Toroidal azulenoids

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

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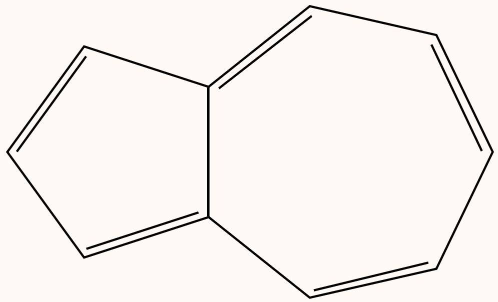
Outline

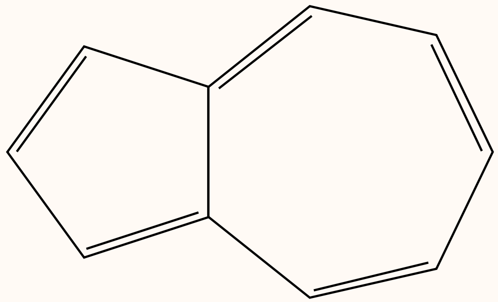
1. Motivation
2. Translation to tiles
3. Tools
4. Methods
5. Results

Azulenoids



Azulene

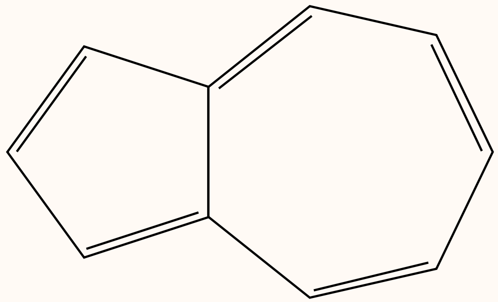
Azulenoids



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

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

Azulenoids



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

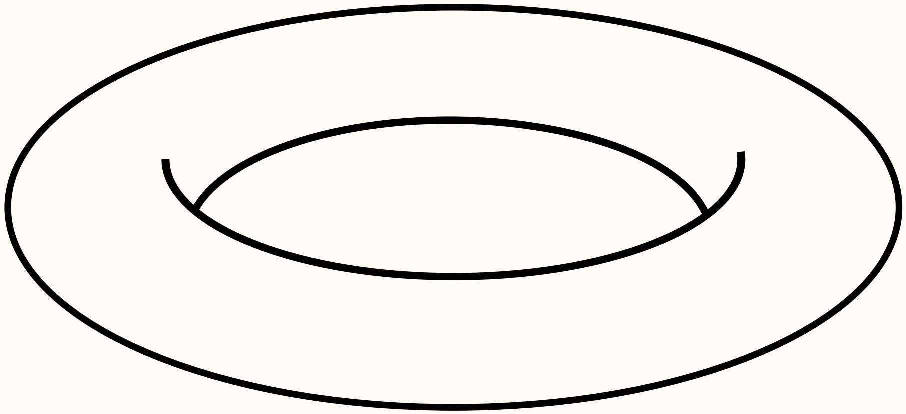
Question

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



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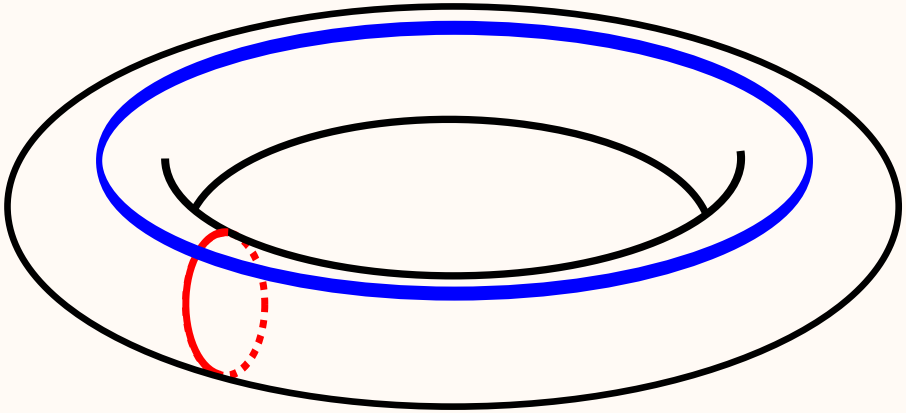

