Toroidal azulenoids

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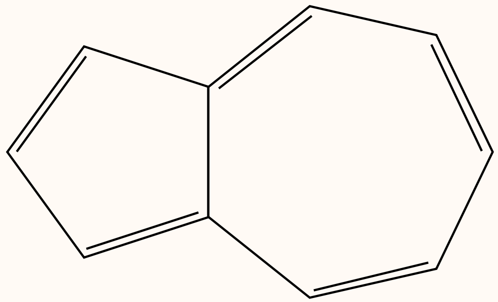
(Joint work with Gunnar Brinkmann, Olaf Delgado-Friedrichs and Edward Kirby)

Outline

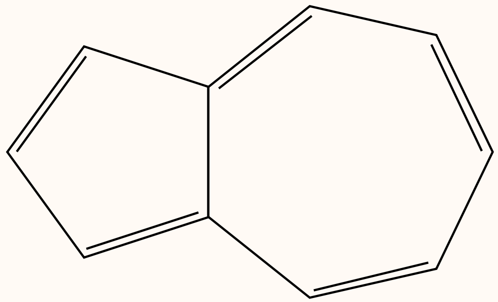
1. Motivation
2. Translation to tiles
3. Tools
4. Methods
5. Results

Azulenoids



Azulene

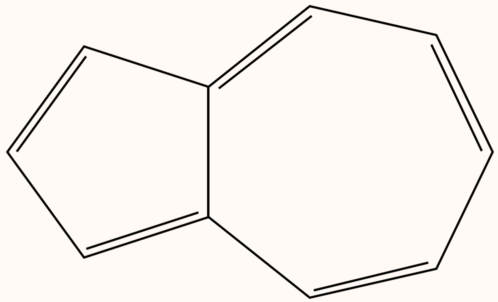
Azulenoids



- $4n + 2$ annulene with a bridging bond
- if a π-electron migrates towards the five membered ring then in principle two 'aromatic-sextets' could be formed

$\Rightarrow$ aromatic behaviour might be expected within Huckel theory

Azulenoids



Consistent with this view is that it has a small dipole moment, and does indeed show some aromatic properties, under milder conditions.

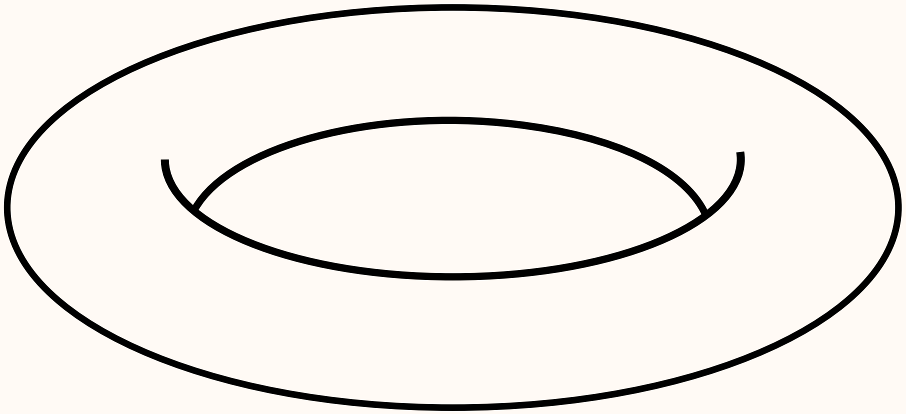
Question

We don't yet know whether and how the electron mobility might manifest itself among azulenes embedded within a fullerene-style network.

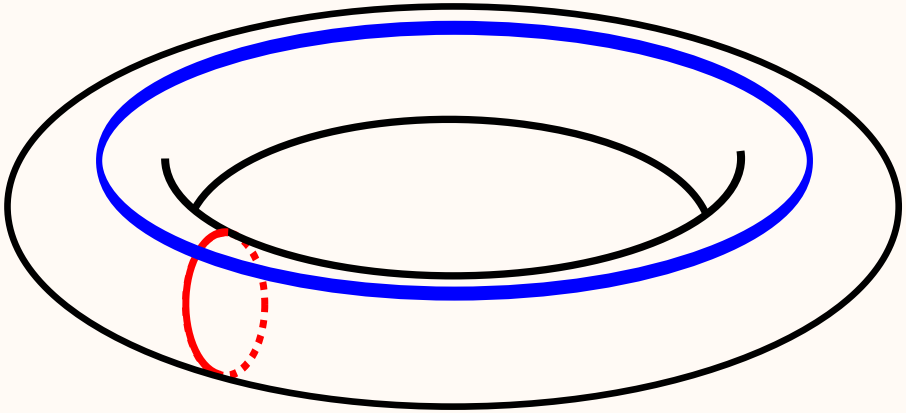
How many variations of such networks are theoretically possible?

Edward Kirby

Torus



Torus



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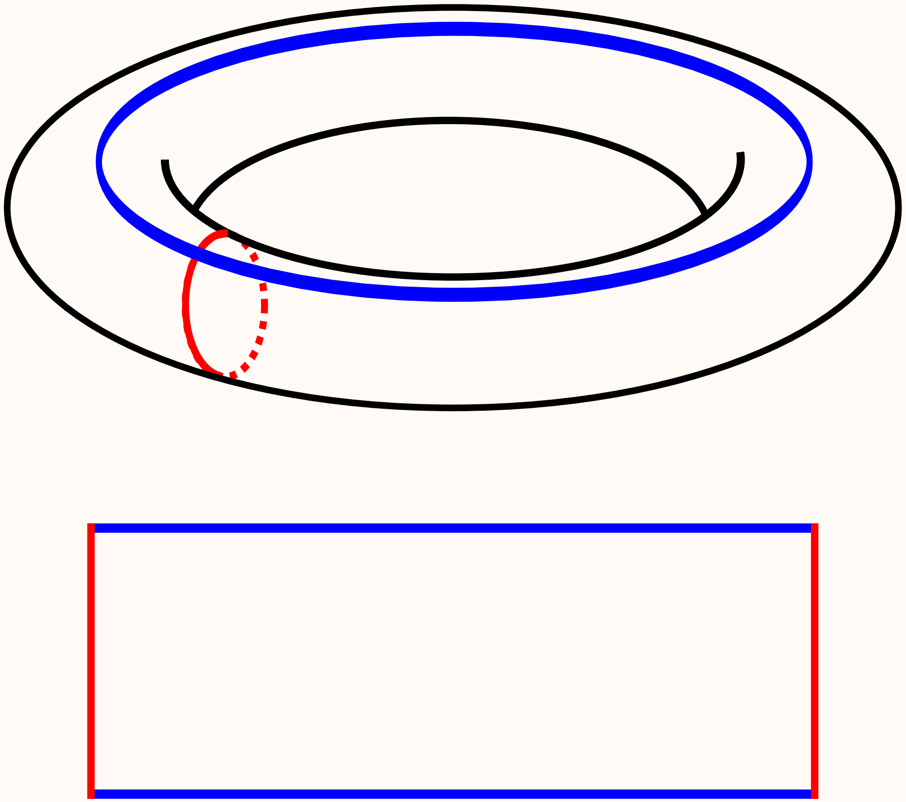

Tiling

- a subdivision of the plane into faces (or tiles)
- everything is locally finite
- the intersections of two different tiles are points or lines or are empty.

Tiling

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- everything is locally finite
- the intersections of two different tiles are points or lines or are empty.

