A Catalogue of Periodic Fully-Resonant Azulene-Transitive Azulenoid Tilings Analogous to Clar Structures

Gunnar Brinkmann, a,*, Olaf Delgado-Friedrichs, b Edward C. Kirby, c and Nicolas Van Cleemput a

a Ghent University, Applied Mathematics and Computer Science, Krijgslaan 281 S9, Ghent, B-9000, Belgium
b The Supercomputer Facility, Australian National University, Canberra, Australia
1 Resource Use Institute, Pitlochry PH16 5DS, Scotland UK

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Abstract. A reference catalogue of 1274 fully-resonant azulenoid tiling patterns with a symmetry group that operates transitively on the azulenes has been generated, and may be consulted at http://caagt.ugent.be/azul. Such networks are analogous to Clar structures and fully-naphthalenoid structures among benzenoids.

Keywords: azulenoid, Clar structure, tiling, fullerene, nanotube, torus

INTRODUCTION

The conjugated cyclic hydrocarbon benzene (C 6H 6) is the archetypal aromatic hydrocarbon, and it is now well known that among benzenoids, those with a chemical graph that can be partitioned into a set of disjoint hexagons, are among the more stable members of this group. This class, of what Clar 1 called 'fully-benzenoid' structures, was later generalised by use of the term 'fully-arenoid', when 'fully-naphthalenoid' structures came to be being studied and enumerated. 2 − 5 Similarly, a fully-resonant-azulenoid, 6 exemplified by Figure 1(c), is a structure in which all the vertices may be accounted for by a set of disjoint azulene graphs.

It should be noted that in this paper we use the term 'fully-resonant azulenoid' rather than just 'fully-azulenoid' when making formal reference to this class.

This is to avoid confusion with the pentaheptite or simply all-azulenoid tilings, because Clar's term 'fully' has sometimes been used in both of these senses.

The term 'azulene' (or 'azu line') was introduced by Piesse 7−9 in the nineteenth century for the unknown constituents of some essential plant oils responsible for the pleasingly blue colours observed during steam distillation and other processes. Such colouration had been known for several centuries, but it was not until well into the 20th Century that the structure responsible for it was identified. 10 The position of the long wavelength peak within the visible spectrum – and therefore a particular azulene's colour – varies according to the nature and the location of any substituent groups present. The term azulene is now used both as a specific name for the parent hydrocarbon C 10H 8 (Figure 2), and as a generic term for all structures containing this carbon ring system.

Like naphthalene, azulene (Figure 2) is a fully-conjugated bicyclic system, and it is iso-electronic with naphthalene. Its structure, however, consists of a five-ring and a seven-ring – rather than the two six-rings of naphthalene – and shares two carbon atoms and a bond.
When talking about the plane graphs representing the molecules the notion of a ring is equivalent to the mathematical notion of a face. On the basis of chemical reactivity, azulene behaves partly like an aromatic system – under generally milder conditions – and partly as a cyclopolyolefin. More relevant to the motivation for this investigation is the fact that azulene has a modest dipole moment and there is a tendency for electron migration from the seven-ring towards the five-ring. This is no more than a tendency in its ground state – it is its polarizability under external influence that is important. It is often rationalised as an attempt by azulene to stabilize the 7-ring as a positively charged aromatic sextet (the tropylium ion). As a result, the 5-ring tends to acquire a negative charge, particularly at the 1(3) positions. This fact gives rise to speculation as to how an extended fully-azulenoid structure, like Figure 1(c) for example, might behave, chemically and electronically, if formed into analogues of graphene (single layer graphite strips), nanotubes (capped or uncapped) or tori. It is not clear whether such azulenic behaviour would survive embedding of the system within a network, nor quite what the consequences would be if it did. Azulene’s chemical behaviour is quite sensitive to steric hindrance, but that would not of necessity affect electrical conductivity. However, even if it turns out that azulenic properties as we know them do not appear, we feel that enumeration of this well-defined set of networks is still useful as a contribution towards the structural taxonomy of carbon networks as a whole.