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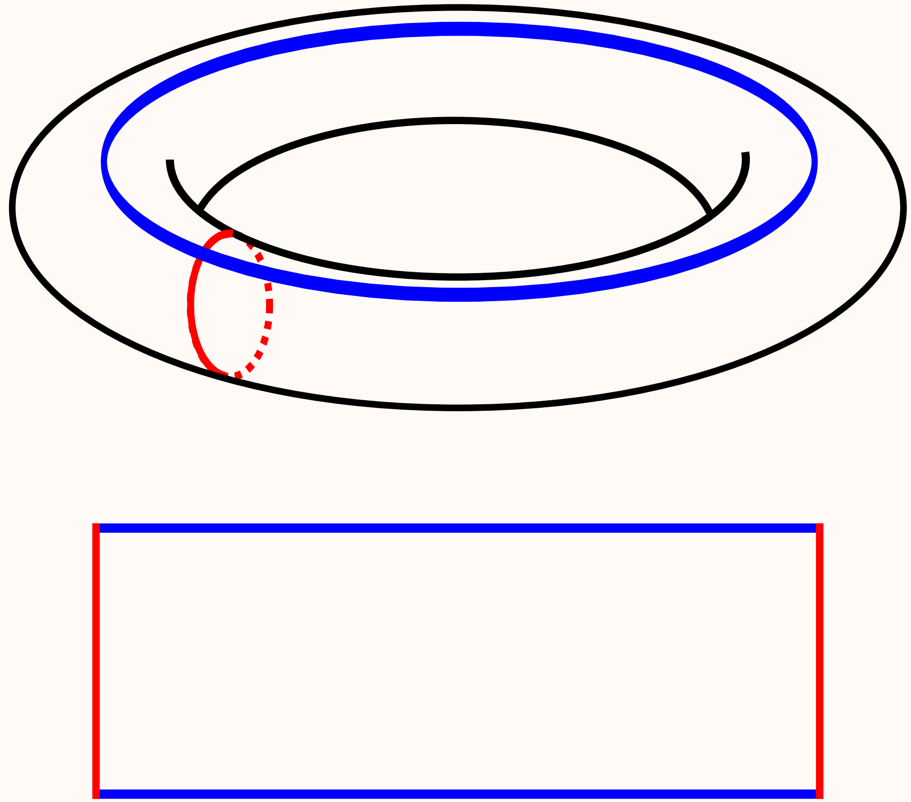

Tiling

Tiling T = set of tiles $t_1, t_2, \ldots$ with $t_i \subset \mathbb{E}^2$, t_i homeomorph to $\overline{B}(0,1)$ that satisfy the following conditions:

1. $\bigcup_{t \in T} t = \mathbb{E}^2$
2. $\forall t_i, t_j (i \neq j) \in T : t_i^\circ \cap t_j^\circ = \emptyset \wedge t_i \cap t_j \in \{\emptyset, \{\text{points}\}, \{\text{lines}\}\}$.
3. $\forall x \in \mathbb{E}^2 : x$ has a neighbourhood that only intersects a finite number of tiles.

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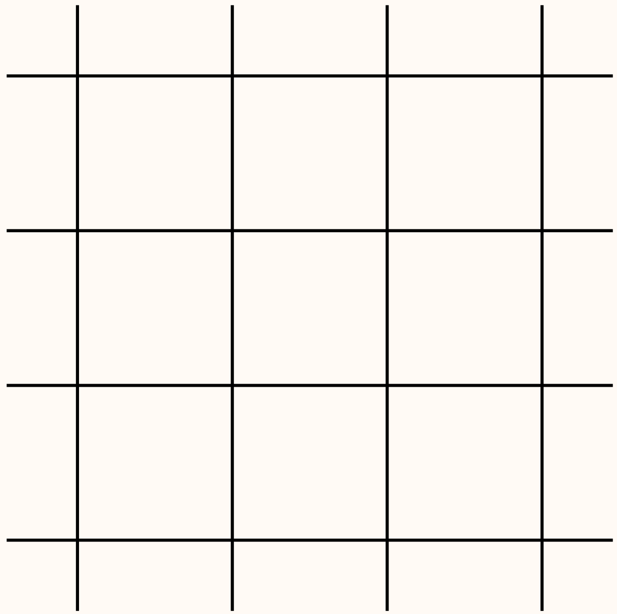
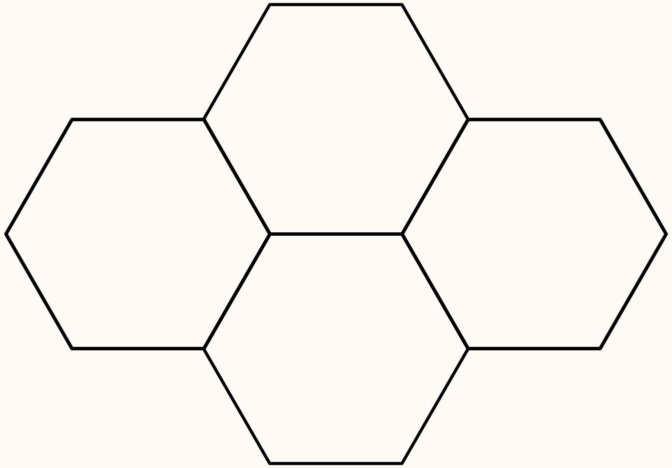
Periodic tiling $\iff$