Periodic tiling $\Longleftrightarrow$

up to symmetry there are only a finite set of tiles

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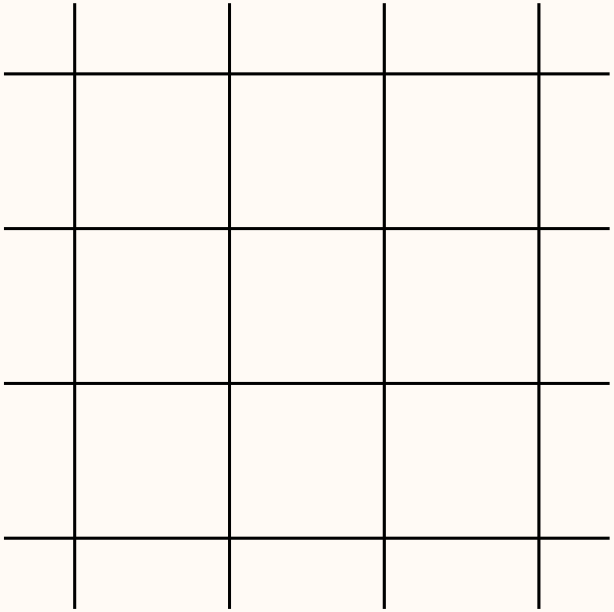
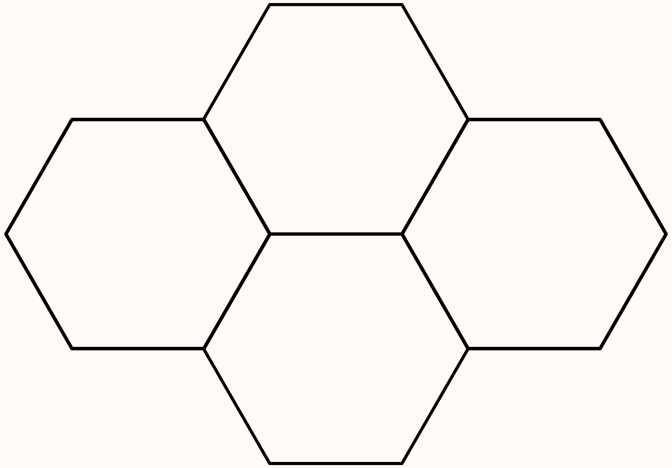
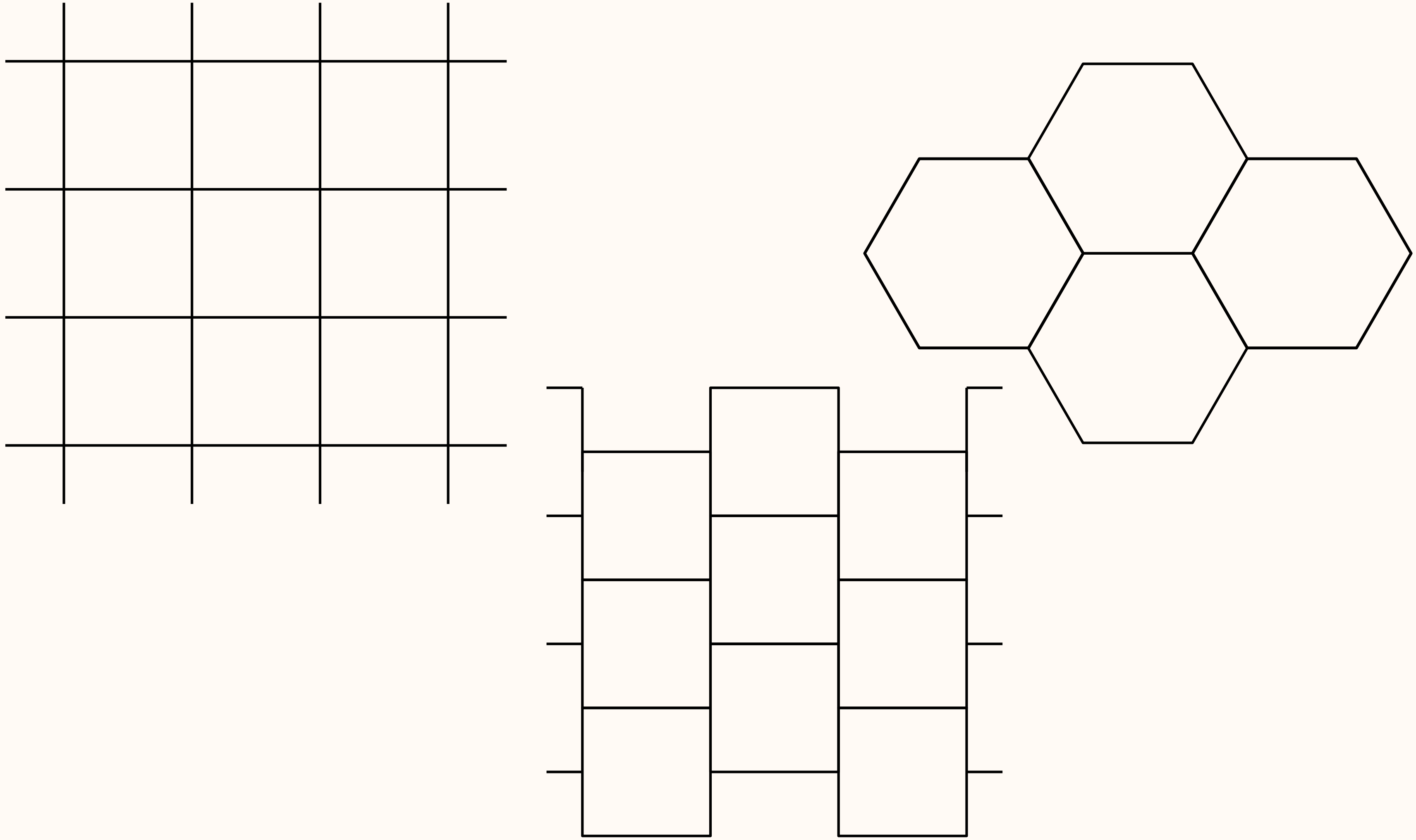
Example tiling



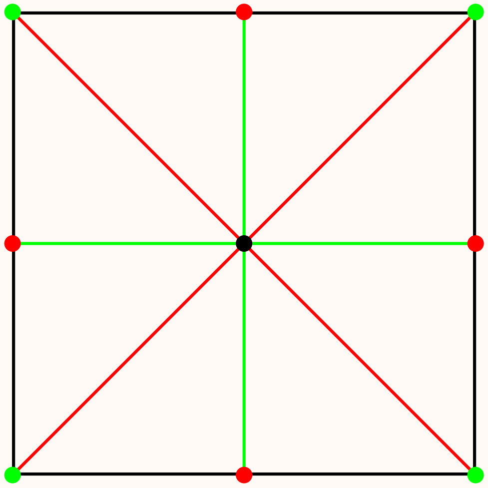


Example tiling



Barycentric subdivision

- For each face: one point
- For each edge: one point
- For each vertex: one point



$\Rightarrow$ subdivision consists of triangles

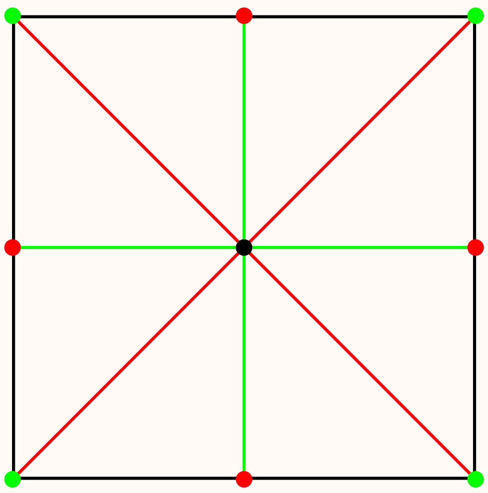
Chamber system

Define $\Sigma = \langle \sigma_0, \sigma_1, \sigma_2 | \sigma_i^2 = \mathbb{1} \rangle$

σ_0 : change the green point (vertex).

σ_1 : change the red point (edge).

σ_2 : change the black point (face).



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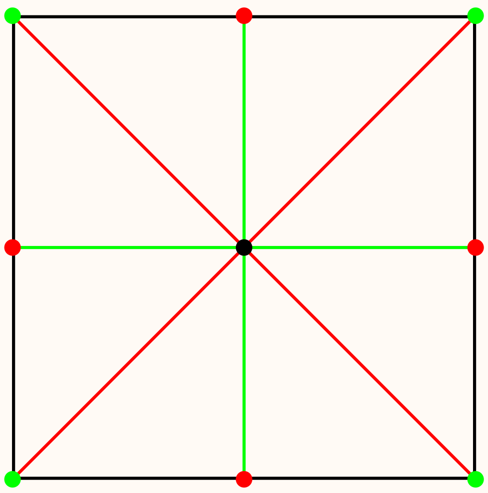

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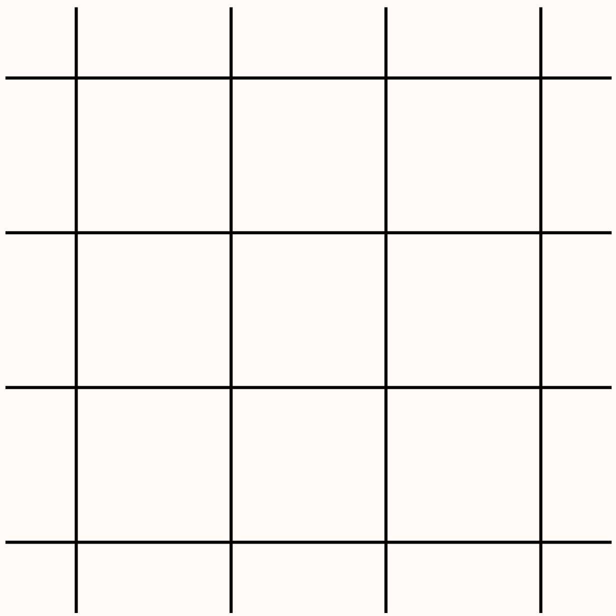
Chamber system $\mathcal{C}$ of T = barycentric subdivision together with Σ

Delaney/Dress graph

The Delaney/Dress graph $\mathcal{D}$ of a periodic tiling is the set of *equivalence classes of the chambers* of the chamber system of the tiling under the symmetry group, together with the actions of Σ.