However, before any serious theoretical study can be made, it is desirable to know what and how many tiling patterns there are within the class described as fully-resonant-azulenoid. One of us has published some preliminary studies based on ad hoc trial & error methods. A small number of patterns were identified, and some networks covering cylinders, tori, and spherical objects have been drawn. It was always suspected, however, that other patterns and tilings were possible, and our study has confirmed this on a systematic basis.

The total number of possibilities is obviously not only infinite but even uncountably infinite. This can easily be seen by modifying the directions and the neighbouring faces of the azulenes in a single strip in Figure 1(c). By doing this we can use a single strip to code an infinite 0,1-sequence proving the existence of an uncountably infinite variety of tilings even if we don’t modify the other strips. So the maximum ring size in this tiling is still 8. We restrict our attention to the following class which we call fully-resonant azulene-transitive azulenoid tilings:

**Definition:** A fully-resonant azulene tiling is an infinite tiling of the plane where every vertex has degree 3 and there exists a spanning subgraph (a subgraph that contains every vertex of the tiling) so that every connected component is isomorphic to the graph of azulene.

A fully-resonant azulene-transitive azulenoid tiling is a fully-resonant azulenoid tiling so that this spanning subgraph can be chosen in such a way that the symmetry group of the tiling acts transitively on the connected components (the azulenes).

Note that the definition always just requires the existence of such a spanning subgraph – it is not required that it is uniquely determined.

In mathematical terms azulene-transitive means that there is only one orbit of the symmetry group on the azulenes. The mathematical use of the word “orbit” is quite different from the one in chemistry and physics. We will show that there are precisely 1274 such fully-resonant azulene-transitive azulenoil tilings. A periodic tiling is a tiling where you have only finitely many orbits of vertices, edges and faces. So a fully-resonant azulene-transitive azulenoil tiling is also a periodic tiling.

A periodic tiling of the plane stays periodic if one restricts the symmetries to a subgroup of the symmetry group that is generated by two independent translations. Taking the quotient of the plane by this subgroup places the fundamental domain on a torus. This is also used in the program to visualize the structures described at the end of this article.

**TOOLS**

The theory of Delaney-Dress symbols has proven to be a powerful tool for the enumeration of equivalence classes of periodic tilings. A Delaney-Dress symbol is a data structure to encode a tiling of the plane together with its symmetry group. In the case of a periodic tiling, this data structure is finite. In the following we will give a short sketch of this data structure. For a bit more extensive though descriptive definition see Ref. 13 or see Ref. 14 for a more formal one.

A flag of a tiling $T$ is a triple $(v,e,f)$ consisting of a vertex $v$, an edge $e$ and a face $f$ of the tiling such that $v$ lies on $e$, and $e$ lies in $f$. The flag graph of $T$ is an infinite graph together with a partition of the edges in 3 sets. The vertex set is the set of all flags of $T$. The edges of the flag graph are $\sigma_0$-edges which connect the flags that only differ in $v$, $\sigma_1$-edges which connect the flags that only differ in $e$ and $\sigma_2$-edges which connect the flags that only differ in $f$. The Delaney-Dress graph of the tiling has the equivalence classes of flags under the symmetry group as vertices. Two such vertices (equivalence classes) $v, w$ are connected by an edge belonging to the class of $\sigma_0$-edges, $\sigma_1$-edges or $\sigma_2$-edges if and only if one (or equivalently all) flags in $v$ are connected to a flag in $w$ by an edge of the specific class. Note that the same two vertices can be connected to each other by edges from more than one class. An illustrative example
of the process from the tiling over the flag graph to the Delaney-Dress graph is given in Figure 3.