symmetry group contains *two independent translations*

Example tiling





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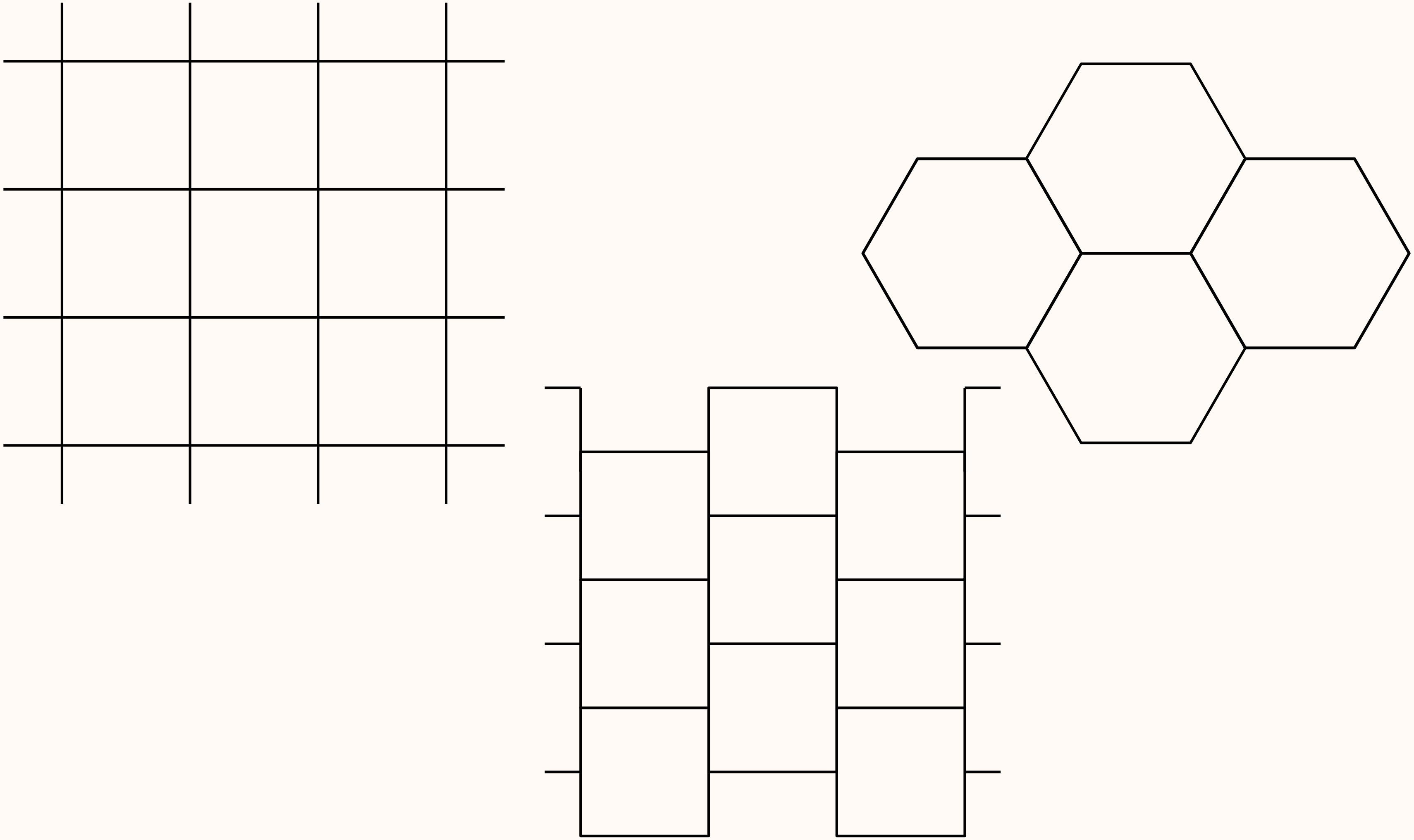
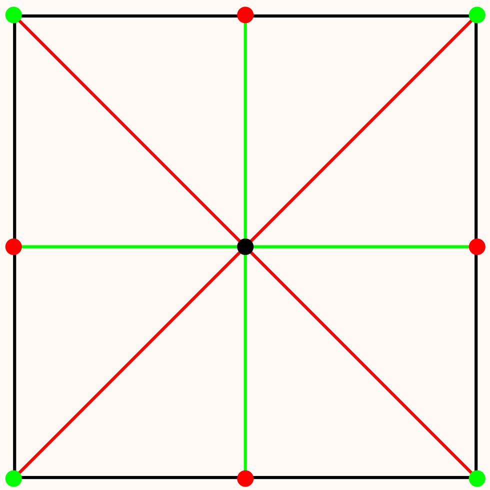


