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Clar chains and a counterexample

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Abstract A fullerene is a 3-regular plane graph with only pentagonal and hexagonal faces. The *Fries* and *Clar* number of a fullerene are two related parameters, and the Clar number is less understood. We introduce the *Clar Structure* of a fullerene, a decomposition designed to compute the Clar number for classes of fullerenes. We also settle an open question with a counterexample: we prove that the Clar and Fries number of a fullerene cannot always be obtained with the same Kekulé structure.

Keywords Fullerenes · Conjugated 6-circuits · Clar number · Fries number · Clar structure · Kekulé structure

1 Introduction

A *fullerene* $\Gamma = (V, E, F)$ is a 3-regular plane graph with only hexagonal and pentagonal faces. A *Kekulé structure* (or perfect matching) $K \subseteq E$ on Γ is a set of edges such that each vertex is incident with exactly one edge in K. The set of faces that have i of their bounding edges in K is denoted by $B_i(K)$. The faces in $B_0(K)$ are called the *void* faces of K; the faces in $B_3(K)$ are called the *benzene* faces of K (also known as *conjugated 6-circuits*, see [6]). The *Fries number* of Γ is the maximum number of benzene faces over all possible Kekulé structures [2]; the *Clar number* of Γ is the maximum cardinality of a set of independent benzene faces over all Kekulé structures [1].

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2 Chains

We define a *Clar structure* of a fullerene Γ to be a set of hexagons C and edges A such that each vertex of Γ is incident with exactly one element of $C \cup A$ and at most two edges in A bound any face of Γ. Given a Clar structure (C, A), choose three alternating edges on each face in C. Together with the edges in A, these edges form a Kekulé structure, K. Note that the faces in C form a maximal independent set of benzene faces in K. Conversely, given a fullerene Γ with a Kekulé structure K, we can form a Clar structure (C, A) associated with K: take C to be a maximal independent set of benzene faces and A to be the remaining edges in K. The Clar number of a fullerene therefore is given by a Clar structure (C, A) with a maximum number of faces in C.

Lemma 1 *Let* Γ *be a fullerene with* $|V|$ *vertices and a Clar structure* (C, A). *Then* $|C| = \frac{|V|}{6} - \frac{|A|}{3}$.

Proof Every face in C contains six vertices and every edge in A contains two vertices. Every vertex of Γ is incident with exactly one element of the Clar structure. Thus $6|C| + 2|A| = |V|$ and solving for $|C|$ gives the result. □

For a face f of Γ, we say that an edge $a \in A$ *exits* f if a shares exactly one vertex with f and that *a lies on f* if both vertices of a are incident with f. For a face f of Γ, any face of C adjacent to f is incident with two adjacent vertices on f, as is any edge from A that lies on f. Thus it is clear that an odd number of edges of A exit a pentagon, an even number of edges of A (possibly zero) exit a hexagon.

For each face f of Γ, we construct a *coupling* of the edges of A exiting f as follows. Choose edges exiting from adjacent vertices to form a couple if such a pair exists. Continue coupling exit edges from adjacent vertices until either: all edges are coupled; only a pair of edges exiting from opposite vertices of a hexagon remains and these can be coupled; only a single exit edge of a pentagon remains. For each pentagon, we call the uncoupled exit edge the *initial* edge for that pentagon. One easily checks that Fig. 1 includes a complete listing of all such couplings. Note that edges of A exit a face f from consecutive vertices around f or f is a hexagon with exactly two edges in A exiting f from opposite vertices.

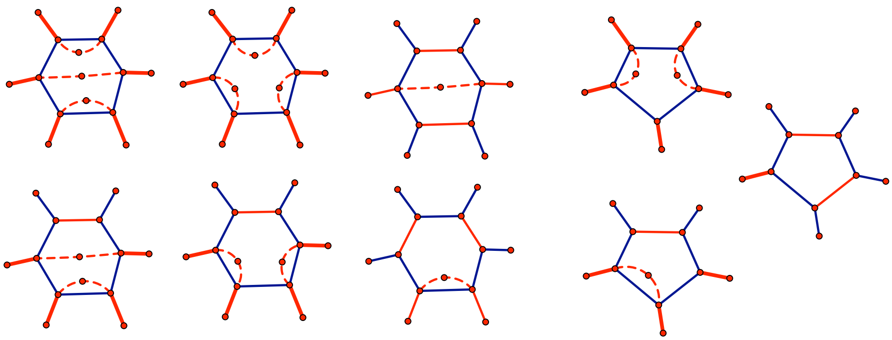


Fig. 1 All possible couplings around a face

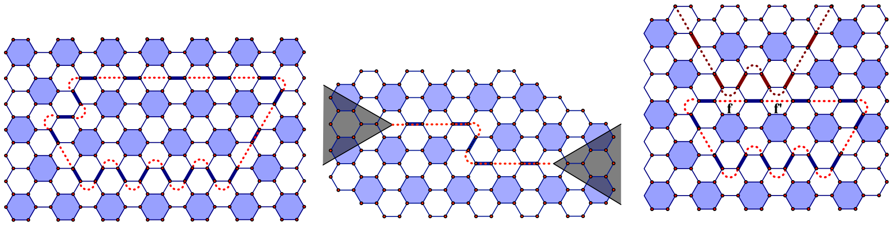


Fig. 2 A closed Clar chain, an open Clar chain, and two Clar chains. To represent pentagons, we insert a $60°$ wedge and identify the two rays bounding the edge

Each edge in A that is not an initial edge has two couplings, one over each face that it exits. Each initial edge has at most one coupling. Given a coupling for a fullerene Γ, define a *Clar chain* in Γ to be an alternating sequence $f_0, a_1, f_1, a_2, \ldots, a_k, f_k$ of faces f_i of Γ and edges a_i in A such that a_i and a_{i+1} are coupled edges exiting f_i for $1 \leq i \leq k-1$, a_1 exits f_0 and a_k exits f_k. If a_1 (or a_k) is not an initial edge, $f_0 = f_k$ and a_1 is coupled with a_k over f_0. If $f_0 = f_k$, we say that the chain is *closed*. A closed chain contains no initial edges and creates a circuit (see the leftmost image in Fig. 2). We say the chain is *open* if it contains initial edges. In this case, a_1 and a_k are initial edges, so f_0 and f_k are pentagons (see Fig. 2 center). A chain $f_0, a_1, f_1, a_2, \ldots, a_k, f_k$ makes a *sharp turn* at f_i if a_i and a_{i+1} exit from adjacent vertices of f_i.

