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Clar and Fries numbers for benzenoids

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Abstract A *Kekulé structure* of a benzenoid or a fullerene Γ is a set of edges K such that each vertex of Γ is incident with exactly one edge in K. The set of faces in Γ that have exactly three edges in K are called the *benzene faces* of K. The Fries number of Γ is the maximum number of benzene faces over all possible Kekulé structures for Γ. The Clar number is the maximum number of independent benzene faces over all possible Kekulé structures for Γ. It is often assumed, but never proved, that some set of independent benzene faces giving the Clar number is a subset of a set of benzene faces giving the Fries number. In Hartung (The Clar structure of fullerenes, Ph.D. Dissertation. Syracuse University, 2012) it is shown that this assumption is false for a large class of fullerenes. In this paper, we prove that this assumption is valid for a large a class of benzenoids.

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

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1 Introduction

A *benzenoid* $\Gamma = (V, E, F)$ is a plane graph with one distinguished face called the *outside face* and with all other faces hexagonal; in addition, we require that all vertices have degree 2 or 3 and all vertices of degree 2 bound the outside face. Benzenoids are also called *hexagonal patches, benzenoid hydrocarbons, graphite patches and graphene patches* in the literature.

By the *boundary* of the benzenoid Γ we mean the boundary of the outside face. Given a benzenoid we may project it onto Λ, the hexagonal tessellation of the plane, by simply tracing its boundary in Λ. Thus we may envision our benzenoid as a region (perhaps self-overlapping) of Λ and as such it inherits the unique 3-coloring of the faces of Λ (up to a permutation of the colors). By the *boundary* of a hexagonal face of Γ we mean the set of vertices and edges it shares with the outside face. The hexagonal faces that have non-empty boundaries are called *boundary faces.* If f is a boundary face, its boundary consists of one or more simple paths called the *boundary segments* of Γ. We denote by $\mathcal{H}$ the class of benzenoids for which the boundary is an elementary circuit and all boundary segments have odd length.

Lemma 1 *A benzenoid Γ is in $\mathcal{H}$ if and only if all boundary faces belong to two of the face color classes.*

Proof Let $f_0, f_1, \ldots, f_k = f_0$ denote the boundary faces of Γ listed in clockwise order. Since the coloring of the faces of Γ is induced by the face 3-coloring of Λ, f_{i-1} and f_{i+1} will be assigned the same color if and only if the boundary segment of f_i separating them has odd length. Hence if $\Gamma \in \mathcal{H}$ all faces with even indices will be assigned the same color and all faces with odd indices will be assigned the same color. Conversely, if the face colors alternate between two colors, all boundary segments will have odd length. □

In view of this lemma, we fix the color classes of the faces for the benzenoids in $\mathcal{H}$. For $\Gamma \in \mathcal{H}$ we choose red for the color class of faces that do not lie on the boundary; we choose blue for the largest of the remaining color classes and yellow for the third color class; we denote these face color classes by R, B and Y, respectively. The central edges on the boundary segments of length 3 and the second and fourth edges on the boundary segments of length 5 are called the *exposed edges*. We let ℓ_B denote the number of exposed edges on blue boundary faces and ℓ_Y denote the number of exposed edges on yellow boundary faces. Finally, let n denote the total length of the boundary. We have computed all of these parameters for the benzenoid in Fig. 1.

Using $|V|$, ℓ_b and ℓ_y as our basic parameters, we have:

Theorem 1 *Let $\Gamma = (V, E, F)$ belong to $\mathcal{H}$. Then*

$$|E| = \frac{3}{2}|V| - (\ell_B + \ell_Y),\ \ |F| = \frac{1}{2}|V| + 2 - (\ell_B + \ell_Y),\ \ n = 4(\ell_B + \ell_Y) - 6,$$
$$|B| = \frac{1}{6}|V| - \frac{1}{3}\ell_Y,\ \ |Y| = \frac{1}{6}|V| - \frac{1}{3}\ell_B,\ \textit{and}\ |R| = \frac{1}{6}|V| - \frac{2}{3}(\ell_B + \ell_Y) + 1.$$