Barycentric subdivision

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



$\Rightarrow$ subdivision consists of triangles

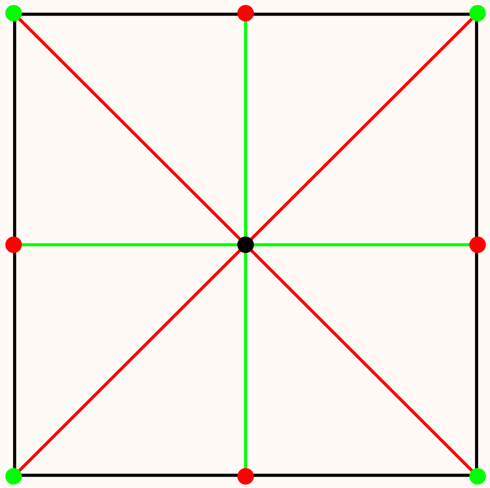
Chamber system

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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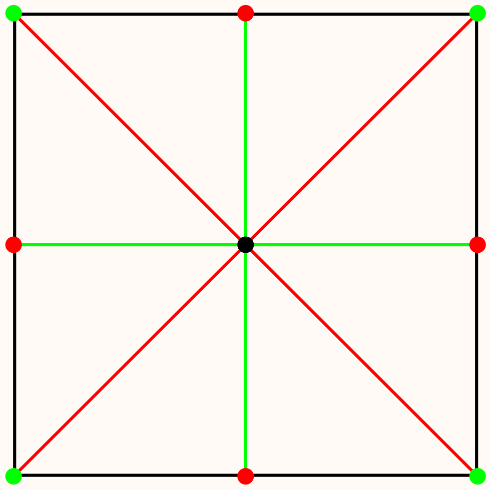
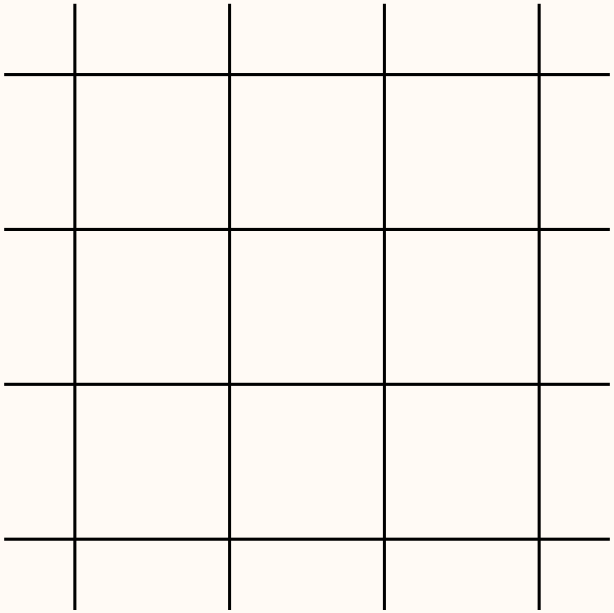


Chamber system $\mathcal{C}$ of T = barycentric subdivision together with Σ

Delaney/Dress graph

The Delaney/Dress graph $\mathcal{D}$ of a periodic tiling is the set of *orbits of the chambers* of the chamber system of the tiling under the symmetry group.