The Delaney-Dress graph alone is not sufficient to encode a tiling. E.g. the Delaney-Dress graphs of all 3 regular tilings (the hexagonal tiling, the square tiling and the triangular tiling) all have the same Delaney-Dress graph consisting of a single vertex and 3 loops – one of every class. To completely encode the tiling we need the Delaney-Dress symbol. The Delaney-Dress symbol \((D,m_{01},m_{12})\) of a tiling consists of the Delaney-Dress graph together with two functions that assign two natural numbers \(m_{01}\) and \(m_{12}\) to every vertex (that is: orbit of flags) of the graph. The number \(m_{01}\) is the size of the faces to which the flags in the orbit belong. The number \(m_{12}\) is the degree of the vertices to which the flags belong. Note that the degrees and face sizes are the same for flags of the flag graph that belong to the same orbit of the symmetry group.

In Figure 3 we have \(m_{12}=3\) for all elements of the Delaney-Dress graph. Furthermore we have \(m_{01}(b) = m_{01}(c) = 8\) because \(b\) and \(c\) belong to 8-gons and \(m_{01}(a)=4\) because \(a\) belongs to a 4-gon.

The combinatorial structure of a tiling together with its symmetry group can be encoded by its Delaney-Dress symbol, but in order to use these symbols for enumeration we also have to have the reverse direction: we have to know which symbols are the symbols of a tiling of the Euclidean plane.

We use the following lemma:\(^{14}\)

**Lemma 1:** A Delaney-Dress symbol \((D,m_{01},m_{12})\) is realizable as a tiling of the Euclidean plane if it satisfies the following conditions:

1. \(D\) is finite and connected;
2. \(m_{01}\) is constant on \(\sigma_0\)-\(\sigma_1\)-components and \(\forall d \in D: d(\sigma_0 \sigma_1)^{m_{01}(d)} = d\)
3. \(m_{12}\) is constant on \(\sigma_1\)-\(\sigma_2\)-components and \(\forall d \in D: d(\sigma_1 \sigma_2)^{m_{12}(d)} = d\)
4. \(\forall d \in D: d(\sigma_0 \sigma_2)^{-1} = d\)
5. \(\sum_{\alpha \in d} \left( \frac{1}{m_{01}(d)} + \frac{1}{m_{12}(d)} - \frac{1}{2} \right) = 0\)

In this notation a \(\sigma_i\)-component is a connected component of the graph consisting only of edges belonging to class \(\sigma_i\) or \(\sigma_i\).

The notation \(d(\sigma_i \sigma_j)^k\) stands for the vertex reached when starting at vertex \(d\) and then \(k\) times walking along the edge belonging to class \(\sigma_i\) first and the edge belonging to class \(\sigma_j\) afterwards.

If you have a fully-resonant azulene-transitive azulenoid tiling with a given set of spanning azulenes and you remove all the edges between the pentagons and heptagons in the azulenes (suppressing the new vertices of degree 2), you get a tiling with a spanning set of disjoint octagons. Note that by suppressing the vertices of degree 2 no faces smaller than 4-gons can be formed.

We will use the inverse process for construction: we split the generation in two parts. In the first part we will generate tilings where every vertex has degree 3 (so \(m_{12}=3\) for all elements in the Delaney-Dress symbol) and that contain a set of disjoint octagons. We will use the inverse of the operation described above and replace these octagons by azulenes in a way that all the azulenes are equivalent under the symmetry group of the tiling. Afterwards we will use the inverse of the operation described above and replace these octagons by azulenes in a way that all the azulenes are equivalent under the symmetry group.

An octagon in the tiling corresponds to a \(\sigma_0\)-\(\sigma_1\)-cycle in the flag graph with 16 vertices. Our restriction is only that all octagons are equivalent under the symmetry group, but we do not distinguish between two isomorphic tilings with this property that only have different symmetry groups. In fact the only possible inner symmetry of an azulene in a fully-resonant azulene-transitive azulenoid tiling is a reflection through the center of the bond separating the 5-gon and the 7-
gon. Removing this symmetry from the symmetry group we get a tiling without inner symmetries but still just one orbit on the azulenes. This tiling together with the induced action of the same symmetry group corresponds to an octagon tiling (with the same group) that has no inner symmetries of the octagon. So we are only interested in octagon tilings that allow a group that acts transitively on the octagons without inner symmetries. So we can restrict the generation to tilings without inner symmetries of the octagon and therefore a 16-cycle representing the octagon in the Delaney-Dress graph.