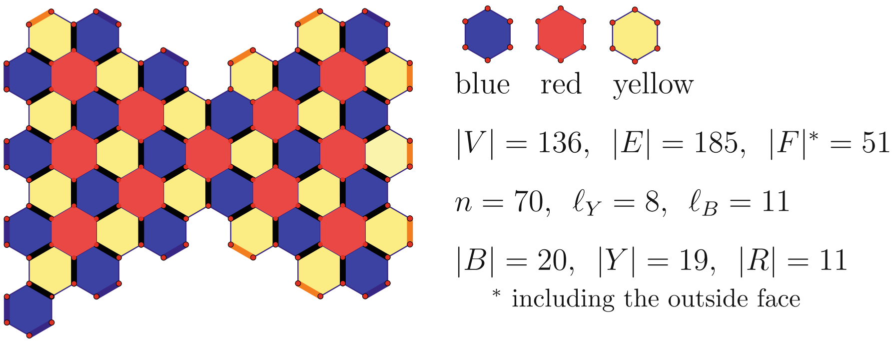

Fig. 1 A simple example

Proof Γ has exactly $2(\ell_B+\ell_Y)$ vertices of degree 2 on its boundary, all of the remaining vertices have degree 3. Hence the sum of the vertex degrees is $3[|V|-2(\ell_B+\ell_Y)]+4(\ell_B+\ell_Y)$ giving $2|E| = 3|V| - 2(\ell_B+\ell_Y)$ and the first equation above.

There are $|F|-1$ faces of degree 6 and one of degree n. Summing the face degrees and adding $2(\ell_B+\ell_Y)$ counts each vertex three times giving:

$$6(|F|-1)+n+2(\ell_B+\ell_Y) = 3|V| \text{ or } |F| = \frac{1}{2}|V| - \frac{n}{6} - \frac{1}{3}(\ell_B+\ell_Y)+1.$$

Then by Euler's formula,

$$|V| - \left[\frac{3}{2}|V| - (\ell_B+\ell_Y)\right] + \left[\frac{1}{2}|V| - \frac{n}{6} - \frac{1}{3}(\ell_B+\ell_Y)+1\right] = 2,$$

which when simplified gives the formula for n above.

Now each blue face covers 6 vertices and the only vertices not covered by the blue faces are covered by exposed yellow edges. Hence $6|B| + 2\ell_Y = |V|$, giving the formula for $|B|$; the formula for $|Y|$ is computed in the same way. Each red face covers 6 vertices and the only vertices not covered by the red faces are the n vertices on the boundary: $6|R| + n = |V|$. Using the previously computed formula for n and solving for $|R|$ gives the last formula listed. Finally, $|F| = |B| + |Y| + |R| + 1$ gives the formula for $|F|$. □

A *fullerene* $\Gamma = (V, E, F)$ is a trivalent plane graph with hexagonal and pentagonal faces. A *Kekulé structure* (or perfect matching) $K \subseteq E$ of a benzenoid or a fullerene Γ is a set of edges such that each vertex is incident with exactly one edge in K. In Fig. 1, the thick edges form a Kekulé structure. Given a Kekulé structure on Γ, a face of Γ may have 0, 1, 2 or 3 of its bounding edges in Γ. The set of faces that have exactly i of their edges in K is denoted $B_i(K)$. 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. (In the chemical literature, benzene faces are often called *conjugated 6-circuits*. See [2].) In our example, $B_1(K)$ and $B_2(K)$ are empty; $B_0(K) = R$ and $B_3(K) = B \cup Y$. It should be noted that a benzenoid may have an odd number of vertices and hence cannot have a Kekulé structure and noted further that those benzenoids that do admit a Kekulé structure usually have many of them. We soon verify that all of the benzenoids in $\mathcal{H}$ admit Kekulé structures.

The *Fries number* of a benzenoid or a fullerene Γ is the maximum number of benzene faces over all possible Kekulé structures for Γ and is denoted by $\phi(\Gamma)$. A set of $\phi(\Gamma)$ benzene faces in some Kekulé structure in Γ is called a *Fries set*. With the given Kekulé structure, our example has 39 benzene faces. Hence the Fries number of this benzenoid is at least 39; in the next section we prove that it actually is 39 for this example.