Example Delaney/Dress graph



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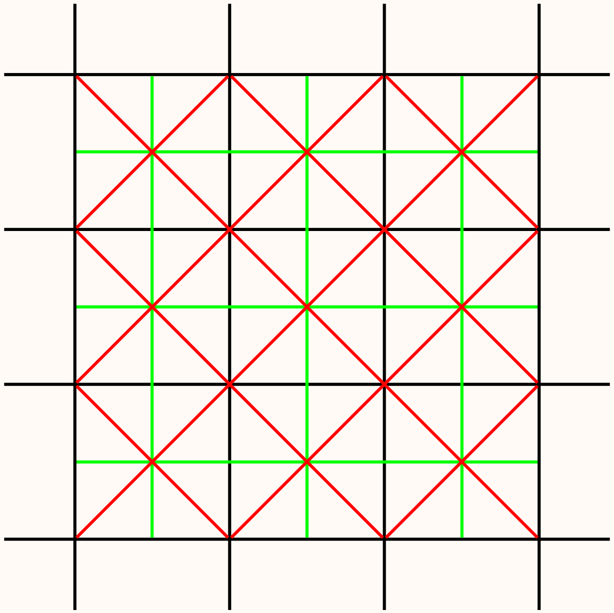

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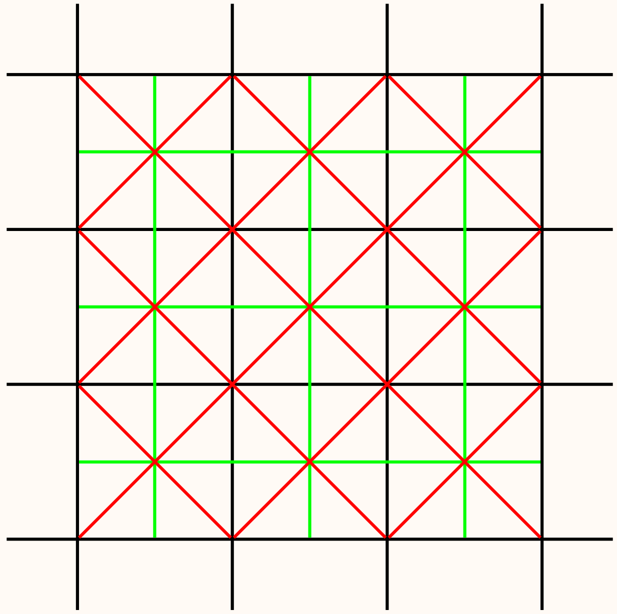

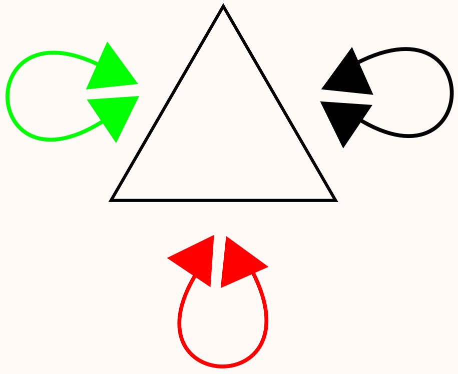

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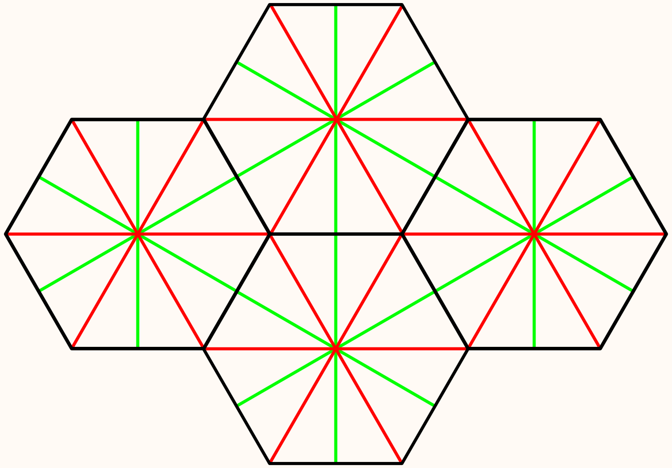

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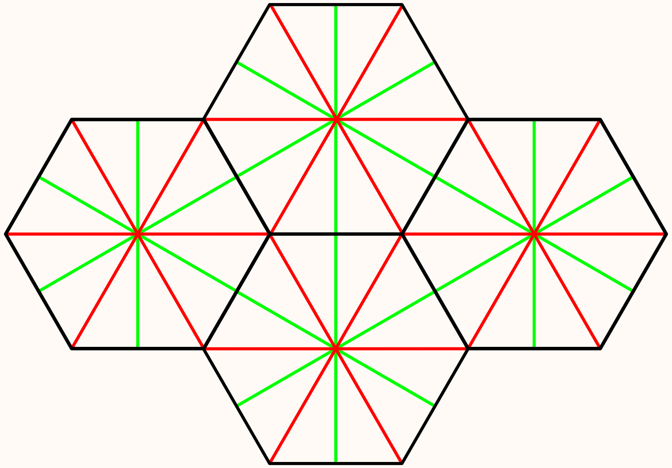