Once we have all non-isomorphic tilings, we can interpret them as having the maximal possible symmetry group. We take the 16-cycle representing the octagon as the starting point of the construction.

Each vertex in the tiling has degree 3. This corresponds to a 6-cycle of $\sigma_1$- and $\sigma_2$-edges in the flag graph. Each vertex is contained in exactly one of the octagons in the spanning set and all 8 vertices of these octagons must be distinct. Furthermore our assumption that the symmetry group does not contain interior symmetries of the octagon also means that these cycles are not mapped onto each other. Exactly two of the vertices in each 6-cycle belong already to the octagon. This gives us the partial Delaney-Dress graph containing at least $16 + 32 = 48$ flags and the connecting edges depicted in Figure 4.

Since each orbit corresponding to a vertex needs to have a non-empty intersection with the orbit of special octagons, the partial Delaney-Dress graph in Figure 4 contains all the vertices and there are only some $\sigma_0$-edges missing to form the Delaney-Dress graph of a tiling.

Because all the vertices are of degree 3, we know that $m_{12}$ is a constant function of value 3. For the flags corresponding to the octagon we have that $m_{01}=8$. This gives us the possibility to enumerate the values of $m_{01}$ for the remaining flags using condition 5 for the realizability of Delaney-Dress symbols. To simplify this process we use that due to condition 2 the flags in Figure 3 that do not belong to the octagon are grouped in eight groups of 4 chambers each. So we need to find all combinations of 8 numbers $n_1,...,n_8$ satisfying the formula

$$\sum_{i=1}^{8} \frac{1}{n_i} = \frac{3}{2}$$

This gives us the following 12 sets of integers (Table 1).

The next step is to systematically try all possible distinct assignments of these numbers to the remaining flags in the partial Delaney-Dress symbol and then add the missing $\sigma_0$-edges in all possible ways compatible with conditions 2 and 4 in Lemma 1.

There are several reasons why some $\sigma_0$-edges would not lead to a valid Delaney-Dress symbol:

- $m_{01}$ might not be constant on a $\sigma_0 \sigma_1$-component,
- the size of a $\sigma_0 \sigma_2$-orbit might not be a divisor of $2m_{01}$,
- the size of a $\sigma_0 \sigma_2$-orbit might not be a divisor of 2.

Using this method we find that there are exactly 255 non-isomorphic tilings satisfying these conditions. Due to the relatively small number of tilings we did not use

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more sophisticated ways to avoid the generation of isomorphic tilings but simply used a list and compared new tilings with those already in the list.

As can be seen in Figure 5 it is possible that a tiling contains two different sets of octagons that satisfy the property that each vertex is contained in exactly one of the octagons in the set. In a tiling with two different spanning sets of symmetry-equivalent octagons, the replacement by an azulene would in principle have to take place for every set in order to get the complete set of azulenoid tilings. But in fact the tiling in Figure 5 is the only tiling for which this happens and here both sets of octagons are equivalent under the symmetry group and would give isomorphic azulenoid tilings.

The last step is to replace the octagons by azulenes. Each octagon can be replaced by an azulene in 8 ways – some of which lead to isomorphic tilings. It is also possible that inserting an azulene in two different octagon tilings produces isomorphic tilings at some point. Again we simply used a list to avoid isomorphisms. We obtained a list of 1274 pairwise non-isomorphic fully-resonant azulene-transitive azulenoid tilings.

