{j(A_2)}(A(G)) \right| \geq \left| \prod_j \theta_{j(A_2)}(A(G'')) \right|, \quad (19)$$

which, according to (10) and (11) means that

$$|\det A(\overline{G/X})| \geq |\det A(\overline{G''/X''})| \quad (20)$$

since, by (13), $\det A(G/X_{A1}) = \det A(G''/X''_{A1})$. In conjunction with (9), (20) gives

$$|\det A(\overline{G/X})| \geq \left| 2 \det A(\overline{G'/X'}) - \det A(\overline{G/X}) \right|. \quad (21)$$

Thus $\det A(\overline{G/X}) \neq 0$, since G' is the graph of a conjugated cone with nonzero positive determinant. In addition (21) requires $\text{sgn} \det A(\overline{G/X}) = \text{sgn} \det A(\overline{G'/X'})$, so, according to the first paragraph of the previous section, we finally have

$$\theta_{(n+1)/2}(A(G)) > 0 > \theta_{(n+3)/2}(A(G)) \quad (22)$$

for the series of radicals with a single pentagon at tip. If $\theta_{(n+1)/2}(A(G))$ is a degenerate eigenvalue, the radical is unstable to Jahn–Teller distortions. In any event (22) implies the existence of an infinite series of closed-shell anions, realized by putting an electron in the last bonding state of each radical.

7. The threefold symmetric radicals

Will the decomposition of the quotient graphs carried out for the fivefold symmetric radicals also apply to the series of threefold symmetric radicals with three pentagons at the tips? There is actually only one additional hurdle, represented by the double edge occurring in $\overline{G/X}$ for this series, as shown in figure 8. Due to this edge, the bipartite subgraphs of $\overline{G/X}$ and $\overline{G''/X''}$ are isomorphic to graphs not strictly qualifying for class \mathcal{A} ; the double edge is equivalent to a circuit of length $4s + 2$ with $s = 0$, and class \mathcal{A} is only defined for $s > 0$. To determine whether or not the determinant formula of theorem 2 still holds when double edges are introduced in class \mathcal{A} graphs, we must take a look at the background for the definition.

In a bipartite graph H with $n = \nu + \nu$ vertices, color the first ν vertices red, and the remaining vertices blue. A spanning directed subgraph of H , where exactly one arc goes out from every red (blue) vertex, and exactly one arc terminates in every blue (red) vertex, is called a *red (blue) separation* [24], and the union of one red and one blue separation gives a linear directed subgraph L of H [33]. Further, a red (blue) separation can be represented as a permutation of the labels of the blue (red) vertices such that a *parity* can be assigned to every factor (perfect matching) K of H . Let k_+ and k_- denote the numbers of factors with, respectively, positive and negative parity. Then the determinant of the adjacency matrix of H is given by Dewar and Longuet-Higgins [34].

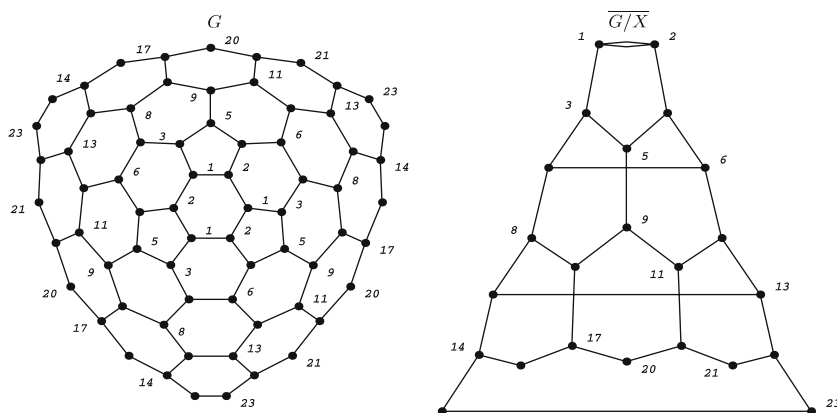


Figure 8. The undirected graph $\overline{G/X}$, which is co-spectral to the quotient graph G/X , where the cells of X are the orbits of the C_3 operation on G . As in figure 4, a fraction of the orbits in G and corresponding vertices in $\overline{G/X}$ are indicated with numbers.