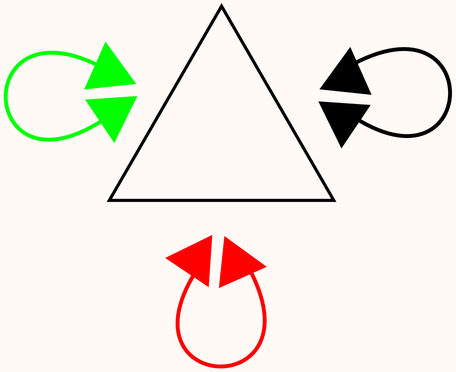

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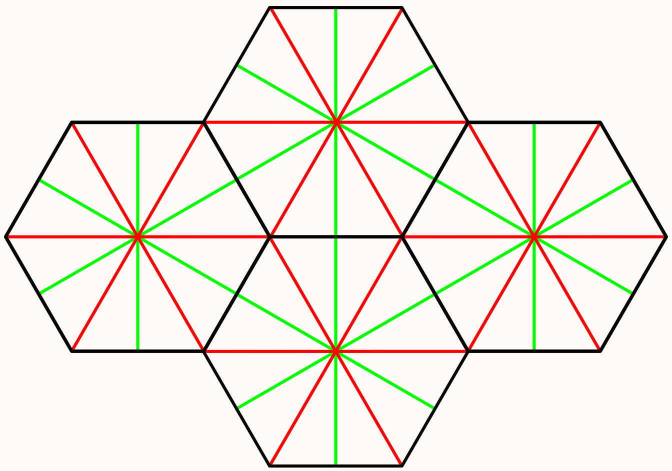
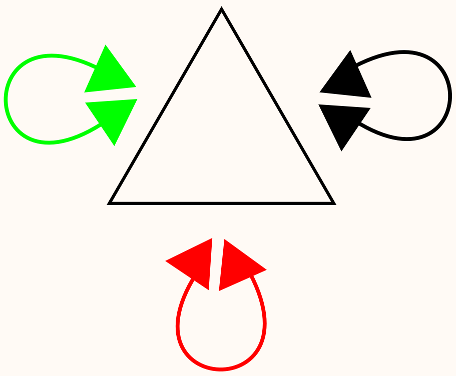




$\Rightarrow$ Delaney/Dress graph is not sufficient to distinguish between tilings!

Delaney/Dress symbol

Define functions $r_{ij} : \mathcal{C} \longrightarrow \mathbb{N}; c \mapsto r_{ij}(c)$ with $r_{ij}(c)$ the smallest number for which $c(\sigma_i \sigma_j)^{r_{ij}(c)} = c$.

Delaney/Dress symbol

Define functions $r_{ij} : \mathcal{C} \longrightarrow \mathbb{N}; c \mapsto r_{ij}(c)$ with $r_{ij}(c)$ the smallest number for which $c(\sigma_i \sigma_j)^{r_{ij}(c)} = c$.

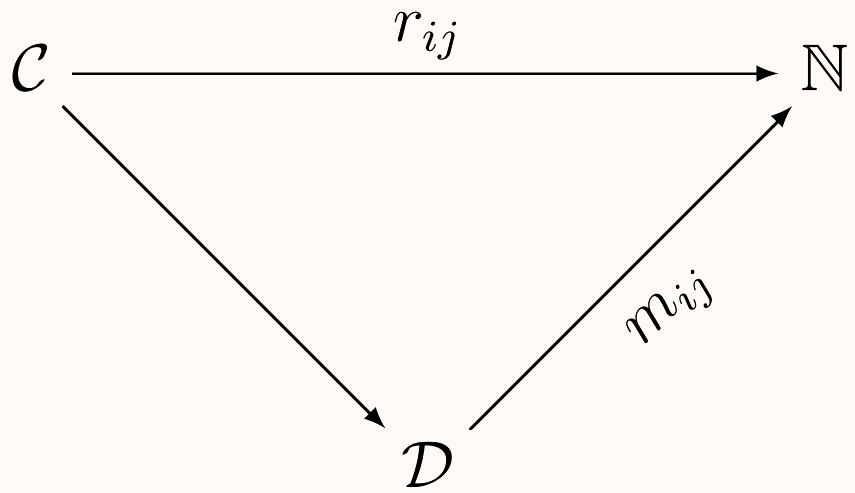
r_{02} is a constant function with value 2.