Example Delaney/Dress graph



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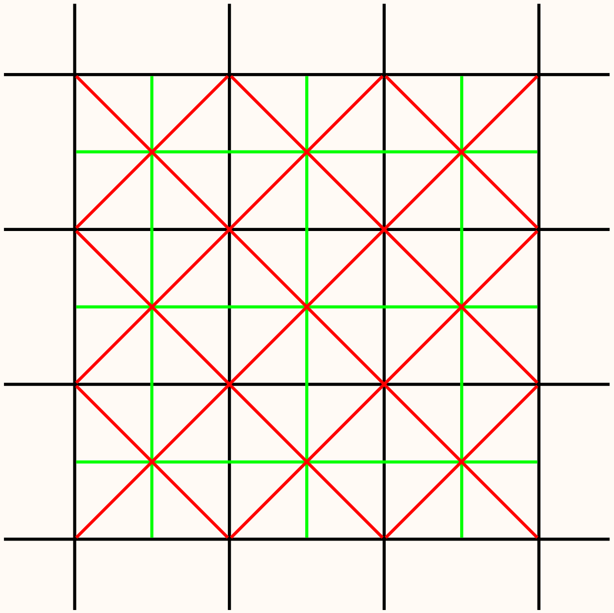

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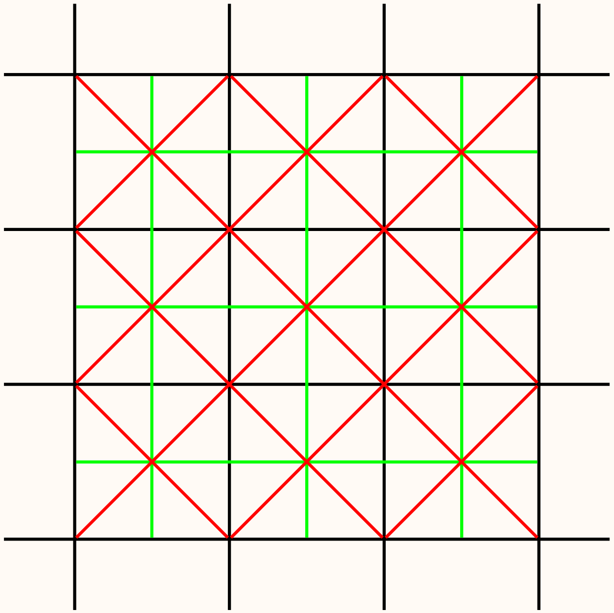

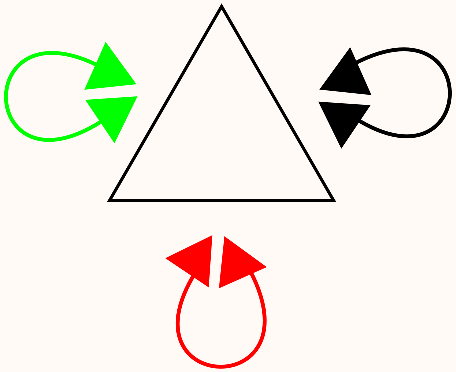

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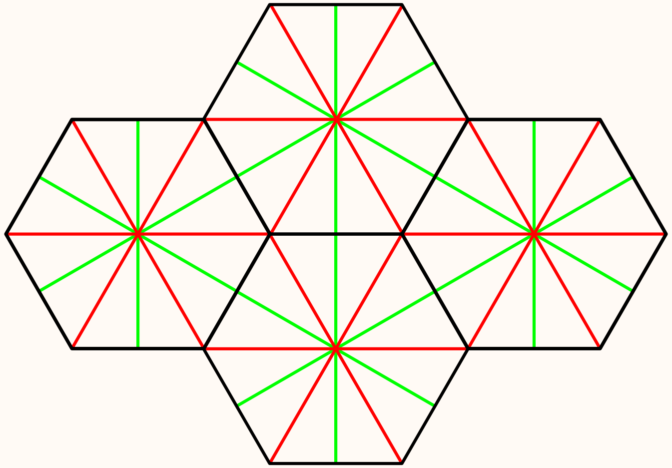

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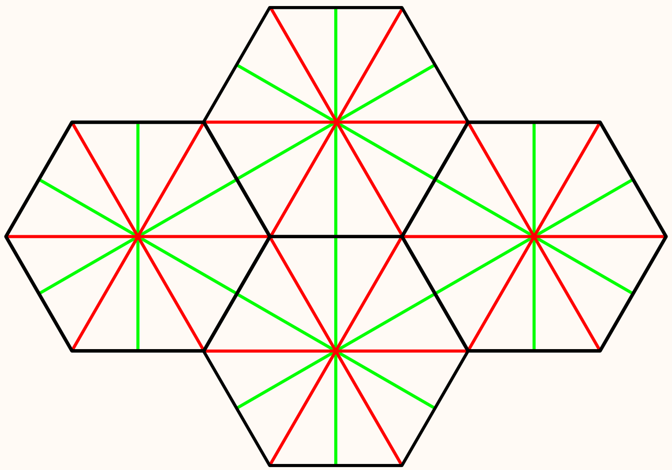

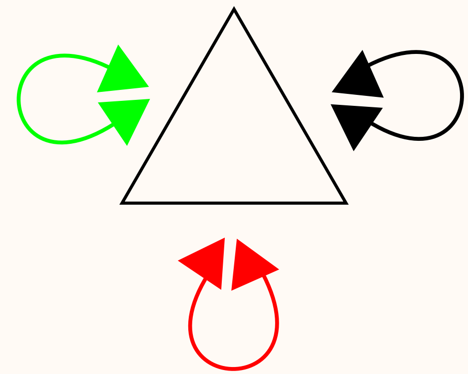

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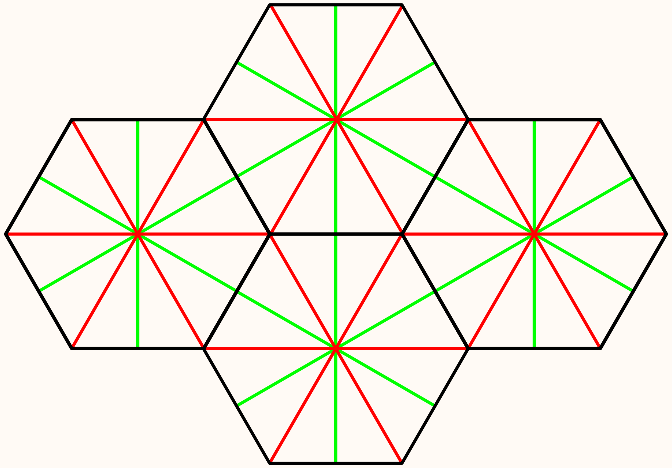

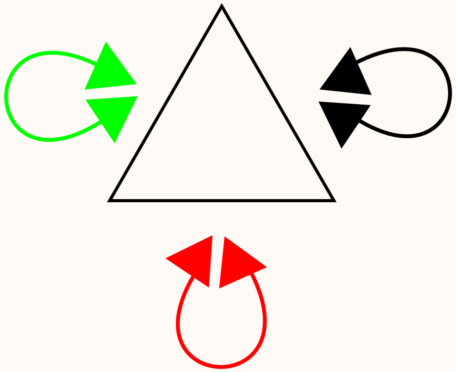

$\Rightarrow$ Delaney/Dress graph is not sufficient to distinguish between tilings!

Delaney/Dress symbol

Define functions $m_{ij} : \mathcal{D} \rightarrow \mathbb{N}$

$m_{01}(d)$ is the size of the face of T that belongs to d.
$m_{12}(d)$ is the number of faces that meet in the vertex that belongs to d.

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$m_{01}(d)$ is the size of the face of T that belongs to d.
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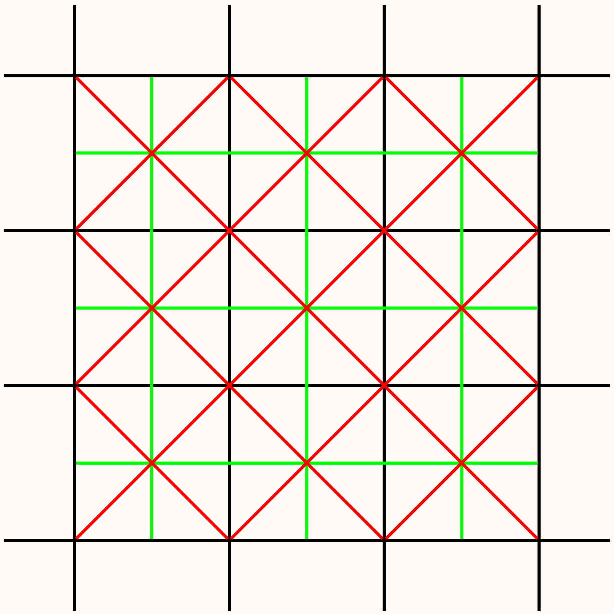
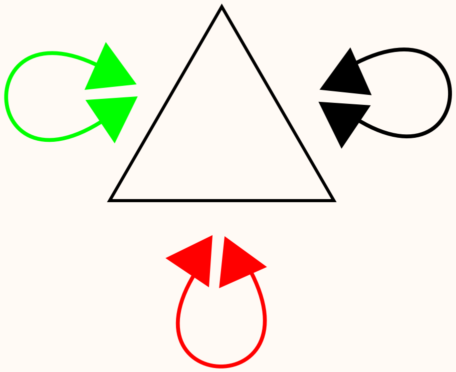
Delaney/Dress symbol of the tiling is $(\mathcal{D}; m_{01}, m_{12})$