Theorem 3.

$$\det A = (-1)^{\nu} (k_+ - k_-)^2. \quad (23)$$

Comparing with theorem 2, it is understood that all factors of a class \mathcal{A} graph have the same parity. Starting with the Coefficients Theorem, it can be proved that this happens iff the union of edge sets from any two factors forms an even number of circuits of length $4s$ ($s = 1, 2, \dots$) [35].

Now, the bipartite subgraphs of $\overline{G/X}$ and $\overline{G''/X''}$ for the series of threefold symmetric radicals are identical to those of the fivefold symmetric series, except for the double edges. Since at most one of the double edges can be part of any factor, each factor of a bipartite subgraph belongs to the same class \mathcal{A} graph, and theorem 2 still applies. The decomposition of $\overline{G/X}$ for the threefold symmetric radicals can therefore be carried out exactly as in the preceding sections, with (21) as the final result. However, according to point (b) at the end of section 3, the graph G' obtained by removing the outer ring of carbons now belongs to a conjugated cone with negative determinant. Thus,

$$\theta_{(n-1)/2}(A(G)) > 0 > \theta_{(n+1)/2}(A(G)) \quad (24)$$

for the threefold symmetric radicals, which implies an infinite series of closed-shell conic cations obtained by removing the single electron in the first antibonding state of each radical.

8. The radicals with five pentagons at the tip

Figure 9, which must be read with the same filter as figure 8, shows the molecular graph G and the quotient graph $G/X_{A'}$ for a radical with five pentagons at the tip. These radicals have only one plane of reflection normal to the paper, and the cells of their equitable partitions are the orbits of the point group C_s . On these cells, the eigenvectors that transform in accordance with the A' representation are constant, while those of the A'' representation sum to zero, and the group has no additional irreducible representations. The decomposition carried out in the preceding sections will not apply here, so we now make a slightly different approach, which is partly based on continuity of the eigenvalues of normal matrices. In addition to the previously exposed quotient graphs, each radical with one or three pentagons at the tip has a quotient graph analogous to that of 9, and this approach will also apply in an alternative derivation of the eigenvalue bonds obtained for these radicals.

Since the 2-valent vertex lying in the σ_v -plane of G is mapped into an end-vertex of $G/X_{A'}$, the Coefficients Theorem allows the decomposition of $G/X_{A'}$ into $G'/X'_{A'}$ plus a loop and a disjoint set of cycles, as indicated in figure 9, with pairs of oppositely directed arcs represented by edges. It is seen that $G'/X'_{A'}$ is the

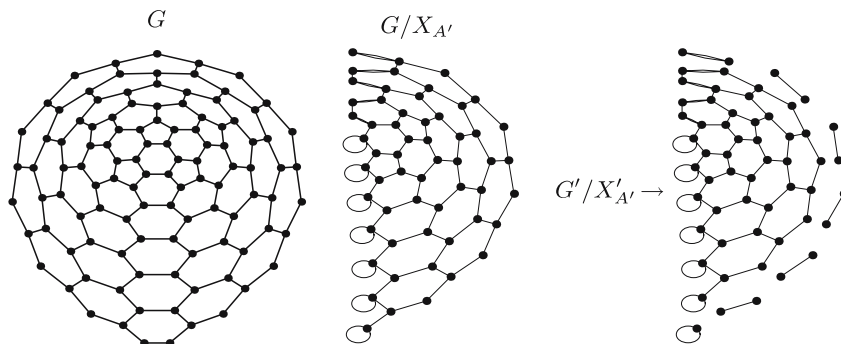


Figure 9. The molecular graph G and quotient graph $G/X_{A'}$ of a C_s symmetric radical with five pentagons at the tip. Decomposition of $G/X_{A'}$ in accordance with the Coefficients Theorem is shown to the right.