Clar chains will not cross one another by the definition of a coupling. However, Clar chains may share faces. The rightmost image in Fig. 2 shows two chains sharing the faces f and f'.

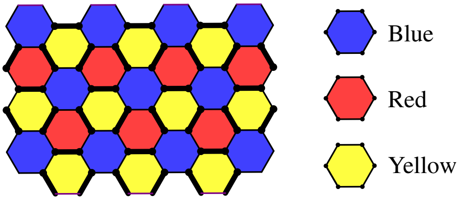
Lemma 2 *Let Γ be a fullerene with a Clar structure (C, A) and a coupling assignment. There are exactly six open Clar chains connecting pairs of pentagons. There may additionally be closed Clar chains.*

Proof We know from Euler's formula that a fullerene has exactly twelve pentagons. From the fullerene $\Gamma = (V, E, F)$ with a coupling, construct a new graph with vertex set V and edge set A together with edges between coupled pairs. In this graph, the twelve initial vertices exiting pentagons have degree 1 and the remaining vertices have degree 2 (one edge from A and one from the coupling). Such a graph decomposes into paths, circuits and isolated vertices. The six paths that terminate at initial vertices of pentagons correspond to the six open Clar chains, and any remaining circuits correspond to closed Clar chains. □

3 Face 3-colorings

We define a *hexagonal patch* to be a plane graph in which all faces are hexagons except for one *outside face*, all vertices are of degree 2 or 3 and all vertices of degree 2 are incident with the outside face. The hexagonal patches of interest to us may be thought of as regions of the hexagonal tessellation of the plane. Such a hexagonal patch inherits a face 3-coloring that is unique up to interchanging the color classes

Fig. 3 Kekulé structure with face 3-coloring. The void faces are in the *blue color class*. *Thick edges* represent edges in the Kekulé structure. (Color figure online)



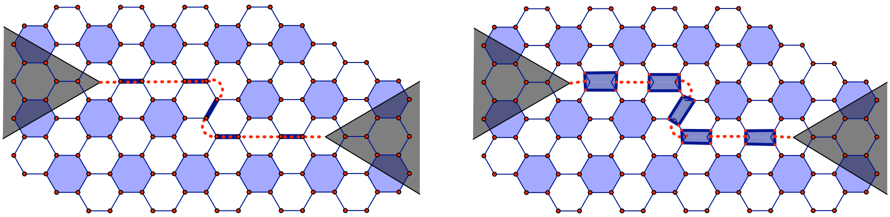


Fig. 4 An open chain in a fullerene and in the expansion

and each color class is a maximal face-independent set. We construct a partial Kekulé structure over such a patch in the following way: choose one color class to be the set of void faces. Let all of the edges not bounding a void face be in the Kekuké structure. On the interior of this patch, all of the faces in the other two color classes are benzene faces. Figure 3 shows a patch with a face 3-coloring and associated Kekulé structure. The blue faces are the void faces, the red and yellow faces are all benzene faces and this set is part of a potential Fries set. Furthermore, either the red faces or the yellow faces can be chosen as part of a potential Clar set. This partial Kekulé structure over a face 3-colored hexagonal patch is "ideal" in the sense that there is no loss to the count of benzene faces or independent benzene faces.

Over a patch of faces that includes a pentagon, a face 3-coloring is clearly not possible. Thus any face coloring of a fullerene using three colors is an *improper face 3-coloring*. We now use the Clar structure of a fullerene to construct an improper face 3-coloring of Γ.

We define the *expansion* $\mathcal{E}(C, A)$ to be the graph obtained by the following operation: widen the edges in A into quadrilateral faces. Each vertex incident with an edge in A becomes an edge, and each edge in A splits lengthwise into two edges (see Fig. 4). We show that $\mathcal{E}(C, A)$ is face 3-colorable using the following result, which appears as Theorem 2.5 in Saaty and Kainen [7].

Theorem 1 *A 3-regular plane graph is face 3-colorable if and only if each face has even degree.*

Lemma 3 *Let* Γ *be a fullerene with a Clar structure* (C, A)*. The expansion* $\mathcal{E}(C, A)$ *is face 3-colorable. All faces of* $\mathcal{E}(C, A)$ *corresponding to faces in* C *and edges in* A *in* Γ *are in one color class of* $\mathcal{E}(C, A)$*. Furthermore,* Γ *has an associated improper face 3-coloring for which the only improperly colored faces are those that share edges in* A*. For a Clar chain* $f_0, a_1, f_1, a_2, f_2, \ldots, a_k, f_k$ *in this improper 3-coloring, the* *faces f_i are all in one of the remaining two color classes, and the faces incident with edges in A over the chain are all in the third color class.*

Proof Let f be a face of degree d in the fullerene Γ. If j edges from A exit f, then the corresponding face in $\mathcal{E}(C, A)$ has degree $d + j$. Pentagons in Γ are exited by an odd number of edges from A, hexagons by an even number of edges from A. Thus every face in $\mathcal{E}(C, A)$ is of even degree, and $\mathcal{E}(C, A)$ is face 3-colorable by Theorem 1. Since every vertex of Γ is incident with exactly one element of $C \cup A$, the faces of $\mathcal{E}(C, A)$ corresponding to the faces in C and the edges in A comprise one color class. Suppose that these faces are blue.

Let $f_0, a_1, f_1, a_2, f_2, \ldots, a_k, f_k$ be a Clar chain (where $f_k = f_0$ if the chain is closed). Consider a face f_i exited by the edges a_{i-1} and a_i. Let d_i and g_i be the faces incident with a_i. In the expansion $\mathcal{E}(C, A)$, the face a_i' is blue. Assume that f_i is red. Then g_i and d_i must each be in a third color class, yellow, since they are each incident with a_i' and f_i. The edge a_i is also incident with the face f_{i+1}, and f_{i+1} is adjacent to g_i, d_i, and a_i' in the expansion, so f_{i+1} must also be in the red color class. Hence each face f_j in the chain is red and all faces incident with an edge a_j in the chain are yellow.