The *Clar number* of a benzenoid or a fullerene Γ is the maximum number of independent benzene faces over all possible Kekulé structures for Γ and is denoted by $\gamma(\Gamma)$. An independent set of $\gamma(\Gamma)$ benzene faces in Γ is called a *Clar set*. In any benzenoid, a color class is an independent set of faces. So in our example, both B and Y are independent sets of benzene faces; hence $\gamma \geq 20$. However, in this case we can do better by choosing the 11 leftmost blue faces and the 10 rightmost yellow faces giving $\gamma \geq 21$. In Sect. 3, we show that the Clar number of this example is in fact 21.

In our example, the Clar set just described is a subset of the Fries set, $B \cup Y$. It has generally been assumed that for any benzenoid or fullerene, some Clar set is a subset of some Fries set, or equivalently that there always exists a Kekulé structure that simultaneously gives the Fries and Clar numbers. Hartung [1] described a class of fullerenes for which this assumption is false. In this paper, we prove that the assumption is valid for all benzenoids in $\mathcal{H}$.

2 The Fries number

Lemma 2 *Let $\Gamma = (V, E, F)$ be a benzenoid that admits a Kekulé structure K. Let K_b denote the number of edges of K on the boundary of Γ. Then*

$$|B_3(K)| = \frac{|V|}{3} - \frac{|B_1(K)| + 2|B_2(K)| + |K_b|}{3}, \tag{1}$$

and if $\Gamma \in \mathcal{H}$, then

$$\phi(\Gamma) \leq \frac{|V|}{3} - \frac{\ell_B + \ell_Y}{3}. \tag{2}$$

Proof The sum $3|B_3(K)| + 2|B_2(K)| + |B_1(K)| + |K_b|$ counts each edge in K twice. Setting the sum equal to $|V| = 2|K|$ and solving for $|B_3(K)|$ gives formula (1). Thus Γ attains its Fries number when $|B_1(K)| + 2|B_2(K)| + |K_b|$ is minimized. We note that the edges in K that match a vertex of degree 2 to another vertex must belong to K_b. For $\Gamma \in \mathcal{H}$, the number of degree 2 vertices is $2(\ell_B + \ell_Y)$ and $|K_b| \geq \ell_B + \ell_Y$. Therefore, $|B_1(K)| + 2|B_2(K)| + |K_b| \geq \ell_B + \ell_Y$ which combined with (1) gives (2). □

Theorem 2 *For a benzenoid in $\mathcal{H}$ the unique Fries set is $B \cup Y$, the union of the two color classes that appear on the boundary, and*

$$\phi(\Gamma) = \frac{|V|}{3} - \frac{\ell_B + \ell_Y}{3}.$$

Proof We must construct a Kekulé structure in which $B_1(K) = B_2(K) = 0$ and $K_b = \ell_B + \ell_Y$. This is achieved by taking K to be the edges incident with both a blue and a yellow face plus the exposed edges. One easily checks that with this Kekulé structure each blue and yellow face is a benzene face and each red face is void. Hence, $B_1(K) = B_2(K) = 0$. Furthermore the only boundary faces in this Kekulé structure are the exposed edges, so $K_b = \ell_B + \ell_Y$.

To see that this Kekulé structure is unique in attaining this bound we note that to achieve this bound we must have $B_1(K) = B_2(K) = 0$ and $K_b = \ell_B + \ell_Y$. These conditions imply that all boundary faces are benzene faces. The condition $B_1(K) = B_2(K) = 0$ also implies that if three faces have a common vertex two are benzene faces and one is void. We note that if f is a red face adjacent to a boundary face, it shares a vertex with two boundary faces and must be void. But then all of the blue and yellow faces adjacent to f must be benzene faces. Thus working inward from the boundary we see that all red faces are void and all blue and yellow faces are benzene faces. □

3 The Clar number

Define a *vertex covering* (C, A) of a plane graph Ω to be a set of faces C and edges A such that all vertices of Ω are incident with exactly one element of the covering. Recall that the *Clar number*, $\gamma(\Gamma)$, of a benzenoid or fullerene $\Gamma = (V, E, F)$ is the maximum set of independent benzene faces over all Kekulé structures for Γ. Let K be a Kekulé structure for Γ. If C is an independent set of benzene faces with respect to K and A is the set of edges in K that are not incident with faces in C, then (C, A) is a vertex covering. We use the term *Clar structure* for vertex coverings obtained in this way from a Kekulé structure. In [1], the following result was proved for fullerenes:

Lemma 3 *Let $\Gamma = (V, E, F)$ be a fullerene or a benzenoid with a vertex covering (C, A). Then (C, A) is a Clar structure for some Kekulé structure of Γ. Furthermore,*

$$|C| = \frac{|V|}{6} - \frac{|A|}{3}. \tag{3}$$

This result also holds for benzenoids as the proof below from [1] is valid in that setting too.