Example Delaney/Dress symbol





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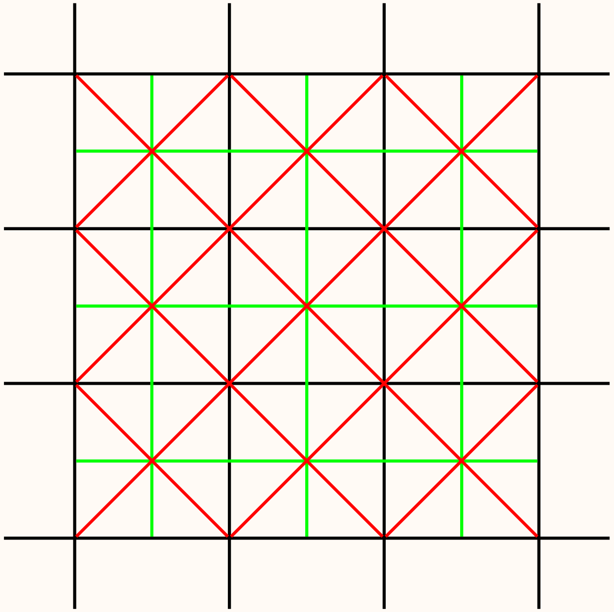
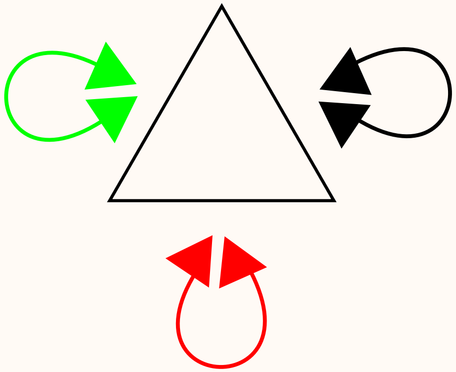
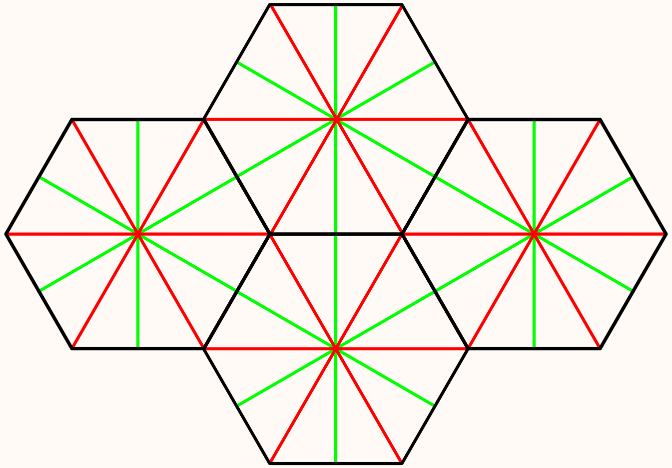


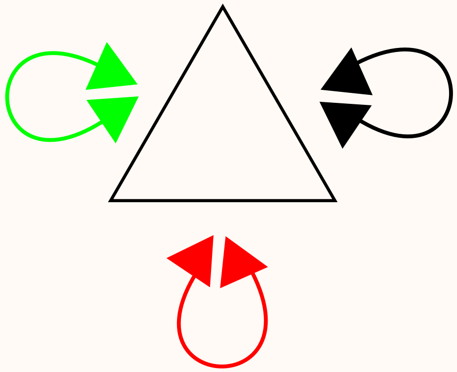


$$m_{01} = 4$$

$$m_{12} = 4$$

Example Delaney/Dress symbol





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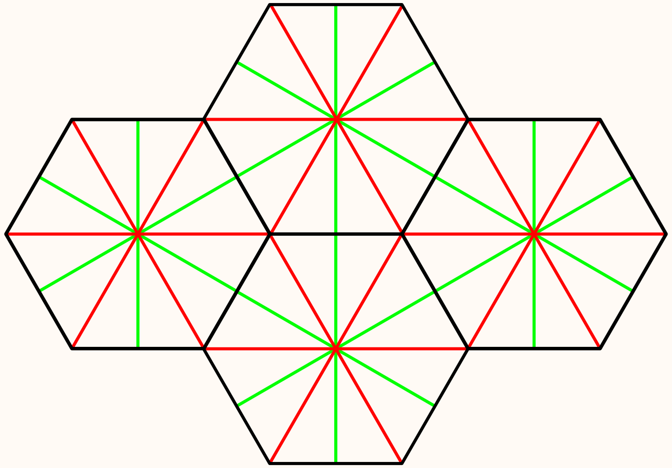
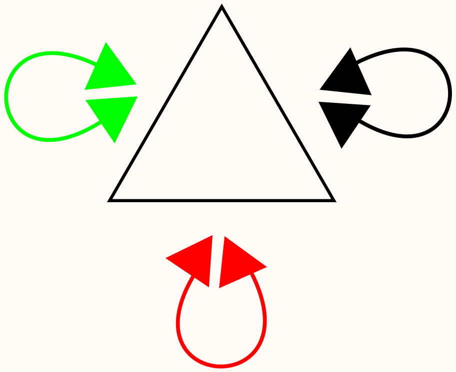
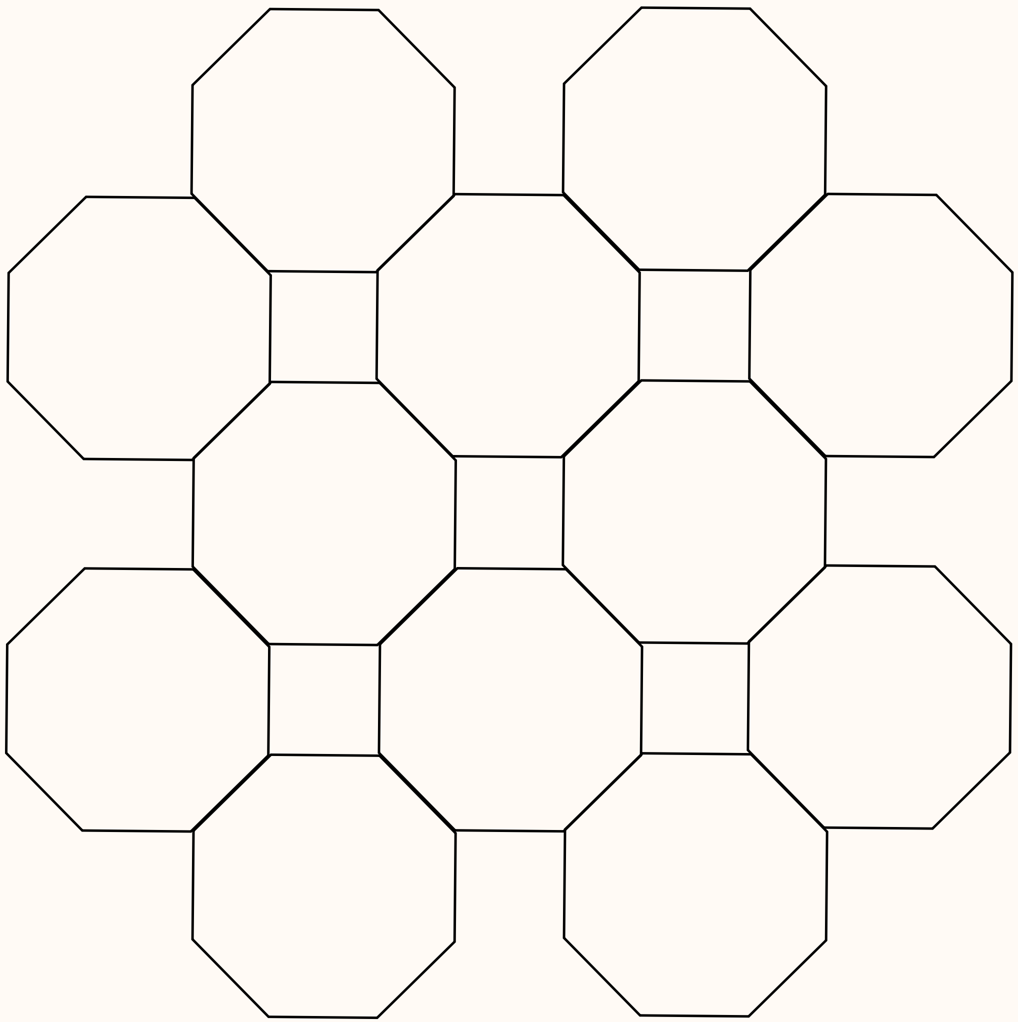