We associate this face 3-coloring of $\mathcal{E}(C, A)$ with an improper face 3-coloring of Γ. We return to the fullerene Γ by collapsing each quadrilateral of $\mathcal{E}(C, A)$ back into an edge in A while retaining the coloring of the remaining faces. Two faces of Γ that share an edge in A correspond to opposite faces around a quadrilateral of $\mathcal{E}(C, A)$, and accordingly have the same color. Two faces of Γ that share an edge not in A share the same edge of $\mathcal{E}(C, A)$ and hence are assigned different colors. □

We now consider closed Clar chains and determine when they exist. Let $\mathcal{C} = \{f_0, a_1, f_1, a_2, f_2, \ldots, a_k, f_k = f_0\}$ be a closed Clar chain. The faces of the fullerene are now partitioned into three parts: the faces $f_0, f_1, \ldots, f_k$ of the chain and two patches. We say that the patch containing the least number of pentagons is the *interior* of $\mathcal{C}$ and the patch on the other side of the chain is the *exterior*. If both sides contain the same number of pentagons, we arbitrarily choose one patch to be the interior. Suppose some face f_i in a closed Clar chain $\mathcal{C}$ is a pentagon. Then f_i is joined by an open Clar chain to another pentagon p. This open Clar chain is either exclusively in the interior or the exterior of $\mathcal{C}$ since chains do not cross one another. We say that $\mathcal{C}$ *contains the pentagon* p if p is in the interior of $\mathcal{C}$ or if the open chain initiated by p is contained in the interior of $\mathcal{C}$. Thus any closed Clar chain contains an even number of pentagons.

Lemma 4 *Let Γ be a fullerene with a Clar structure (C, A) and an associated coupling. If $|C|$ is the Clar number for Γ, then every closed Clar chain contains a pentagon.*

Proof Consider a closed Clar chain containing no pentagons. There may additionally be nested closed chains in the interior; let $\mathcal{C} = \{f_0, a_1, f_1, a_2, f_2, \ldots, a_k, f_k = f_0\}$ be the innermost closed Clar chain. For $i = 1, 2, ..., k$, let g_i and d_i be the faces incident with a_i on the interior and exterior of the chain, respectively. Give Γ the improper face 3-coloring associated with (C, A), and assume that C is contained in the blue color class. By Lemma 3, all faces f_i belong to a second color class, say yellow, and all g_i and d_i are in the remaining color class (red). Since Clar chains do not cross one another, there are no edges from A in the interior of this innermost Clar chain and thus all the faces on the interior of $\mathcal{C}$ are properly 3-colored. Consider two faces g_i and d_i that share an edge a_i of the chain. The faces g_i and d_i are red, and are each adjacent to the yellow faces f_{i-1} and f_i. The interior face g_i conforms with the proper face 3-coloring of the interior of the chain. If the interior coloring continued to the exterior face d_i, then d_i would be blue. We see that this is the case for all of the improperly colored faces d_j, g_j incident with edges a_j over the chain for $1 \leq j \leq k$. The faces $\{d_j\}$ together with the set of blue faces in the interior of the chain form an independent set. If we interchange the blue and red color classes within the interior of the chain, then the set of faces in the interior together with the faces $\{d_j\}$ are properly face 3-colored. All vertices on the chain and its interior are then incident with exactly one blue face. Let C'' be the collection of all blue faces and let $A'' = A \setminus \{a_1, a_2, \ldots, a_k\}$. Now (C'', A'') is a Clar structure, and $|C''| > |C|$ by Lemma 1, so $|C|$ is not the Clar number for Γ. □

The position of the two faces of a fullerene in relation to one another is given by their *Coxeter coordinates*. A shortest dual path between nearby faces can be drawn as two straight line segments with a 120° left turn between them, or in some cases, as one straight line segment. In the case with a 120° left turn, the Coxeter coordinates are given as the ordered pair (m, n): a straight line segment containing m faces before a 120° left turn, and another with n faces after the turn. In the case with one straight line segment of length m, the coordinate is given just as (m) (see Figs. 5, 6).

Define a *straight chain segment* to be an alternating chain $f_0, a_1, f_1, a_2, \ldots, a_k, f_k$ of edges in A and hexagons f_i such that the edges a_i and a_{i+1} exit from opposite vertices of f_i for each i. A straight chain segment with k edges in A connects a pair of faces with Coxeter coordinates (k, k). We can visualize a straight chain segment with k edges as the diagonal of a parallelogram with edges of length k through faces and with the straight chain along the diagonal of the parallelogram (see Fig. 5). Note that every Clar chain in a fullerene Γ is a sequence of straight chain segments with only sharp turns.

We say that a Clar structure (C, A) has a coupling with *non-interfering* Clar chains if for every pair of pentagons p_1 and p_2 joined by a Clar chain, there is no other pentagon that has a vertex in common with any shortest chain joining p_1 and p_2 in any coupling of (C, A). For the rest of this paper, we consider pairs of pentagons that can be joined by non-interfering Clar chains. When more than two pentagons interact, chains can become quite complicated (see [5]).

Lemma 5 *Assume two pentagons are joined by a non-interfering Clar chain. Then any shortest Clar chain joining them is composed of alternating right and left turns.*

Proof If a Clar chain takes two consecutive right turns, we have turned 120° and are traveling toward the first straight chain segment. Thus a face reached by two consecutive right turns could be reached by two shorter segments. □

Suppose the chain connecting pentagons p_1 and p_2 consists of a straight chain segment with k edges in A, then a sharp left turn followed by a straight chain segment with l edges in A. If we position p_1 at the “origin,” the first straight chain segment goes

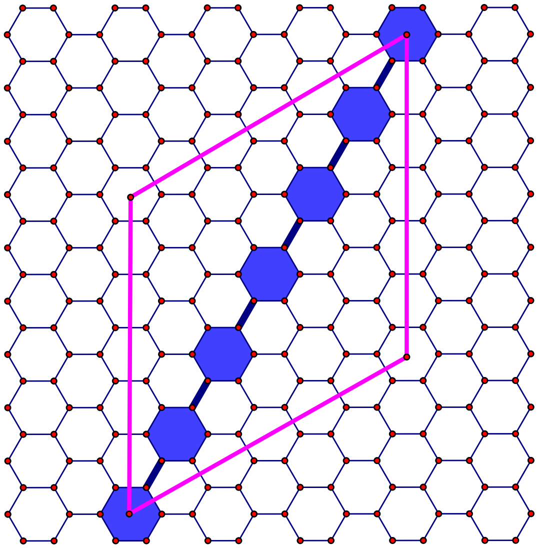


Fig. 5 A straight chain segment with 6 edges in A joining a pair of faces with Coxeter coordinates (6,6). *Thick edges* represent edges in A

to the face with Coxeter coordinates (k, k). The side of the second parallelogram goes backwards 2l faces along the side of the first parallelogram (in the first coordinate) and l faces in the positive direction in the second coordinate. If $2l \leq k$, the second parallelogram ends at p_2 with coordinates $(k - 2l, k + l)$. (See Fig. 6a.) If we instead have a sharp right turn and $2l \leq k$, then the coordinates are reversed, and the segment has Coxeter coordinates $(k + l, k - 2l)$.