quotient graph of the conjugated cone obtained by removing the outer ring of the radical. According to our previous work, $A(G')$ has to satisfy (3), so $\det A(G'/X'_{A'})$, and thus $\det A(G/X_{A'})$, must be non-zero. Each eigenvector of A'' type equals zero on each vertex lying in the σ_v -plane of G , so their corresponding eigenvalues are all non-zero, as they are contained in the spectrum of the graph obtained by removing only the 2-valent of these vertices from G , and this graph also belongs to a conjugated cone of the type that has to satisfy (3). The point of these considerations is that $A(G)$ is non-singular, i.e. invertible.

We can now go on to find the inverse of $A(G)$, which by appropriate labeling of the vertices can be written in the form

$$A(G) = \begin{pmatrix} B & V \\ V^T & C \end{pmatrix}, \tag{25}$$

where $B = A(G')$ and C is the adjacency matrix of the outer ring of G , connected to G' by V . By exploiting the non-singularity of B and C in the solution of

$$\begin{pmatrix} M & N \\ Q & R \end{pmatrix} \begin{pmatrix} B & V \\ V^T & C \end{pmatrix} = I$$

with the blocks M, N, Q , and R as unknowns, the inverse of $A(G)$ is found to be

$$A^{-1}(G) = \begin{pmatrix} (B - VC^{-1}V^T)^{-1} & -(B - VC^{-1}V^T)^{-1}VC^{-1} \\ -(C - V^TB^{-1}V)^{-1}V^TB^{-1} & (C - V^TB^{-1}V)^{-1} \end{pmatrix}. \tag{26}$$

Since we know that this matrix actually exists, the expansions

$$\begin{aligned} (B - VC^{-1}V^T)^{-1} &= B^{-1} + B^{-1}VC^{-1}V^TB^{-1} \\ &+ B^{-1}VC^{-1}V^TB^{-1}VC^{-1}V^TB^{-1} + \dots \end{aligned} \tag{27}$$

and

$$(C - V^T B^{-1} V)^{-1} = C^{-1} + C^{-1} V^T B^{-1} V C^{-1} + C^{-1} V^T B^{-1} V C^{-1} V^T B^{-1} V C^{-1} + \dots \quad (28)$$

have to converge at some point. Now we multiply each entry of V and V^T in $A(G)$ with a scaling factor ρ , and let ρ increase continuously from zero. Since $A^{-1}(G)$ exists, the expansions above converges for $\rho = 1$, and thus clearly converge for any value of ρ between 0 and 1, so no eigenvalues become equal to zero when ρ is in this interval. This chain of matrices are Hermitian, and the eigenvalues of a Hermitian matrix vary continuously with the matrix. This particular consequence of *Weyl's Perturbation Theorem* [36] is in fact true for any normal matrix [25]. Thus, no eigenvalues pass through zero as ρ increases from 0 to 1, so the number of negative eigenvalues of $A(G)$ equals the number of negative eigenvalues of $B = A(G')$ plus the number of negative eigenvalues of C , the adjacency matrix of the outer ring. Then we have

$$\text{sgn det } A(G) = \text{sgn det } A(G') \cdot \text{sgn det } C = \text{sgn det } A(G') \quad (29)$$

since, as mentioned in section 5, the Coefficients Theorem shows that the determinant of an odd circuit equals 2. From the chemical formula given in section 2 it then follows that $\text{det } A(G)$ is positive for all radicals of this series. Thus, according to point (a) of section 3, the eigenvalue bounds

$$\theta_{(n+1)/2}(A(G)) > 0 > \theta_{(n+3)/2}(A(G)) \quad (30)$$

hold, except for the smallest member of the series. The latter radical consists of a single carbon ring around a conjugated cone for which we do not know if (3) applies; our previous analysis was restricted to cones where each edge is part of a hexagon. However, direct calculation shows the above inequality to hold also for the first graph of figure 3. As for the series with one pentagon at the tip, this inequality implies an infinite series of closed-shell conic anions. An important difference is that, except for accidental degeneracies, all the eigenvalues of $A(G)$ are now simple, so the C_s symmetry of the molecular graphs is presumably preserved in the real radicals. For the two other series we are currently – perhaps permanently – unable to predict the multiplicity of the highest occupied levels; we have no evidence that this multiplicity is an invariant of each series, although direct calculation of a few systems suggests that it may be.