$$m_{01} = 6$$

$$m_{12} = 3$$

Example Delaney/Dress symbol



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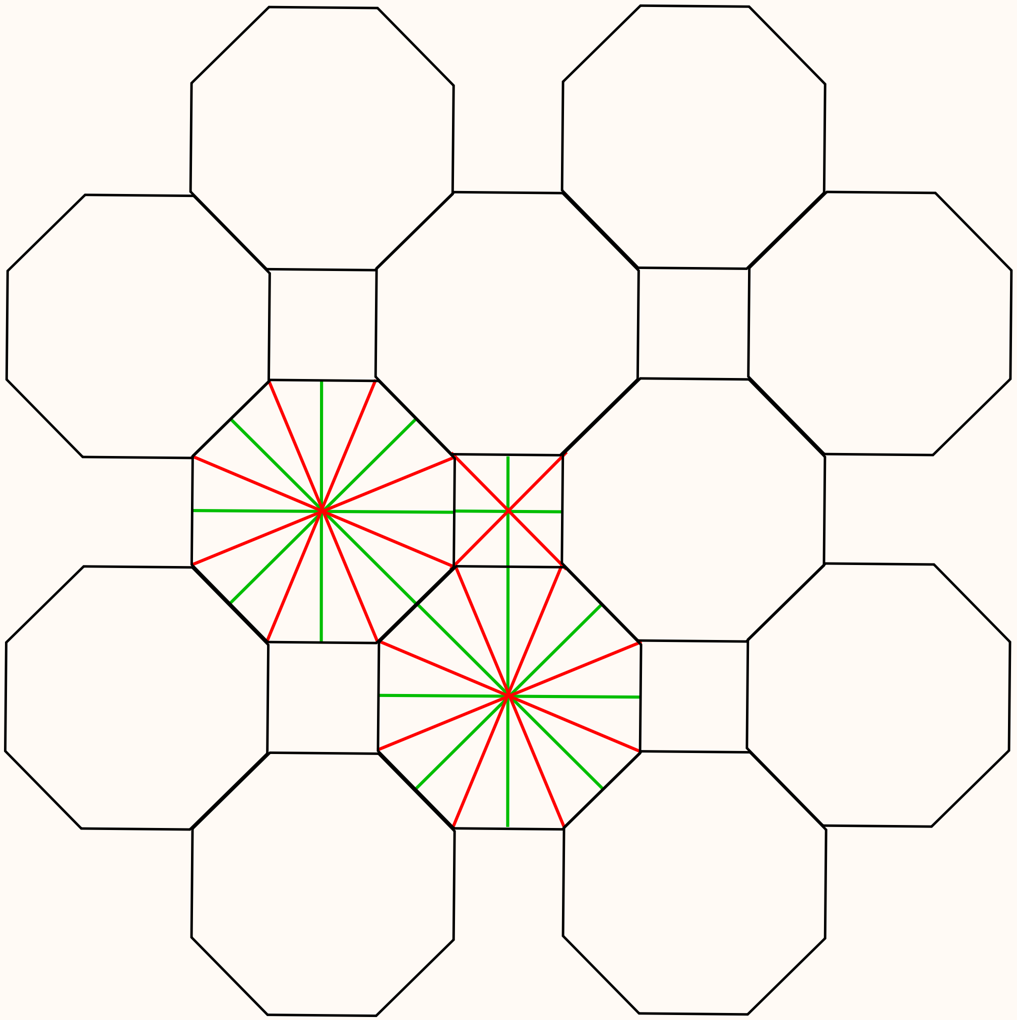

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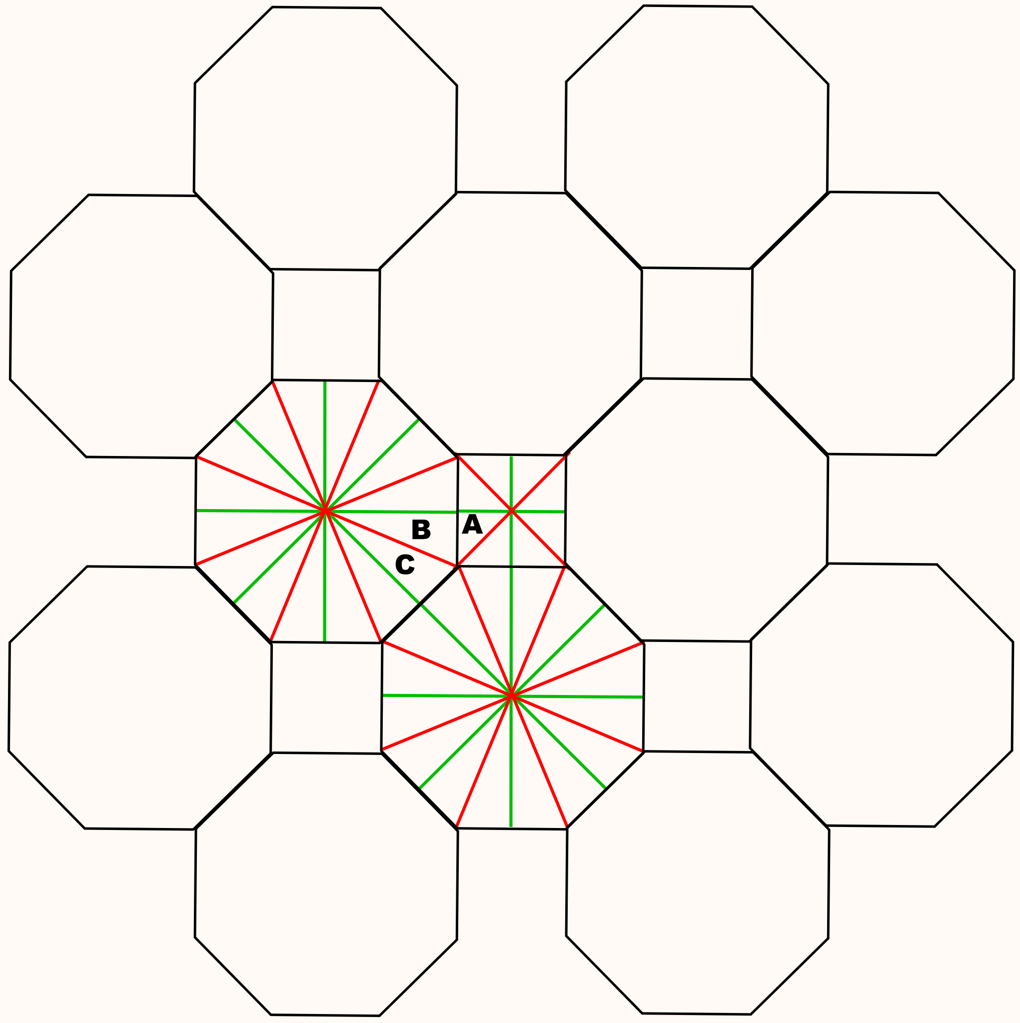

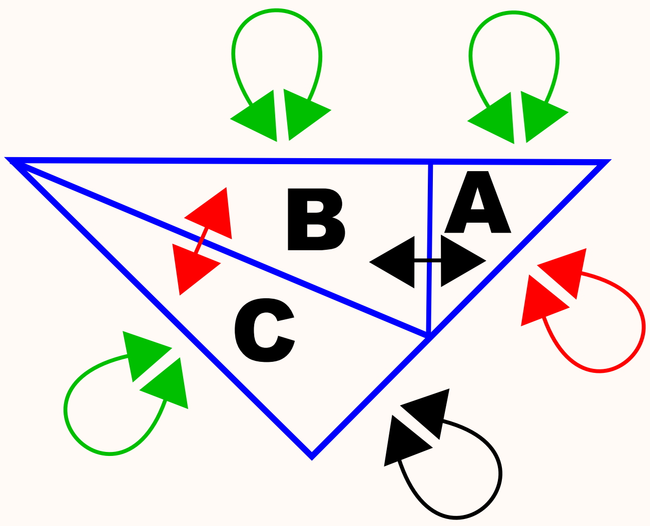

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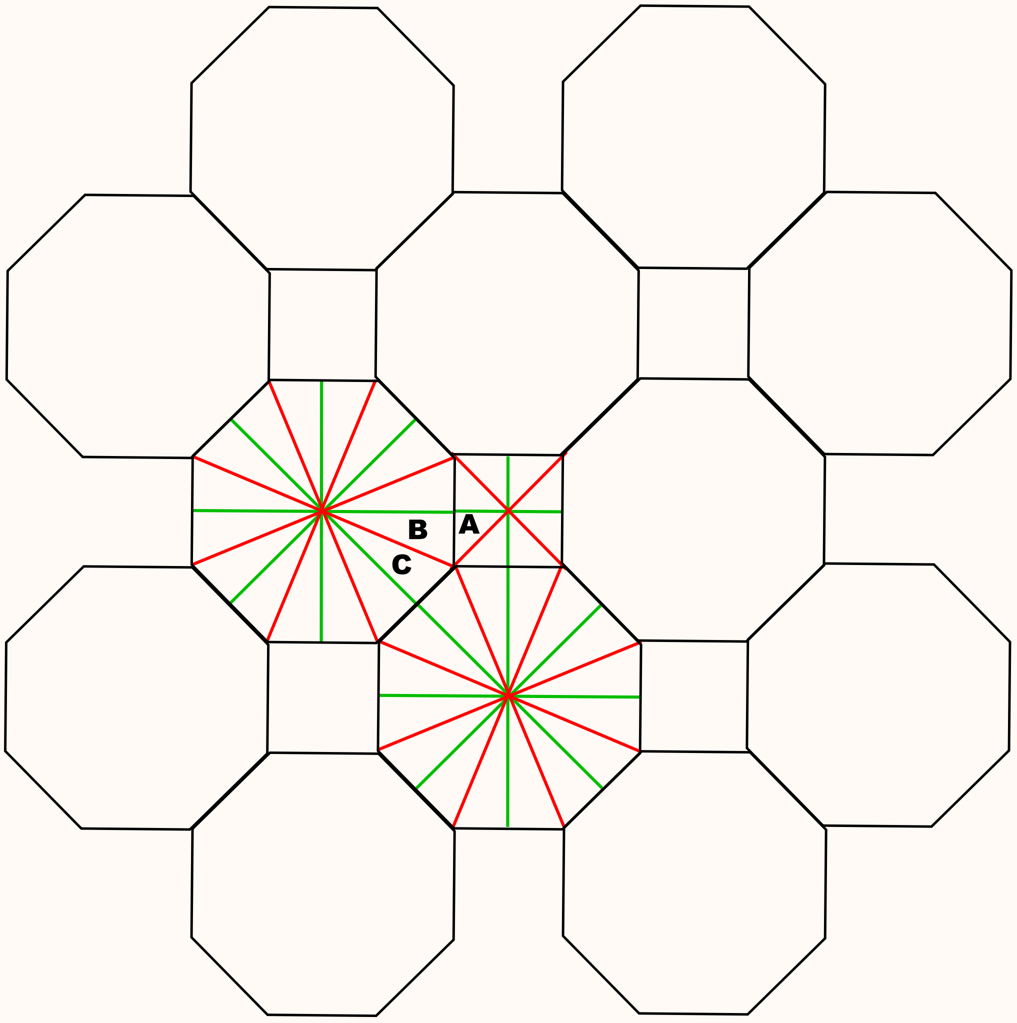