If $2l > k \geq l$, then going backwards $2l$ faces in the first coordinate after a sharp left turn takes us to $k - 2l < 0$. Since this is negative, we re-orient the segment so that it is in the positive direction, and we have $2l - k$ as our second Coxeter coordinate. In the case of a sharp left turn, going backwards $2l$ faces takes us past the point (k); it takes us to the coordinate $(2k - 2l, 2l - k)$. Going forwards l faces in the now-first coordinate takes us to $(2k - l, 2l - k)$. (See Fig. 6b.) For a sharp right turn, the Coxeter coordinates of the segment are $(2l - k, 2k - l)$.

Lemma 6 *Suppose we want to connect two faces of a fullerene* Γ *by a Clar chain and the orientations of the parallelograms are given. If the segments alternate between right and left turns, the sum of the edges in A over the Clar Chain is the same regardless of the number of turns.*

Proof If a chain alternates between right and left turns, the jth parallelogram is in the same orientation as the first parallelogram for j odd, and in the same orientation as the second for j even since all turns are at 60° angles. Any parallelograms with the same orientation are adding edges to A in the same direction. Thus one parallelogram with k edges in $|A|$ reaches the same face as r parallelograms with $k_1, k_2, \ldots, k_r$ parallelograms in the same orientation such that $k_1 + k_2 + \cdots + k_r = k$. So a parallelogram with k edges in A followed by a parallelogram with l edges in A reaches the same point as any number of parallelograms with alternating turns such that diagonals of

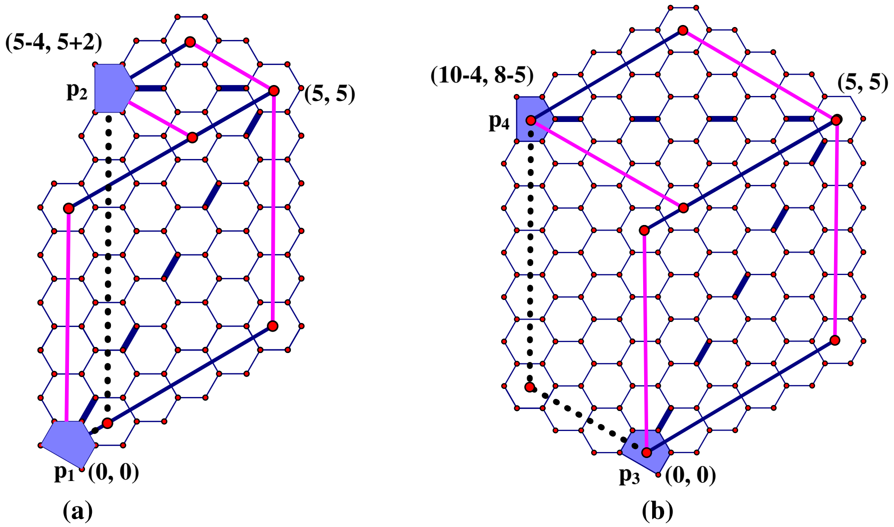


Fig. 6 Pairs of pentagons connected by two straight chain segments. **a** A straight chain segment of length $k = 5$ followed by a straight chain segment of length $l = 2$. The Coxeter coordinates between p_1 and p_2 are (1, 7). **b** A straight chain segment of length $k = 5$ followed by a straight chain segment of length $l = 4$. The Coxeter coordinates between p_3 and p_4 are (6, 3).

the odd-numbered parallelograms add up to k and the diagonals of the even-numbered parallelograms add up to l. □

4 Calculating the number of edges in A over a Clar chain

To find the Clar number for classes of fullerenes, we would like to calculate the number of edges in A over Clar structures (C, A) for these fullerenes, since $|C| = \frac{|V|}{6} - \frac{|A|}{3}$. By Lemmas 5 and 6, a chain with at most a single turn contributes a minimum number of edges to A.

Consider two pentagons p_1 and p_2 that are joined by a Clar chain. Start with the hexagonal tessellation and at each pentagon, cut out a 60° wedge and identify the rays bounding the wedge. Assign the faces the improper face 3-coloring given by the chain. The chain and the two wedges split our region and the face 3-colorings above and below the split must match when the wedges are collapsed (see Fig. 7). For any Clar structure (C, A), the edges in A in the Clar chain between p_1 and p_2 together with the faces in C must contain each vertex of the patch exactly once.

Suppose that the Coxeter coordinates of the segment between p_1 and p_2 are (m, n). We can assume without loss of generality that $m \geq n$. Begin with p_1 at the origin and consider a parallelogram with sides parallel to the directions of the Coxeter coordinates (see Fig. 7). We define the chain to be of *Type 1* if each vertex of p_1 outside of the parallelogram is covered by a face in C. The chain is of *Type 2* if exactly two of the vertices outside of the parallelogram are covered by a face in C. The chain is of *Type*

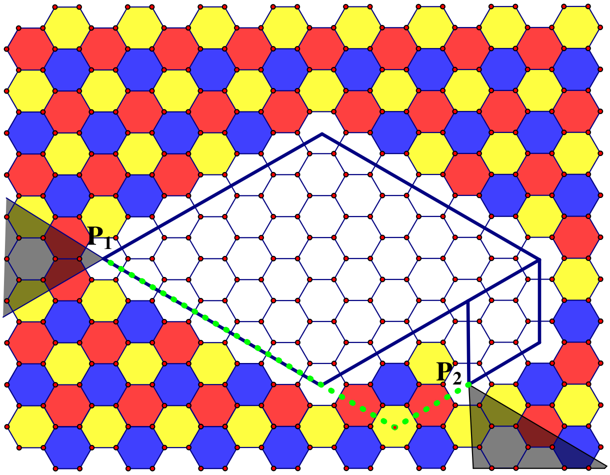


Fig. 7 If the *yellow faces* contain the set C, this chain is of Type 1. If the *red faces* contain C, the chain is of Type 2. If the *blue faces* contain C, it is of Type 3. (Color figure online)

3 if none of the vertices outside of the parallelogram is covered by a face in C. The following Lemma is tedious but not difficult to prove, for details see [5].