Proof First, we may simply select three alternating edges around each face in C. Those edges plus the edges in A form a Kekulé structure for Γ. Next note that every face in C contains 6 vertices and every edge in A contains 2 vertices and that every vertex of Γ is incident with exactly one element of the vertex covering. Hence $6|C| + 2|A| = |V|$, and solving for $|C|$ gives the equation. □

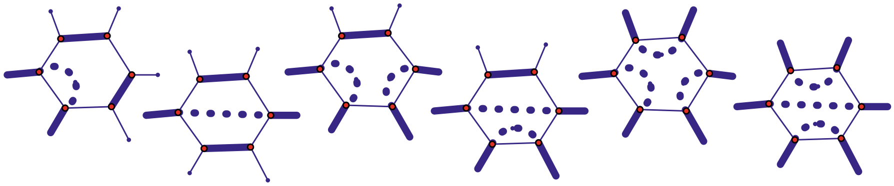

Fig. 2 Possible couplings

Hence a benzenoid attains its Clar number with a vertex covering (C, A) that minimizes $|A|$. Let $\Gamma \in \mathcal{H}$. We proved in the last section that the Fries set for Γ is the union of the two color classes that appear on the boundary. Since each color class is independent, one good choice for the Clar set is the larger of these two color classes, the blue faces. The Clar structure corresponding to the blue faces is (B, E_Y) where E_Y is the set of exposed yellow edges and, as we have already shown, $|B| = \frac{1}{6}|V| - \frac{1}{3}\ell_Y$.

This is an easily computed lower bound but, as we saw with our basic example, the actual value could be larger. The key concept needed to understand when and how we can improve on this bound is that of "Clar chains." Clar chains were introduced in [1] and used there to produce fullerenes with no Kekulé structure that gives both the Fries and Clar numbers. Since properties of Clar chains are worked out in detail in that paper, we only discuss those properties relevant for the benzenoids in $\mathcal{H}$ and some of the proofs are only sketched here, referring to [1] for the details.

Given a Clar structure (C, A) let A^* denote those edges in A that do not lie on the boundary. We say that an edge $e \in A^*$ *exits* a face f if e and f share exactly one vertex. If $f \in C$, no edge of A^* exits f; if f is any other hexagonal face, 0, 2, 4 or 6 edges of A^* exit f depending on whether f shares 3, 2, 1 or 0 edges with faces in C. In [1], it was shown that the edges exiting a hexagonal face f may be *coupled* by segments across that face so that coupled edges either exit by adjacent vertices or exit directly across from one another and that the coupling segments never cross. The six possible coupling schemes for a face are pictured in Fig. 2.

Now construct a simple auxiliary graph with vertex set V, the edges in A^* and edges corresponding to the coupling segments joining endpoints of edges in A^* across hexagonal faces. In this graph, the vertices on the faces in C have degree 0; vertices that lie on the boundary and are endpoints of edges in A^* have degree 1; the remaining endpoints of edges in A^* have degree 2. Hence this auxiliary graph consists of isolated vertices, paths that join one vertex on the boundary to another vertex on the boundary and circuits. Given a path, consider the sequence $f_0, e_1, f_1, e_2, \ldots, e_k, f_{k-1}, e_k, f_k$ where $f_0 = f_k$ is the outside face, the e_i are the edges of the path in A^* and f_i is the face that contains coupling segment joining e_i to e_{i+1}. This sequence of faces and edges is called an *open Clar chain*. Circuits are also represented by such sequences where $f_0 = f_k$ is not the outside face and and the end points of e_k and e_1 are coupled across f_0; these are called *closed Clar chains*.