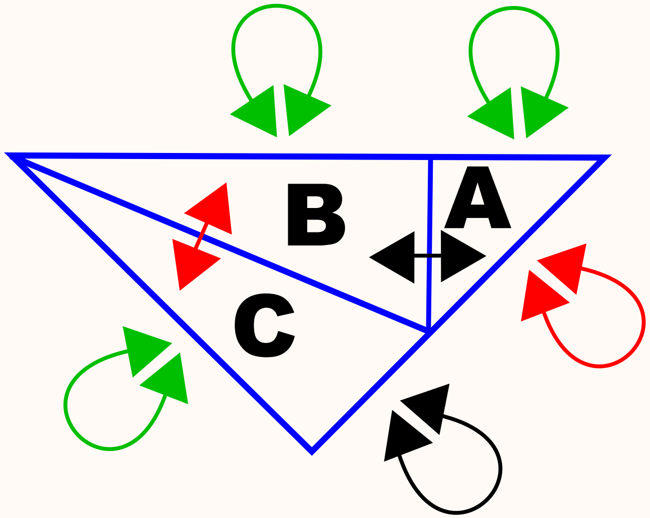

	m_{01}	m_{12}
A	4	3
B	8	3
C	8	3

Delaney/Dress symbol

$(\mathcal{D}; m_{01}, m_{12})$ is the Delaney/Dress symbol of a periodic tiling of the plane iff.

1. $\mathcal{D}$ is finite
2. Σ works transitively on $\mathcal{D}$
3. m_{01} is constant on $\langle\sigma_0, \sigma_1\rangle$ orbits and $\forall d \in \mathcal{D} : d(\sigma_0\sigma_1)^{m_{01}(d)} = d$
4. m_{12} is constant on $\langle\sigma_1, \sigma_2\rangle$ orbits and $\forall d \in \mathcal{D} : d(\sigma_1\sigma_2)^{m_{12}(d)} = d$
5. $\forall d \in \mathcal{D} : d(\sigma_0\sigma_2)^2 = d$
6. $\sum_{d\in\mathcal{D}}(\frac{1}{m_{01}(d)} + \frac{1}{m_{12}(d)} - \frac{1}{2}) = 0$

Refined question

How many variations of fullerene-style networks for which there exists a partition of the atoms into azulenes are theoretically possible, assuming there is only one equivalence class of azulenes?

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Translation

Restrictions azulenoid:

- 1 equivalence class of azulenes
- every atom part of exactly one azulene

Translation

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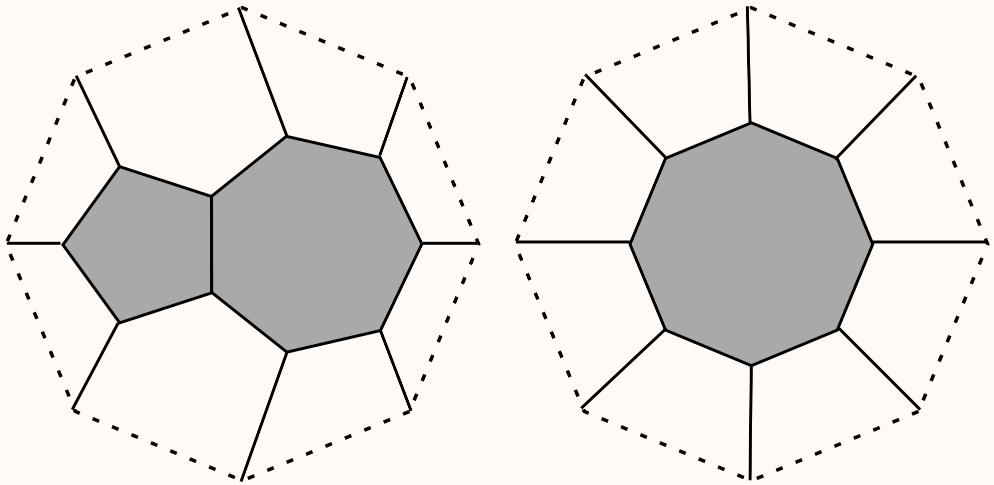
Restrictions Delaney/Dress symbol:

- $\exists \sigma_0 \sigma_1$ orbit $O : m_{01}(O) = 8 \wedge \forall \sigma_1 \sigma_2$ orbit $V : O \cap V \neq \emptyset$



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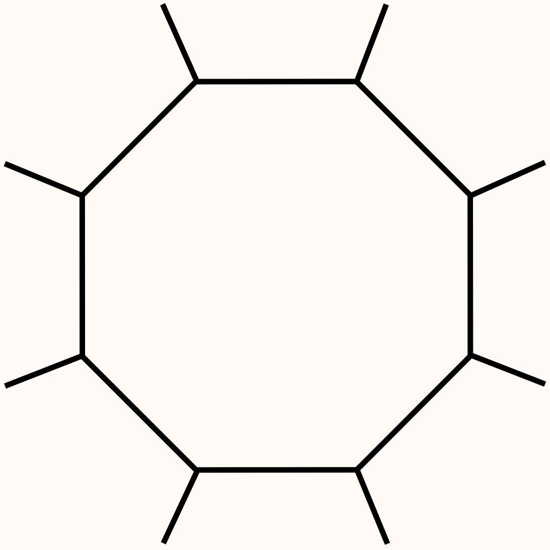
- $\displaystyle\sum_{d\in\mathcal{D}}\left(\frac{1}{m_{01}(d)} + \frac{1}{m_{12}(d)} - \frac{1}{2}\right) = 0$

Method

- Octagon and the different vertex orbits



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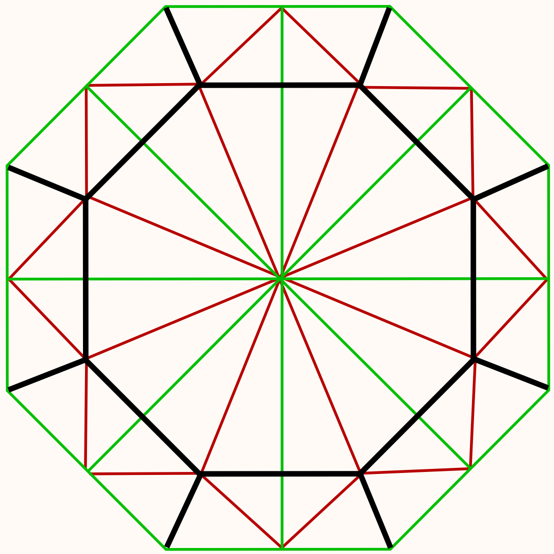
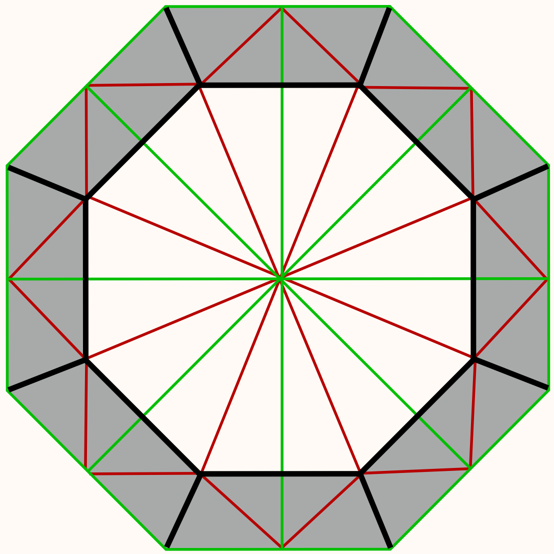


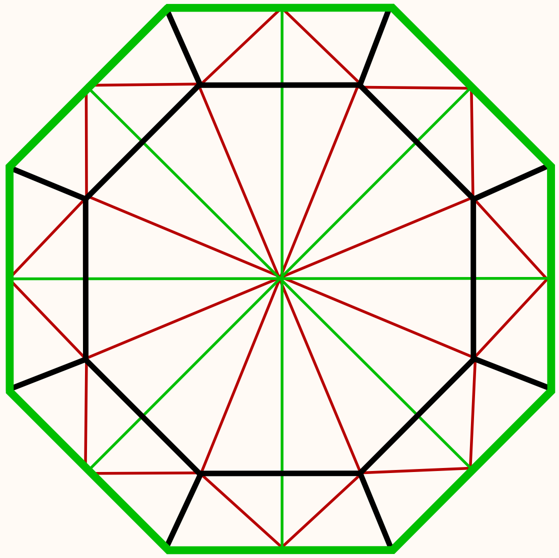
Method

- Octagon and the different vertex orbits
- Calculate and assign remaining m_{01} values