Lemma 7 *Let p_1 and p_2 be two pentagons joined by a chain and let (m, n) [or (m)] be Coxeter coordinates of the segment between them, where $m \geq n$. Then $m \equiv n$ (mod 3) and*

(i) *A chain of Type 1 contributes m edges to A;*
(ii) *A chain of Type 2 contributes $m + n$ edges to A;*
(iii) *A chain of Type 3 contributes $3m + 2$ edges to A.*

Lemma 8 *Let Γ be a fullerene with a Clar structure (C, A) and a coupling. If $|C|$ is the Clar number for Γ, then any closed chain $\mathcal{C}$ containing exactly two pentagons p_1 and p_2 together with the open Clar chain connecting the pentagons contributes the same number of edges to A as a Clar chain of Type 3 between p_1 and p_2.*

Proof Let $\mathcal{C} = \{f_0, a_1, f_1, a_2, f_2, \ldots, a_k, f_k = f_0\}$ be a closed Clar chain containing exactly two pentagons p_1 and p_2. There must be some open Clar chain $p_1, e_1, h_1, e_2, h_2, \ldots, e_l, p_2$ joining p_1 and p_2 that is contained in $\mathcal{C}$. Give Γ an improper face 3-coloring associated with the Clar structure (C, A). By Lemma 3, we can assume without loss of generality that the faces of C are blue in this face 3-coloring, and that the faces $f_0, f_1, f_2, \ldots, f_k = f_0$ of $\mathcal{C}$ are red.

Suppose the Coxeter coordinates between p_1 and p_2 are (m, n) with $m \geq n$. Note that a closed chain surrounding p_1 and p_2 has at least $2(m + 1)$ edges in A, as well as edges from A in the open chain.

Consider the case in which the faces $p_1, h_1, h_2, \ldots, p_2$ of the open chain are also in the red color class. We can remove the closed chain by interchanging the colors blue and yellow in the interior. After this change, the pentagons p_1 and p_2 are still red. Since they are not in the color class containing C, the chain between the pentagons is of Type 1 or Type 2. We know from Lemma 7 the chain contributes at most $m + n$ edges to A. Therefore, deleting the closed chain and interchanging the interior face colors decreases A. Such a closed chain does not exist in a Clar structure that attains the Clar number.

Consider the case in which the faces of the open chain $p_1, h_1, h_2, \ldots, p_2$ are in the yellow color class. Removing the closed chain interchanges the colors of the blue and yellow faces, so p_1 and p_2 would be in the blue color class. Since the pentagons cannot be in the set C, we no longer have a vertex covering (C, A). This results in a chain of Type 3: there are $3m + 2$ edges in A connecting the pentagons, and all vertices of the pentagons are covered by edges in A. Therefore, the open chain $p_1, e_1, h_1, e_2, h_2, \ldots, e_l, p_2$ (at least m edges) together with the closed chain $f_0, a_1, f_1, a_2, f_2, \ldots, a_k, f_k = f_0$ contributes at least $3m + 2$ edges to A. If it does not contribute exactly $3m + 2$ edges to A, this Clar structure would not attain the Clar number. □

Let Γ be a fullerene that allows a coupling of a Clar structure with non-interfering Clar chains. Let (m_i, n_i) be the Coxeter coordinates of the segments between each pair of pentagons connected by a Clar chain for $1 \leq i \leq 6$. For an arbitrary Clar structure of Γ, there are three choices for the set of faces containing C outside of the regions containing the pairs of pentagons. These three choices give three distinct Clar structures. Given one of these Clar structures, the number of edges contributed to $|A|$ by the pair with Coxeter coordinates (m_i, n_i) is given by Lemma 7. For each of the three choices, we determine the total number of edges in $|A|$ and let M be the minimum of these three sums. We define such a pairing of pentagons to be *widely separated* over the fullerene if for any two pentagons that are not paired together, one of the Coxeter coordinates of the segments joining them is at least $\frac{M}{2} - 2$.

Lemma 9 *Let Γ be a fullerene over which the pairs of pentagons are widely separated. If (C, A) is a Clar structure that attains the Clar number for Γ, then (C, A) cannot include a closed chain containing more than two pentagons.*

Proof Suppose (C, A) is a Clar structure that attains the Clar number for Γ, and that (C, A) includes a closed Clar chain $\mathcal{C} = \{f_0, a_1, f_1, a_2, f_2, \ldots, a_k, f_k = f_0\}$ containing more than two pentagons. Any closed chain contains an even number of pentagons, so $\mathcal{C}$ must contain at least 4 pentagons. By definition of widely separated, $\mathcal{C}$ contains at least two pairs of pentagons for which one of the Coxeter coordinates of the segments joining them is at least $\frac{M}{2} - 2$. Therefore the length of $\mathcal{C}$ is at least $2(\frac{M}{2} - 2) + 2 = M - 2$. There are additional edges in A for each of the six chains between paired pentagons, so the total contribution to $|A|$ is greater than M. Thus, (C, A) does not attain the Clar number for Γ. □

Theorem 2 *Let Γ be a fullerene over which the pairs of pentagons are widely separated. Let M be the minimum sum of the edges in A over the three possible choices for the face set containing C. Then $\frac{|V|}{6} - \frac{M}{3}$ is the Clar number for Γ.*

Proof By Lemma 2, any Clar structure (C, A) over Γ contains six Clar chains connecting pairs of pentagons. Let M denote the minimum number of edges in A over the

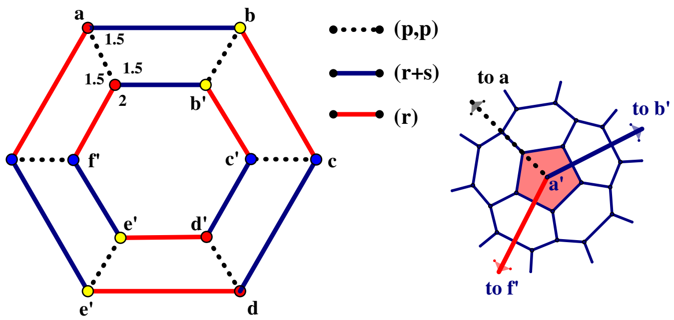


Fig. 8 The *left figure* shows the auxiliary graph for this class of fullerenes. The pentagon a' in the fullerene represented by the auxiliary graph is on the *right*

three possible choices for the set C. If a different pairing is chosen for any pentagon, then there are at least two new pairs of pentagons. For each new pair, one of the Coxeter coordinates is at least $\frac{M}{2} - 2$ since the original chains were widely separated. Chains connecting the other four pairs each contribute at least one edge to A, giving a total of at least M edges in A. By Lemma 9, any closed Clar chain containing more than one pair of pentagons increases the size of A. Thus any other Clar structure contains at least M edges in A. The conclusion follows by Lemma 1. □

5 Calculating the Clar number for an infinite family of fullerenes

We use the methods of the previous section to calculate the Clar number for a class of fullerenes as an example. This class is taken from Graver's "A Catalog of All Fullerenes with Ten or More Symmetries" [3], and the Clar number is found when the parameters are such that we have pairs of pentagons that are widely separated.