9. Reduced representations and eigenvalue sum rules

Since we now have the critical spectral information about three entire classes of radicals and their associated anions and cations, it seems worthwhile to extract some additional chemically relevant facts from the quotient graphs. As in

the preceding section, it is implicitly understood that the symmetries and transformation properties refer to the graphs, and that their physical realization as conic carbon radicals may be prevented by Jahn–Teller distortions. The reduced representations and sum rules derived in this sections still have immediate for the anions and cations, and for the interpretation of the spectra of the real radicals.

For the threefold symmetric radicals, we already have the reduced representations; the number of $A1$ and $A2$ states are found by counting vertices in G/X_{A1} and $\overline{G/X}$, and the C_{3v} point group has only three non-equivalent irreducible representations, so the reduced representation of a threefold symmetric radical with r concentric rings reads

$$\Gamma = \frac{r^2 + 3r - 2}{2} \cdot A1 + \frac{r(r + 1)}{2} \cdot A2 + (r^2 + 2r - 1) \cdot E. \quad (31)$$

In the same manner the number of $A1$ and $A2$ appearances in the reduced representation of the fivefold symmetric radicals are found. However, the C_{5v} group has two non-equivalent two-dimensional irreducible representations, $E1$ and $E2$, that cannot be resolved by any quotient graph. As mentioned in the previous section, for both series there is one additional equitable partition of the vertices, where the cells are the orbits of the σ_v elements of the point groups. However, the spectra of the resulting quotient graphs contain the eigenvalues of all E states in addition to the $A1$ states, and thus provide no additional group theoretical information. For the fivefold symmetric radicals we must therefore turn to the standard approach of representation theory. For each of the 10 elements (automorphisms) of the C_{5v} group, the character $\chi_i(\Gamma)$ equals the number of vertices that are unchanged by the operation of the i th element, and the number of times $E1$ appears in Γ is given by

$$n(E1) = \frac{1}{10} \sum_i^{10} \chi_i(E1) \cdot \chi_i(\Gamma). \quad (32)$$

Only for the identity operation and reflections through the σ_v -planes is $\chi_i(\Gamma)$ non-zero, so from the character table we get

$$n(E1) = \frac{1}{10} \cdot 2 \cdot n = n/5 = r^2 \quad (33)$$

and the reduced representation of the fivefold symmetric radicals becomes

$$\Gamma = \frac{r(r + 1)}{2} \cdot A1 + \frac{r(r - 1)}{2} \cdot A2 + r^2 \cdot E1 + r^2 \cdot E2. \quad (34)$$

The trace of a matrix equals the sum of its eigenvalues, and each loop of a quotient graph contribute a “1” on the diagonal of its adjacency matrix. The

sum of eigenvalues which corresponding eigenvectors are of A1 or A2 type is thus an invariant for each of the two series;

$$\sum_j \theta_{j(A1/A2)}(A(G))^{(3)} = \sum_j \theta_j(A(G/X))^{(3)} = \sum_j \theta_j(A(\overline{G/X}))^{(3)} = 0 \quad (35)$$

and

$$\sum_j \theta_{j(A1/A2)}(A(G))^{(1)} = \sum_j \theta_j(A(G/X))^{(1)} = \sum_j \theta_j(A(\overline{G/X}))^{(1)} = 2, \quad (36)$$