Method

- Octagon and the different vertex orbits
- Calculate and assign remaining m_{01} values
- Assign remaining σ_0's



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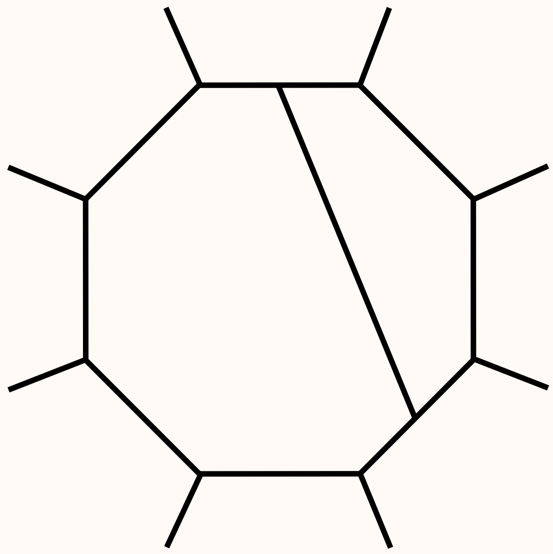
- Replace octagon with azulene



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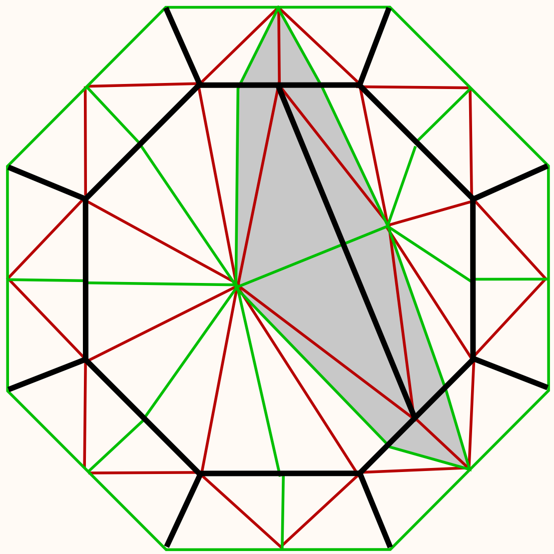
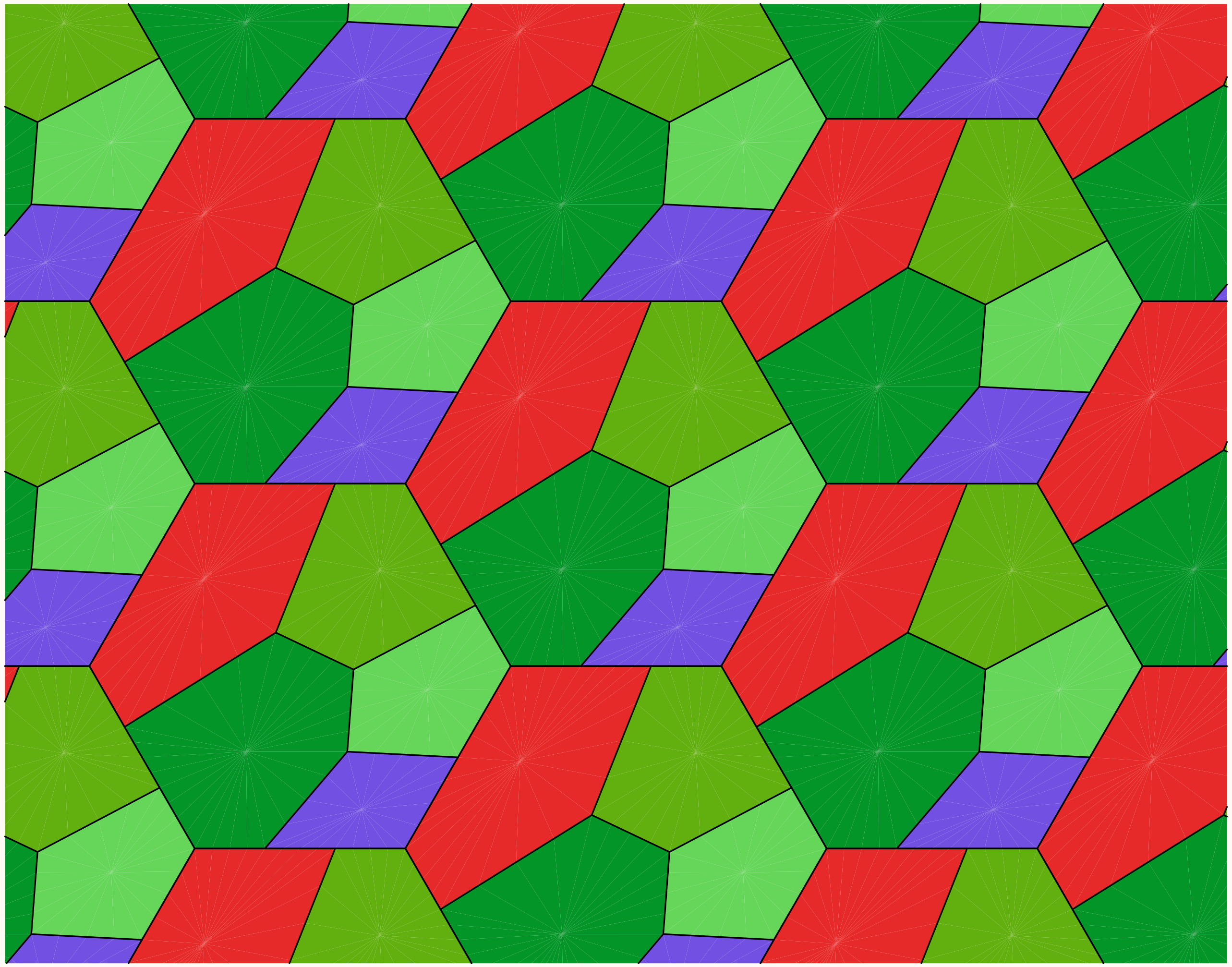


Visualisation



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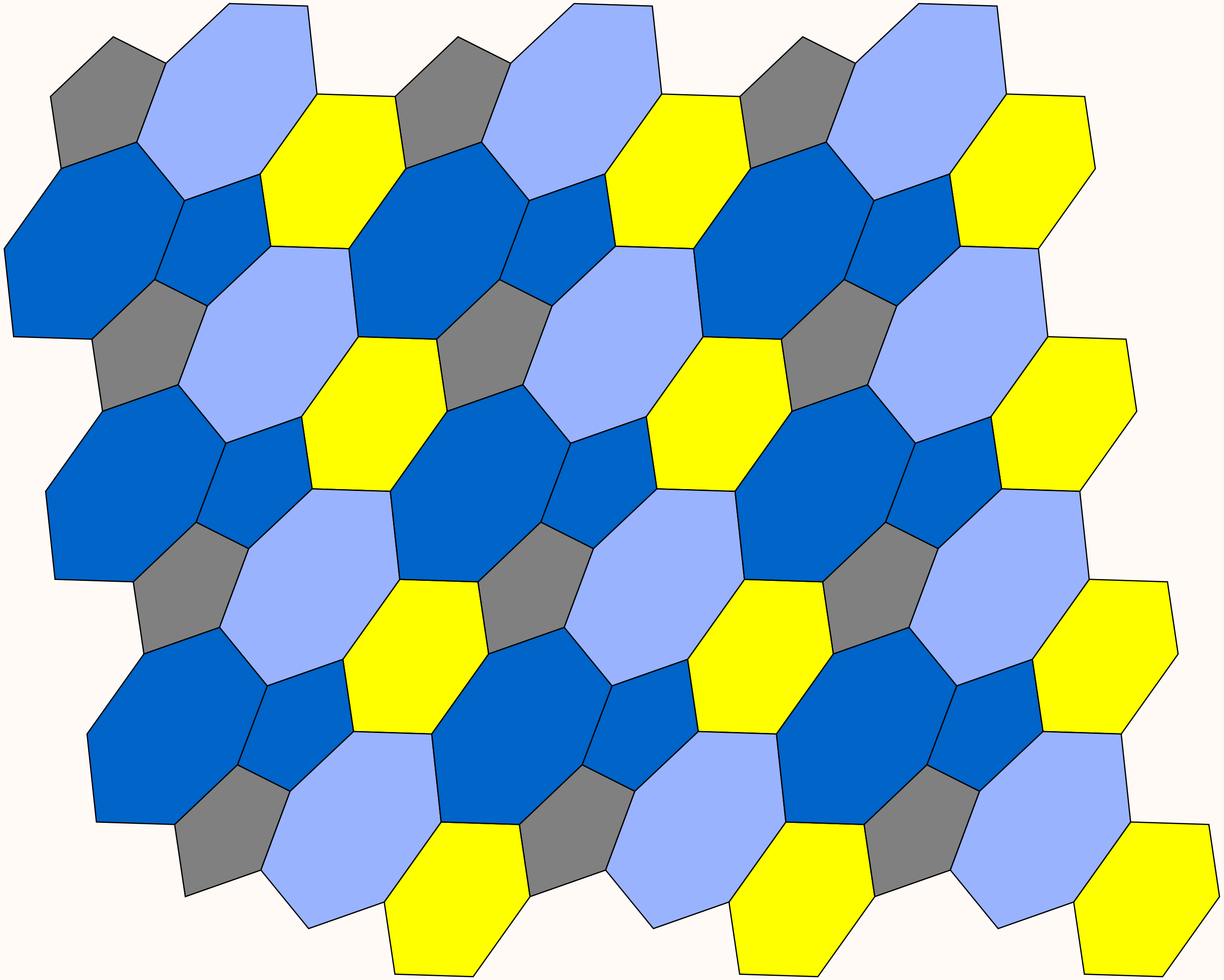