Lemma 4 *Let $\Gamma \in \mathcal{H}$, let (C, A) be a Clar structure for Γ and let $f_0, e_1, f_1, e_2, \ldots, e_k$, f_k, e_{k+1} be a Clar chain. Then all of the faces on the chain are in the same color class (red if it is an open chain). Furthermore when traversing the chain, all of the faces*

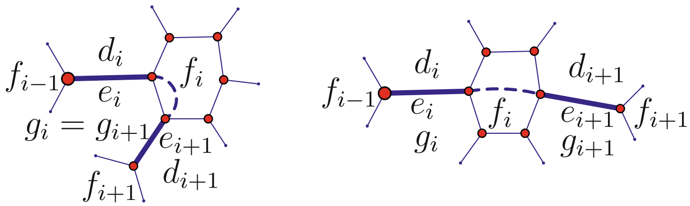

Fig. 3 Clar chains

adjacent to the e_i on the right are in a second color class and all of the faces adjacent to the e_i on the left are in the third color class.

Proof Since $\Gamma \in \mathcal{H}$ we may extend the face 3-coloring to include the outside face colored red. For the rest of this proof refer to Fig. 3. Since d_i, g_i and f_i share a common vertex, they are assigned different colors. Now the six faces around f_i alternate in the colors of d_i and g_i. If the chain makes a sharp right turn, $g_{i+1} = g_i$ and d_{i+1} is assigned the same color as d_i. The same argument holds for a sharp left turn. If e_{i+1} exits opposite from e_i, g_{i+1} is separated by one face from g_i and hence is assigned the same color as g_i; similarly d_{i+1} is assigned the same color as d_i. Since f_{i-1} shares a vertex with both d_i and g_i its color must be different from the colors assigned to d_i and g_i; the same is true of f_i. Hence f_{i-1} and f_i must be assigned the same color. Inductively then all of the f_i are in one color class, all of the d_i in a second color class and all of the g_i in the third color class. □

Lemma 5 *Let $\Gamma \in \mathcal{H}$, let C be a Clar set and let (C, A) be the corresponding Clar structure for Γ. Then there are no closed chains in the chain decomposition given by (C, A).*

Proof Suppose that $e_1, f_1, e_2, \ldots, e_k, f_k, e_1$ is a Clar circuit for the Clar structure (C, A). We may assume that the inside of the circuit is on the right as we traverse it by increasing the indices. Using the notation pictured in Fig. 3, let $g_1, \ldots g_k$ denote the faces on the inside and incident with the e_i. Delete from C all faces that lie inside the circuit to get C' and delete from A all of the edges of the chain and any other edges of A that are inside this circuit to get A'. Note that (C', A') is a vertex cover for all vertices outside the circuit. Now let G denote all of the faces inside the circuit of the same color as the g_i. Since every vertex inside the circuit and every endpoint of an e_i meets a face of this color, $(C' \cup G, A')$ is a vertex cover. Since $|A'| < |A|$, $|C' \cup G| > |C|$, contradicting the fact that C is a Clar set. □

4 Clar and Fries sets

The following is a restatement of Theorem 2–5 from [3]:

Theorem (Saaty and Kainen) *Every trivalent, bipartite plane map admits a unique face three-coloring.*

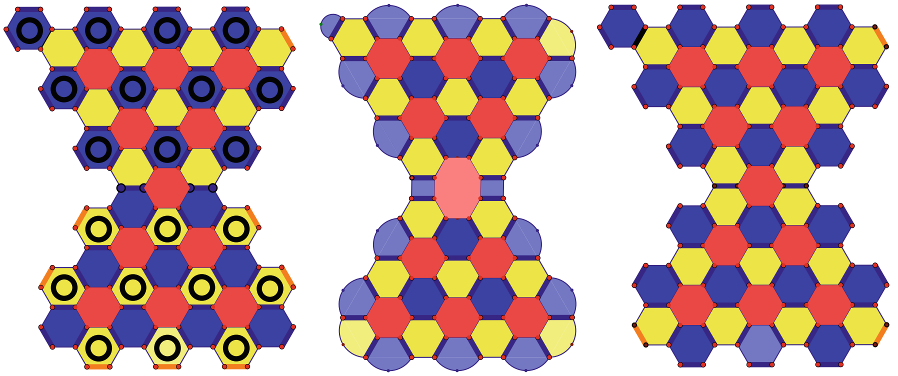

Fig. 4 Using Clar chains

We now have all of the tools in place to prove our main result:

Theorem 3 *Let $\Gamma \in \mathcal{H}$. Then every Clar set for Γ is a subset of the Fries set of Γ.*

Proof Let $\Gamma \in \mathcal{H}$, C be a Clar set and let (C, A) be the corresponding Clar structure. We construct another auxiliary graph called the *expansion* of (C, A) and denote it by $\mathcal{E}(C, A)$. This is a slight variation on the expansion as defined in [1]. First each boundary path of length 3 or 5 is replaced by a single edge. The faces they bound (including some faces in C) now have degree 2 or 4. The Kekulé structure K is also modified along the altered boundary paths. First we note that given a boundary path of length 3 or 5 the vertices of degree 2 can be covered only if all of the exposed edges belong to K or if all of the nonexposed edges on the path belong to K. If the exposed edges of a path are in K, the replacement edge does not belong to K'; if the nonexposed edges of a path are in K, the replacement edge is included in K'. One easily checks that this modification K' of K is a perfect matching for the modified graph and that the corresponding modification (C', A') of (C, A) is still a vertex cover. Note that none of the edges in A^* have been deleted or replaced. The next step in this construction is to "split" the edges in A^* and expand each one into a new square face. The hexagonal faces along a Clar chain are each expanded to octagons or to a face of degree $2m + 6$ if m chains pass through it. If we let $\overline{A^*}$ denote the square faces, $(C \cup \overline{A^*})$ is now a face-only vertex covering of $\mathcal{E}(C, A)$.

This construction is illustrated in Fig. 4. The Clar structure (C, A) that we start with takes the set of 21 faces indicated by circles in the left most patch. The 5 edges in A are the 2 edges of the Clar chain across the center plus the exposed edge of the yellow face in the upper left corner and the 2 exposed edges of the blue faces in the lower left and right corners. Ignoring the face 3-coloring, $\mathcal{E}(C, A)$ is pictured in the center with its modified Kekulé structure K'.

One easily sees that this construction yields a $\mathcal{E}(C, A)$ that is bipartite and trivalent. Hence we may apply the Saaty–Kainen Theorem to get a face 3-coloring of $\mathcal{E}(C, A)$. Since this coloring is unique and the color classes are the only face-only vertex coverings, $(C \cup \overline{A^*})$ is a color class (in our example, the blue color class). We use red for the color class of $\mathcal{E}(C, A)$ containing the outside face, and yellow for the third color class. Finally, shrinking the faces in $\overline{A^*}$ back to the edges in A^* and reinstalling the length-3 and length-5 paths on the boundary, we are back to Γ (on the right in the figure) with an *improper face 3-coloring:* the coloring is a proper face coloring everywhere except that faces sharing an edge from A^* have the same color (yellow in the figure). Here the blue faces are the Clar set. Since the red faces belong to the color class of the outside face, they remain the same in both colorings. In the improper coloring, the blue and yellow faces have been interchanged in the bottom half.

In general the Clar chains from the Clar structure (C, A) for the benzenoid Γ partition Γ into regions. The improper face 3-coloring given by the expansion $\mathcal{E}(C, A)$ maintains the red color class and reverses the blue and yellow faces in alternate regions. Hence C is always a subset of the Fries set $B \cup Y$. □

Returning to our example, can we be certain that the Clar structure that we started with actually achieved the Clar number, i.e. that 21 is indeed the Clar number, not just another lower bound? Note that for the Clar structure (B, Y^*), $|B| = 20$ and $|Y^*| = 8$ and for the Clar structure (C, A) we just constructed $|C| = 21$ & $|A| = 5$. It follows from Eq. 3 that increasing $|C|$ by 1 decreases $|A|$ by 3. So for any improvement on 21, we would need a Clar structure (C, A) with $|A| = 2$. That would require a Clar chain of length 1 or a Clar chain of length 2 that completely separates the blue and yellow exposed edges. One easily checks that a Clar structure with such a Clar chain does not exist.

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