where the superscripts (1) and (3) refer to the five and threefold symmetric series, with, respectively, one and three pentagons at the tips. Since the molecular graphs have no loops, these sums, which hold also for the conjugated cones obtained by removing the outer carbon ring from the radicals, immediately imply

$$\sum_j \theta_{j(E)}(A(G))^{(3)} = 0 \quad (37)$$

and

$$\sum_j \theta_{j(E1/E2)}(A(G))^{(1)} = -2. \quad (38)$$

As there are no quotient graphs that single out the $E1$ or $E2$ states, we are unable to refine the sum (38). On the other hand, counting loops in G/X_{A1} for the two series gives in conjunction with (35) and (36)

$$\sum_j \theta_{j(A1)}(A(G))^{(3)} = r - 1, \quad (39)$$

$$\sum_j \theta_{j(A2)}(A(G))^{(3)} = 1 - r, \quad (40)$$

$$\sum_j \theta_{j(A1)}(A(G))^{(1)} = r + 1, \quad (41)$$

$$\sum_j \theta_{j(A2)}(A(G))^{(1)} = 1 - r. \quad (42)$$

In the same manner, the reduced representations and sum rules for the radicals with five pentagons at the tip are easily derived from the quotient graph of figure 9:

$$\Gamma = \frac{\bar{r}^2 + 21\bar{r} + 42}{2} \cdot A' + \frac{\bar{r}^2 + 19\bar{r} + 38}{2} \cdot A'' \quad (43)$$

and

$$\sum_j \theta_{j(A')} (A(G))^{(5)} = 4 + \bar{r} = - \sum_j \theta_{j(A'')} (A(G))^{(5)}, \quad (44)$$

where \bar{r} is defined in connection with the chemical formula in section 2.

10. Summary and outlook

Beneficial features common to the quotient graphs of the five and threefold symmetric series of radicals, with respectively, one and three pentagons at the tip, allow determination of the nature of their highest occupied and lowest unoccupied Hückel orbitals by purely graph-theoretical considerations. The radicals of threefold topological symmetry are found to have a single electron in the first anti-bonding orbital, each member of the fivefold symmetric series has a vacancy in the last bonding orbital, and none of the two series contain radicals with un-bonding orbitals. As far as the Hückel theory applies, the associated threefold symmetric cations and fivefold symmetric anions are thus stable against Jahn–Teller distortions and otherwise chemically inert. The derivation outlined here of the crucial eigenvalue bonds for these two series of radicals depends on our previous results for conjugated cones, the possibility to split the determinants of the quotient graphs by means of the Coefficients Theorem, and the associated class \mathcal{A} bipartite subgraphs.

The radicals with five pentagons at the tip have the lowest symmetry of the three series we have investigated. The decomposition carried out for the two other series is not possible for these radicals, and the spectral information was obtained by exploiting the continuity of the eigenvalues of the adjacency matrices, which by the Coefficients Theorem were proved to be non-singular. Like the series with one pentagon at the tip, each of these radicals has one vacancy in the last bonding orbital. The approach to the eigenvalue bonds for the radicals with five pentagons at the tip will apply in an alternative derivation of the eigenvalue bonds for the three and fivefold symmetric radicals. As the absolute value of an eigenvalue is restricted by the largest vertex degree [26], the distance between the Hückel levels decreases with the size of the systems investigated in this work, and Hund's rule is likely to set in at some point. Since, except for accidental degeneracies, all the eigenvalues of the anions and neutral conjugated cones with five pentagons at the tip are simple, we expect this to happen first in one of these series.

We found these series of radicals, cations, and anions sufficiently interesting that we supplied the reduced representations together with eigenvalue sum rules derived from the quotient graphs. For curved graphene sheets, the Hückel model is known to work for the valence states. The nature and ordering of the lower-lying virtual π -states, on the other hand, will presumably deviate from the predictions

of this theory. The derived eigenvalue sum rules may help to clarify the limits of the Hückel model when comparative *ab initio* results are available.

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