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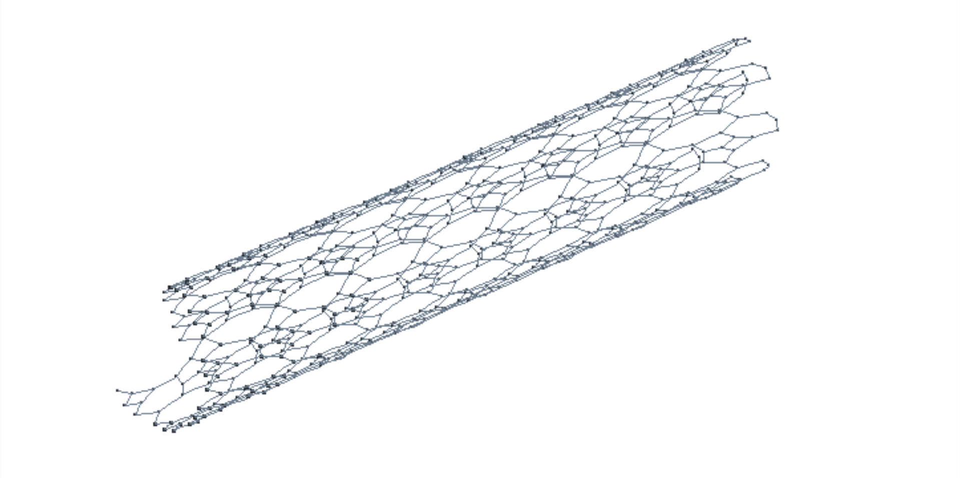
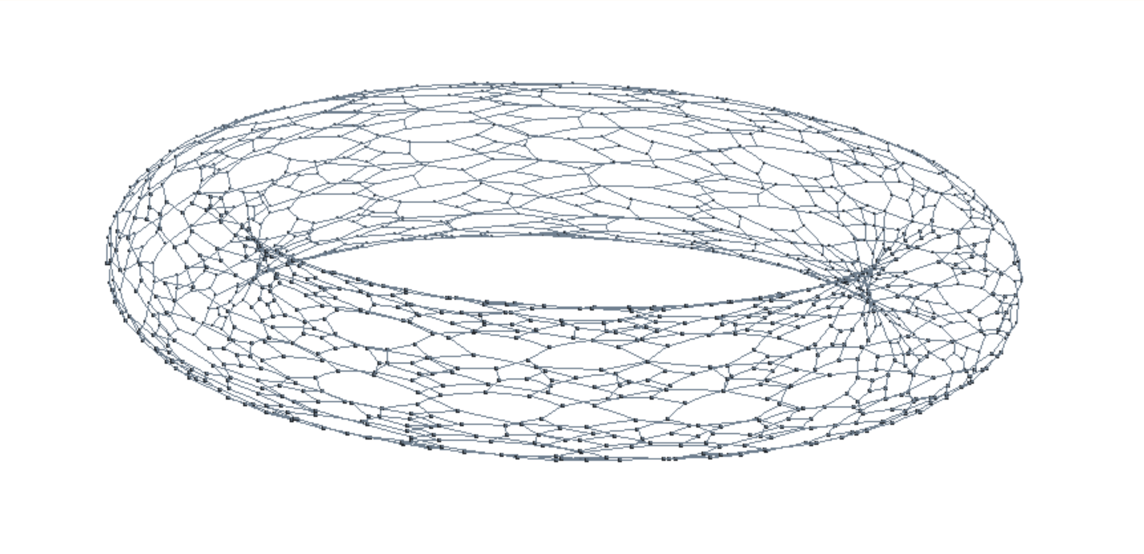




Results

	m_{01} values								# strings	# symbols
1	4	4	4	4	4	6	24	24	21	6
2	4	4	4	4	4	8	12	24	42	42
3	4	4	4	4	4	8	16	16	21	48
4	4	4	4	4	4	10	10	20	21	0
5	4	4	4	4	4	12	12	12	7	44
6	4	4	4	4	6	6	8	24	105	0
7	4	4	4	4	6	6	12	12	54	2
8	4	4	4	4	6	8	8	12	105	12
9	4	4	4	4	8	8	8	8	10	160
10	4	4	4	6	6	6	6	12	35	6
11	4	4	4	6	6	6	8	8	70	38
12	4	4	6	6	6	6	6	6	4	25

Results

383 symbols of tilings containing octagons

Results

383 symbols of tilings containing octagons

$$\Downarrow$$

1274 azulenoids

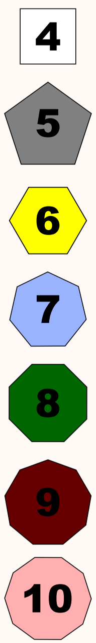
Translation only

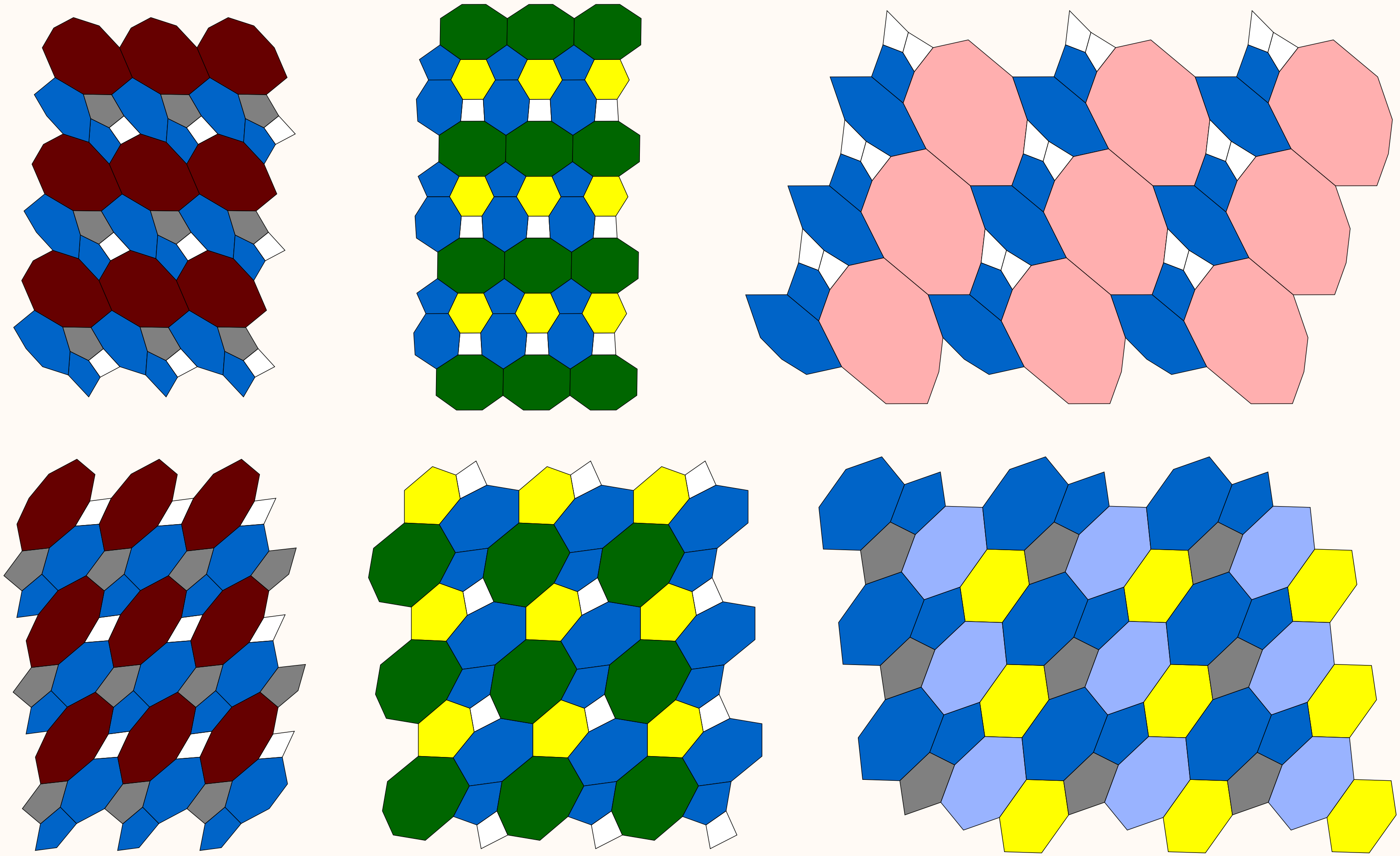
one orbit of azulenes under the subgroup of translations

or

all the azulenes have the same orientation

Translation only





End

Thanks for your attention!