Figure 8 shows an auxiliary graph that represents a general fullerene in this class. The vertices represent the twelve pentagons in the fullerene. The edges represent segments between nearby pentagons, and the colors code the Coxeter coordinates of these segments. The numbers shown represent angle types between two segments joined by a common pentagon, and the meaning of these numerals is shown on the right in Fig. 8. For a detailed description, see [3]. Different choices for parameters r, p, and s result in all fullerenes within this family. Graver showed in [3] that the number of vertices for a fullerene in this family is $12r^2 + 2s^2 + 12rs + 12p(2r + s)$. These fullerenes are widely separated when p is much smaller than r (an inequality is given shortly). In this case, the six open Clar chains must pair pentagons joined by segments with Coxeter coordinates (p, p). There are several cases depending on the congruence classes of r and s modulo 3. We consider the case in which $r \not\equiv 0 \pmod 3$ and $r \equiv s \pmod 3$, giving $r + s \not\equiv 0 \pmod 3$.

Let a, b, c, d, e, f be pentagonal faces on the fullerene in clockwise order as shown. In a partial face 3-coloring that avoids the Clar chains between segments with Coxeter coordinates (p, p), a and b are in different color classes since the segment between a and b has coordinate $(r + s)$, where $r + s \not\equiv 0 \pmod 3$. Similarly, the segment between b and c has Coxeter coordinate (r), and so b and c are in different color classes. Since $r \not\equiv 0$ but $r \equiv s \pmod 3$, $r + s \not\equiv r \pmod 3$, so a and c are in different color classes. Thus a and d are in one color class (red), b and e are in a second color class (yellow), and c and f are in a third color class (blue). Each of these pentagons is paired over a (p, p) segment with another pentagon (a with a', b with b', and so on), so each pair is in the same color class. Note that the Coxeter coordinates between a and the yellow face b are $(r + s)$, the coordinate between d and the yellow face e is (r). There are two possibilities for the position of the yellow color class around a red pentagon. The pentagon a and the pentagon d must each have a different position with respect to the yellow faces. Thus all six possible colorings around these segments are represented. The type of Clar chain only depends on the position of the faces in the color class containing C. This class is symmetric, and regardless of the color chosen, there are two chains of each of the three types. Thus the total contribution to A is $2p + 2(p + p) + 2(3p + 2) = 12p + 4$. The next closest pentagons that are unpaired have coordinates (r). This choice of Clar chains is widely separated when $r \geq \frac{12p+4}{2} - 2 = 6p$. Thus, when the chains are widely separated, the Clar number is

$$\frac{|V|}{6} - \frac{|A|}{3} = \frac{12r^2 + 2s^2 + 12rs + 12p(2r + s)}{6} - \frac{12p + 4}{3}$$
$$= 2r^2 + \frac{1}{3}(s^2 - 4) + 2rs + 4rp + 2p(s - 2)$$

Note that $s \not\equiv 0 \pmod 3$, so $s^2 \equiv 1 \pmod 3$ and the above expression is always an integer. This example illustrates our computational approach to the Clar number. Using these techniques in conjunction with the Catalog [3], the Clar number can be easily computed for many infinite families of fullerenes.

6 Class for which the Clar and Fries number cannot be attained by the same Kekulé structure

It is part of the folklore of fullerenes that a set of independent benzene faces that attains the Clar number for a fullerene is contained in the set of benzene faces that gives the Fries number. In this section, we describe a class of fullerenes for which this does not hold: for fullerenes in this class, any Kekulé structure that attains the Fries number cannot give the Clar number; any Kekulé structure that attains the Clar number cannot give the Fries number.

In the examples we construct here, pairs of nonadjacent pentagons are joined by a single edge, and we refer to such patches as *basic patches*. These basic patches are widely separated to ensure that no other pairing of pentagons could yield the Fries or Clar number. A partial 3-coloring can be constructed except over the basic patches. We can begin to construct a Kekulé structure consisting of edges connecting the faces in one color class as described previously. This structure must be extended inside each basic patch to complete the Kekulé structure.

To achieve the Clar number, this extension must be chosen so that $|A|$ is minimized. We know from [4] that the number of benzene faces over a Kekulé structure K is given

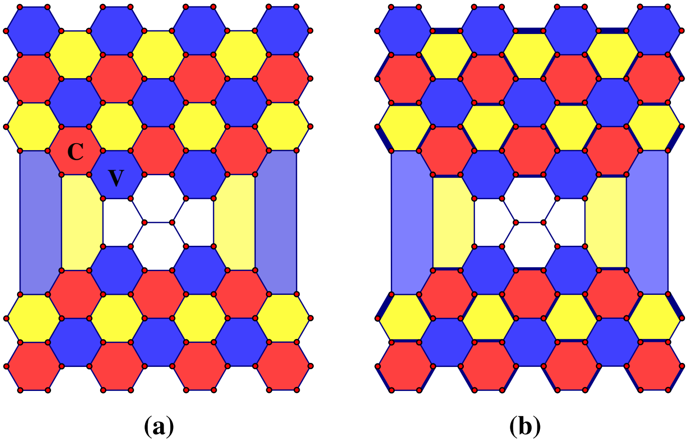


Fig. 9 Around this basic patch, the void faces are *blue*, the Clar faces are *red*. **a** A partial face 3-coloring outside of a basic patch. **b** A partial Kekulé structure given by the choice of void faces. (Color figure online)

by $|B_3(K)| = \frac{|V|}{3} - \frac{|B_1(K)|+2|B_2(K)|}{3}$. To attain the Fries number, this extension must be chosen so that $|B_1(K)|+2|B_2(K)|$ is minimized. We refer to $|A|$ as the *Clar deficit* and $|B_1(K)| + 2|B_2(K)|$ as the *Fries deficit*.