Isomorphism rejection by lists is not a good choice in cases where a huge number of structures are generated and time is critical. But here it is more than sufficient. The whole C-program implementing the algorithm described above takes less than 2 seconds on a 2.2 GHz Pentium Core Duo processor. It is important to not only make sure that the algorithm used is correct, but also test the implementation. The best way to do so is to use an independent program if possible even implementing another algorithm. Olaf Delgado-Friedrichs independently implemented a different algorithm. It is also based on the use of Delaney-Dress symbols but generates in its first phase all tilings in which the tiles are octagons and all related by symmetry, but the vertex degrees may be arbitrary. Relative to the approach described above, the order of adding edges to the Delaney graph (here $\sigma_2$ instead of $\sigma_0$) and generating combinations of numbers (here $m_{12}$ instead of $m_{01}$) in accordance to Lemma 1 is reversed. The $\sigma_0\sigma_1$-cycle representing that tile in the Delaney-Dress symbol is then replaced by the Delaney-graph of Figure 4 and the $\sigma_2$-edges by $\sigma_0$ edges. Also in this approach, a list of the already generated structures in each phase is maintained in order to avoid duplicates. The results of both algorithms agree, allowing us to be very confident in the completeness of the list.

**DISCUSSION**

Within the class described, intuition suggests that tilings with smaller rather than larger rings will be the more useful and interesting – although with a wider range of sizes than fullerenes had in their original strict sense. The largest ring size that occurred is 36 and there are 316 tilings that have a ring larger than 16. Systems with very large rings become more reminiscent of coronoids rather than benzenoids, and for present purposes we regard them as having a lower priority for study. Even so, the number of tilings presented here (1274) is still quite large in practical terms, and, obviously, firm conclusions of any kind must await deeper and more detailed study of the possible structures listed. However, we may make a few preliminary observations, with a view to suggesting some priorities for further study.

In Table 2, we show the numerical occurrence of rings up to size 16 among the 1274 tilings, and for the most part it is the smaller, even rings that predominate (5- and 7-rings are included for completeness, but by definition occur in every tiling).

In terms of practical chemistry and physics, two questions will need to be addressed: (i) would azulenic structures of this type be stable, and show any novel chemical properties, and (ii) would any of them show metallic properties and electrical conductivity?

In respect of chemical properties (i), there seems no reason to suppose that such network structures should not be stable, but these disjoint azulenes are...
likely, perhaps, to add less *extra* stability to a network than their benzenoid analogues. This is because among the most stable *finite planar* benzenoids, the full hexagons are essentially disconnected, *i.e.* no Kekulé structures involve double bonds that merely connect full hexagons rather than forming part of them. In contrast, while obviously the azulenes in a network *can* be disconnected and partitioned in this way, it has been conjectured that they do not have to be, and that no such structure is essentially disconnected.

Infinite fully-resonant azulenoid tilings and their toroidal analogues are never essentially disconnected because the set of all bonds not contained in the azulenes together with the bonds between the 5- and the 7-rings in the azulenes form a Kekulé structure. A similar construction also works for the hexagonal tiling and its toroidal analogues when interpreted as being fully-benzenoid or fully-naphthalenoid.

Besides this question of connectedness, there is the matter of the full versus the empty rings, and this favours azuloids. For planar structures (in the chemical sense) embedded in the plane there is no uncertainty: in a benzenoid, any ring that has degree-2 vertices is part of the periphery, and must always be full, otherwise it is not fully benzenoid. The same argument applies to an azulenoid, with the further stipulation that only azulenes can have degree-2 vertices because they must be full and on the periphery, if the structure is to be fully azulenoid. The set of full-rings is therefore well-defined in both cases.

In toroidal species on the other hand, the full-set of azulenes is still, in general, well-defined, but for a benzenoid, because there is now no periphery, there are three equivalent choices of hexagons to be made, and the set of full rings is not unique. (However, note that this is not true for every azulenoid. Figure 6(a) shows an example where there appear to be two equally valid azulene sets that could be defined as being full.)

Despite the caveat that no infinite and probably also no finite fully-resonant azulenoid is *essentially* disconnected, it is still possible that enough Kekulé structures of the form where azulenes are disconnected may contribute, and endow the azulenoid with a significant degree of basicity.

The other practical possibility to consider, is that the innate polarisability of azulene could render carbon structures constructed from these networks – strips, tubes or tori – unusually good electrical conductors.