$r_{01}(c)$ is the size of the face of T that belongs to c.

$r_{12}(c)$ is the number of faces that meet in the vertex that belongs to c.

Delaney/Dress symbol

Define functions $m_{ij} : \mathcal{D} \to \mathbb{N}; d \mapsto m_{ij}(c)$ in such a manner that the following diagram is commutative:



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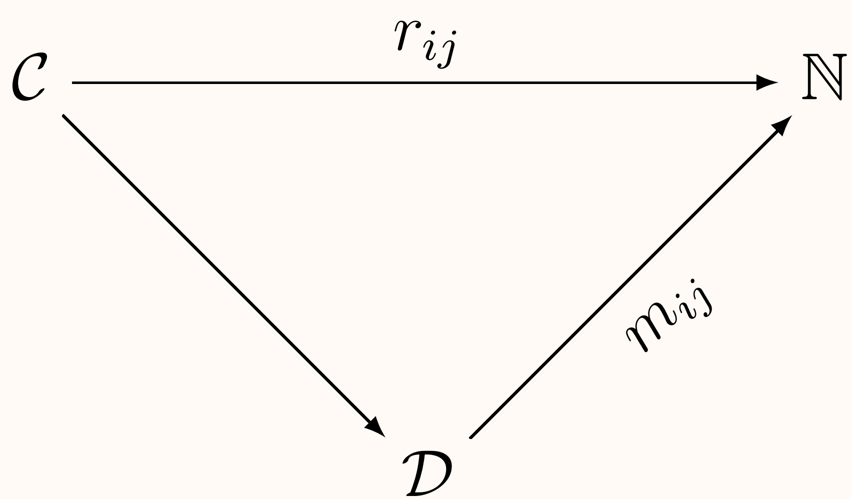
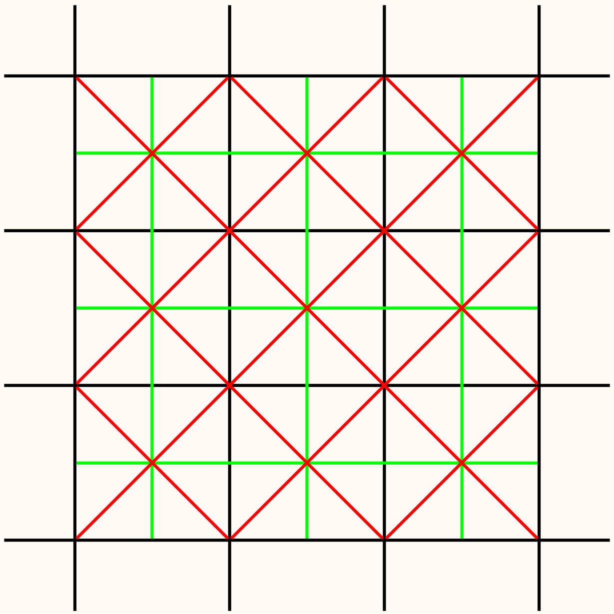
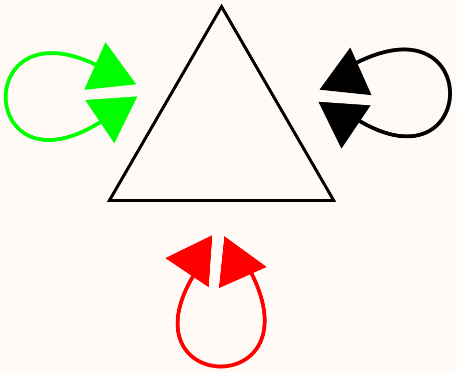