To construct the partial Kekulé structure outside of the basic patches, we choose one color class of independent faces to be the void faces. We must then choose another color class to be the set C contributing to the Clar number. Thus there are six possible options for choosing the partial Kekulé structure and the partial Clar structure. In Sect. 6.1, we show that for exactly one of these six choices around a basic patch, no completion of the Kekulé structure simultaneously minimizes the contribution to $|A|$ and $|B_1(K)| + 2|B_2(K)|$ over the patch. In Sect. 6.2, we construct fullerenes with six basic patches so that for each of the six choices for void and Clar faces, exactly one of these basic patches requires different extensions of the Kekulé structure to minimize the Clar deficit and the Fries deficit. Thus for our class of fullerenes, no Kekulé structure attains both the Fries and the Clar number for the fullerene.

6.1 A choice for the void and Clar faces that requires two Kekulé extensions

Figure 9a depicts a basic patch. For the faces surrounding the basic patch, the blue faces are chosen to be void and the red faces are chosen to be Clar faces. Figure 9b shows the partial Kekulé structure given by this choice of void faces; all edges that join two blue faces are in the partial Kekulé structure. We need to extend this to a Kekulé structure.

Extension 1 We first extend the Kekulé structure to minimize the Clar deficit. Outside the patch, we start with a partial Kekulé structure in which each red hexagonal face is a benzene face (Fig. 9b). None of the ten vertices incident with a pentagon is covered by a face in C, so these vertices must be covered by edges from A in the vertex covering (C, A). In the partial Kekulé structure, every hexagon that is not in C is adjacent to a

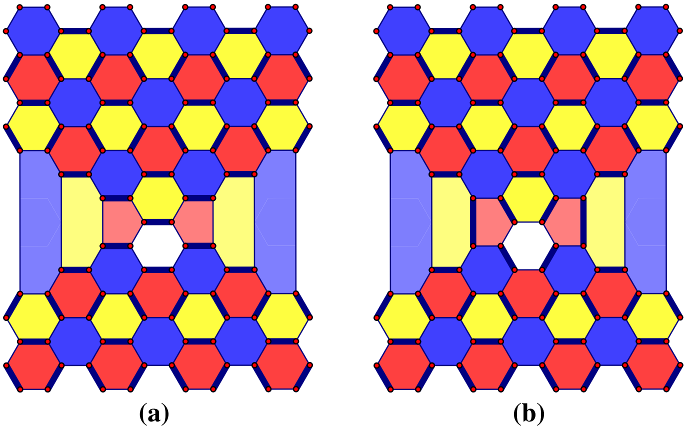


Fig. 10 Extensions 1 and 2 on a basic patch where the Clar faces are *red* and the void faces are *blue*. **a** Extension 1 minimizes the Clar deficit. Here $|A| = 5$ and $|B_1(K)| = 4$, $|B_2(K)| = 6$, $|B_1(K)| + 2|B_2(K)| = 16$. **b** Extension 2 minimizes the Fries deficit. Here $|A| = 8$ and $|B_1(K)| = 2$, $|B_2(K)| = 4$, $|B_1(K)| + 2|B_2(K)| = 10$. (Color figure online)

face in C. Thus no extension can increase $|C|$ over the patch. Any extension that does not reduce $|C|$ must cover only the ten vertices incident with the pentagons. There is only one perfect matching for these ten vertices, and it is shown as a completion of the Kekulé structure in Fig. 10a. Note that this is a Clar chain of Type 3 between the two pentagons. Over the patch in this extension, $|A| = 5$ and $|B_2(K)| = 6$, $|B_1(K)| = 4$, giving $|B_1(K)| + 2|B_2(K)| = 16$.

Extension 2 The Kekulé structure in Fig. 10b has $|A| = 8$ and $|B_2(K)| = 4$, $|B_1(K)| = 2$, giving $|B_1(K)| + 2|B_2(K)| = 10$. While $|A|$ is not minimized, $B_2(K)$ and $B_1(K)$ are both smaller than in Extension 1. Extension 1 is the only extension that minimizes the Clar deficit, and that extension does not minimize the Fries deficit. Thus for this choice of void and Clar faces over a basic patch, any structure that contributes the maximum number of faces toward the Clar number over this patch cannot achieve the maximum number of benzene faces.

6.2 Extending Kekulé structures over basic patches with other choices for the void and Clar faces

We show that the choice for the void faces and faces in C described in Sect. 6.1 is the only case over such a patch for which $|A|$ and $|B_1(K)| + 2|B_2(K)|$ cannot be minimized simultaneously.

Let the blue faces be the void faces and the yellow faces be the Clar faces. Then the Kekulé structure in Fig. 10b has a minimal Fries deficit of $|B_1(K)| + 2|B_2(K)| = 10$. Every yellow hexagon is a benzene face, so we also have a maximum number of faces contributing to the Clar count, with $|A| = 2$ (a Clar chain of Type 2).

Suppose that the void faces are in the color class that includes the pentagons (here, the red faces). Then the edges joining these faces complete a Kekulé structure over

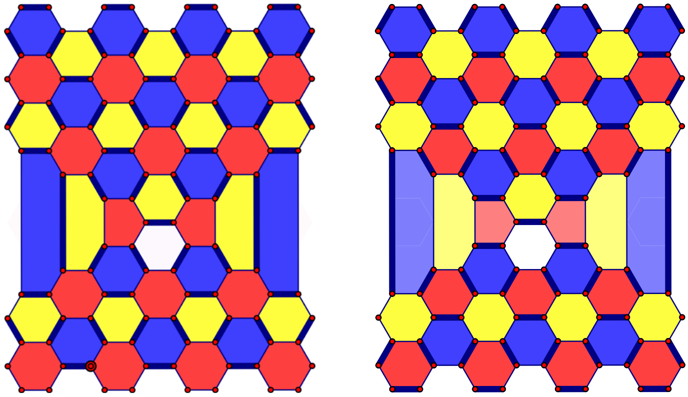


Fig. 11 Over a basic patch, we choose other *color* classes for the void and Clar faces and consider extensions of the resulting Kekulé structure. **a** The *red* faces represent the void faces. **b** The *yellow* faces are void. (Color figure online)

the patch, as seen in Fig. 11a. $|B_1| = |B_2| = 0$, so the number of benzene faces over the patch is clearly maximized. We must also choose a color class to be the Clar faces. Since all hexagons in the remaining two color classes are benzene faces, $|C|$ is also maximized over the patch for either choice.