If we now look very broadly at the collection of tiling patterns, and how one might select some good candidates for further study, with electrical properties in mind, many of them may be put aside for the time being, as having too much variation in the azulenes’ orientation. Since azulene itself has at least some polarity, it is reasonable to assume that an approximately head-to-tail orientation of the azulenes is desirable. Obvious candidates are therefore those with a 2-6’ coupling between azulenes (Figure 6(a) for example). Figure 6(b) has the same coupling, but the rows of azulenes, alternate in direction – an arrangement that seems unattractive, although it might yield some interesting Möbius strips.

\[ \text{Figure 6. Three fully-resonant-azulenoid tilings.} \]

(a) Catalogue number 4: a simple 2-6’ coupling, but with an ambiguous full-set. (b) Catalogue number 34: this too is a 2-6’ coupling and it has the smallest number of ring sizes, but the direction of rows alternate. (c) Catalogue number 5: here the coupling is through the sides of a 4-cycle, one of which is from site 1(3) of one azulene to 5(7) of another.
The relative simplicity of Figure 6(b) raises another question of interest to check: as an alternative structural interpretation, could a subset of the set of empty hexagons in fact be regarded as full, with the azulenes empty? The answer is no, and this can be seen by considering the eight hexagons that surround any given azulene. Six of them will have one edge in common with the central azulene, and two of them will share two edges. For the answer to be yes, these eight hexagons must, in sequence, alternately be full and empty, and there are two ways of choosing a full set. Either choice, however, results in one hexagon of the pair that share two edges with the azulene being full while the other hexagon is empty. It is easy to see that a consequence of this is that the valencies of the azulene bridging bond cannot be satisfied. Similarly, it has been reported that a finite planar benzenoid cannot be both fully-benzenoid and fully-naphthalenoid.

However, while directly in-line arrangements of azulenes appear the most attractive at first sight, it is worth considering again the chemistry of azulene. Referring to Figure 2, it is actually position 1 (or, equally, 3) of azulene that is, by a substantial margin, the preferred point of attack by electrophilic reagents, so that it is possible that 1-5' or 1-7' may be a better coupling, even if the conjugated conduction path is more circuitous. Figure 6(c) shows an example.

In Figure 7, a small sample is shown of some azulene chains, isolated from their wider networks, that occur within some catalogue tilings, and possible conjugation paths through them. Whether, in reality, the polarising tendency of azulene is strong enough to make some network patterns behave conspicuously better than others under the influence of an electrical potential, remains to be seen, and we have yet to examine and compare the eigenvalues of a range of objects tiled with these patterns.

**Sample**

It is difficult to select a sample from the 1274 structures that is interesting and at the same time small enough to be included in the text. We selected the six structures in which the azulenes are all equivalent under a subgroup of the symmetry group that only contains translations. These structures are shown in Figure 8.
CONCLUSIONS

With current knowledge, none of the 1274 tilings that are enumerated here should be ruled out, but we consider that those with rings of no more than ten vertices, and that have a conjugation path from position-1(3) of one azulene to position-5(7) of another, and where all azulenes are arranged in one direction, with a tolerance of, say, around 45°, may prove to be the most interesting in the context of novel graphenes, nanotubes and tori.

REFERENCES

7. Note: Mr S. Piesse is reported to have read a paper "On Azuline" at a meeting of the Chemical Society (London) on 5th November 1863.

*Figure 8.* The six structures where all the azulenes are equivalent under a group of translations.
SAŽETAK

Katalog periodičkih potpuno rezonantnih azuleno-tranzitivnih azulenoidnih popločenja analognih Clarovim strukturama

Gunnar Brinkmann,a Olaf Delgado-Friedrichs,b Edward C. Kirbyc i Nicolas VanCleemputa

aGhent University, Applied Mathematics and Computer Science, Krijgslaan 281 S9, Ghent, B-9000, Belgium
bThe Supercomputer Facility, Australian National University, Canberra, Australia
cResource Use Institute, Pitlochry PH16 5DS, Scotland UK