Suppose that the yellow faces are the void faces. Begin a partial Kekulé structure consisting of all edges that join two yellow faces. Extend this Kekulé structure so that all blue and red hexagons are benzene faces as in Fig. 11b. For either choice of the Clar faces, $|C|$ is clearly maximized over this patch. $|B_1| = |B_2| = 2$, and any local change increases $|B_1(K)| + 2|B_2(K)|$ and decreases the number of benzene faces.

We see that for every case except that described in Sect. 6.1, the same Kekulé structure maximizes the number of faces contributing to the Clar number and the Fries number over the basic excluded patch.

6.3 Fullerenes over which the Clar and Fries numbers cannot be attained simultaneously

To force the existence of a patch in which these parameters cannot be maximized by the same Kekulé structure, we need a fullerene with 6 basic patches so that one of them is the exceptional patch for each the six choices of C and the void faces. One infinite class of examples is the class considered in Sect. 5 and shown in Fig. 8. The dotted edges represent the excluded patches which, in our example, are pairs of pentagons joined by a single edge. Furthermore, the partial face 3-coloring is different around each of the six excluded patches. Thus regardless of which of the six color choices for the color class of the void faces and the color class of the Clar faces is made, one of the six patches is such that one Kekulé structure maximizes the Clar number, while another Kekulé structure maximizes the Fries number, and the two parameters cannot be maximized simultaneously.

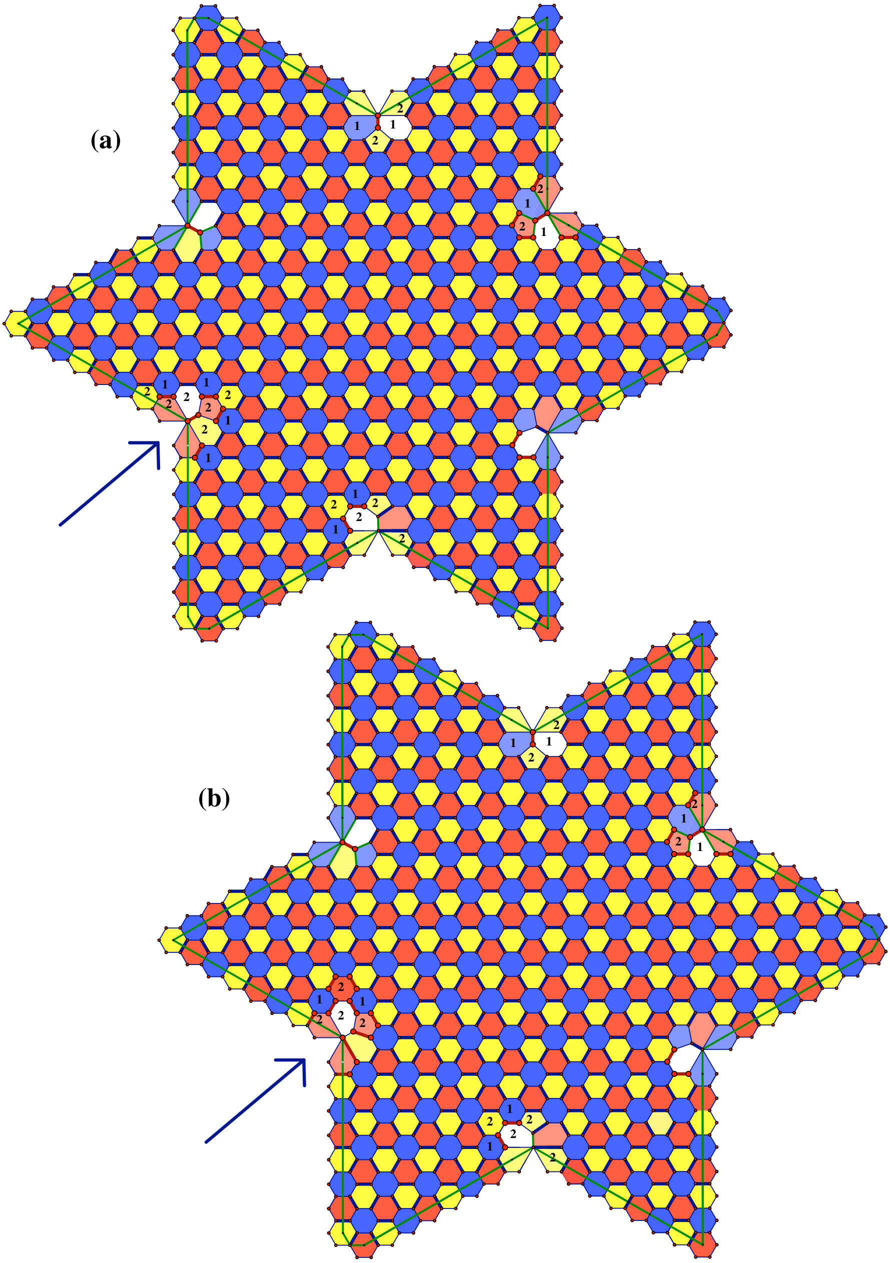


Fig. 12 The Clar faces are *red* and the void faces are *blue*. An *arrow* indicates the patch over which the Fries and Clar deficits cannot be minimized simultaneously. **a** minimizes the Clar deficit, **b** minimizes the Fries deficit. The numerals represent faces in the sets B_1 and B_2. (Color figure online)

An example with $s = 1$, $r = 7$ is shown in Fig. 12. Since fullerenes in this class with $r \geq 7$ are widely separated, the Clar number is achieved by a Kekulé structure with Clar chains between pentagons together in basic patches. In this coloring, the red faces indicate the set containing C and the void set is contained in the blue color class. A pair of pentagons lies in a basic patch on each interior corner. The edges in A are represented by thick red edges and the remaining edges in the Kekulé structure are represented by thick blue edges. An arrow indicates the excluded patch over which the number of faces in C and the number of benzene faces cannot be maximized simultaneously.

In the first figure, there are 272 benzene faces and there are 135 faces in C. In the second figure, there are 274 benzene faces and 134 faces in C. The first figure attains the Clar number but not the Fries number for the fullerene, and the reverse is true for the second. Hence the set of faces that attains the Clar number is not contained in a set of faces that attains the Fries number.

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