Delaney/Dress symbol of the tiling is $(\mathcal{D}; m_{01}, m_{12})$

Example Delaney/Dress symbol





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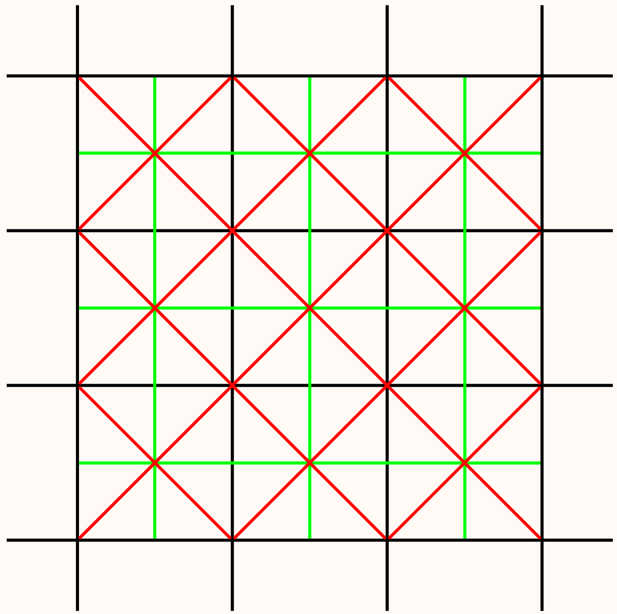
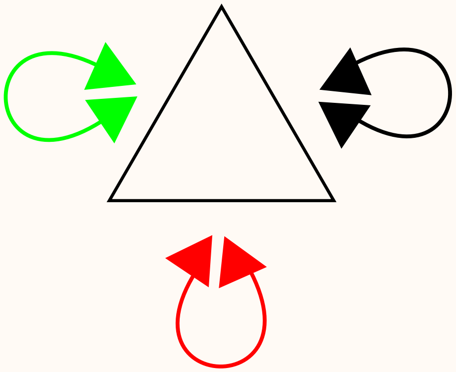
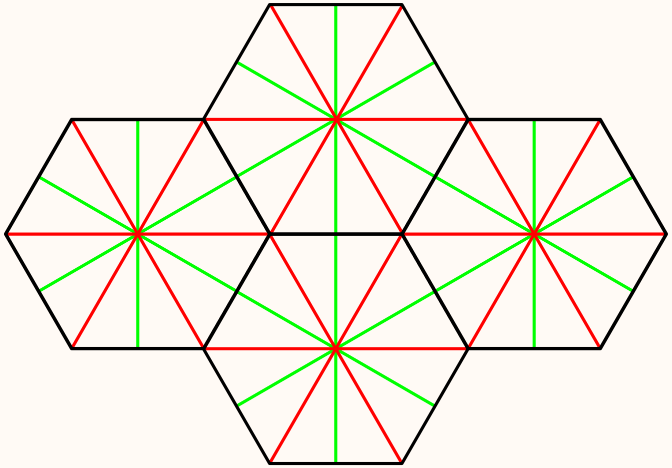


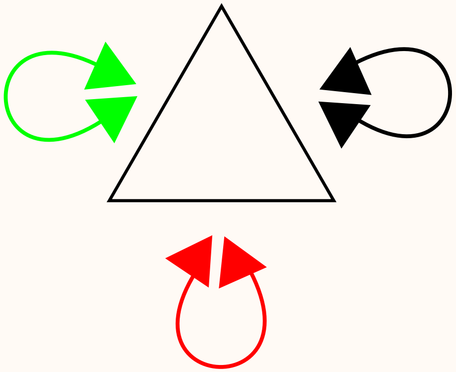


$$m_{01} = 4$$

$$m_{12} = 4$$

Example Delaney/Dress symbol





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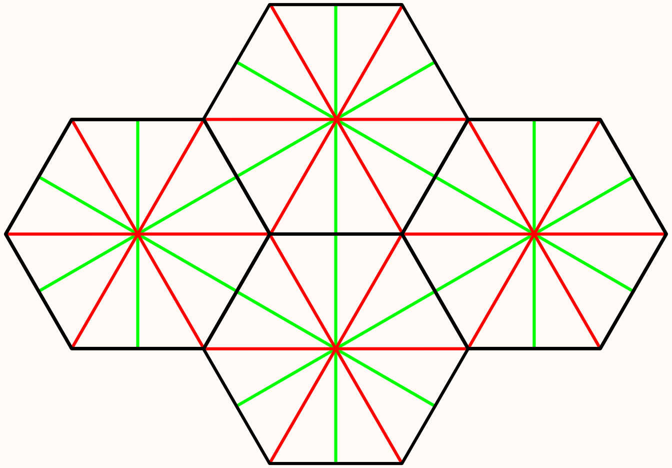
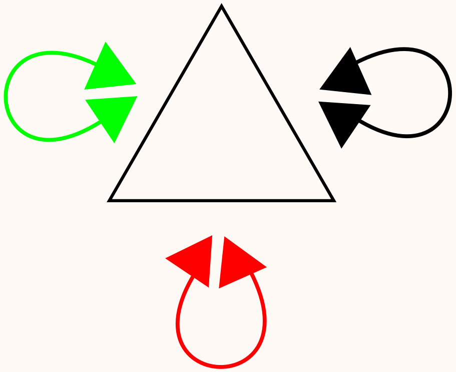
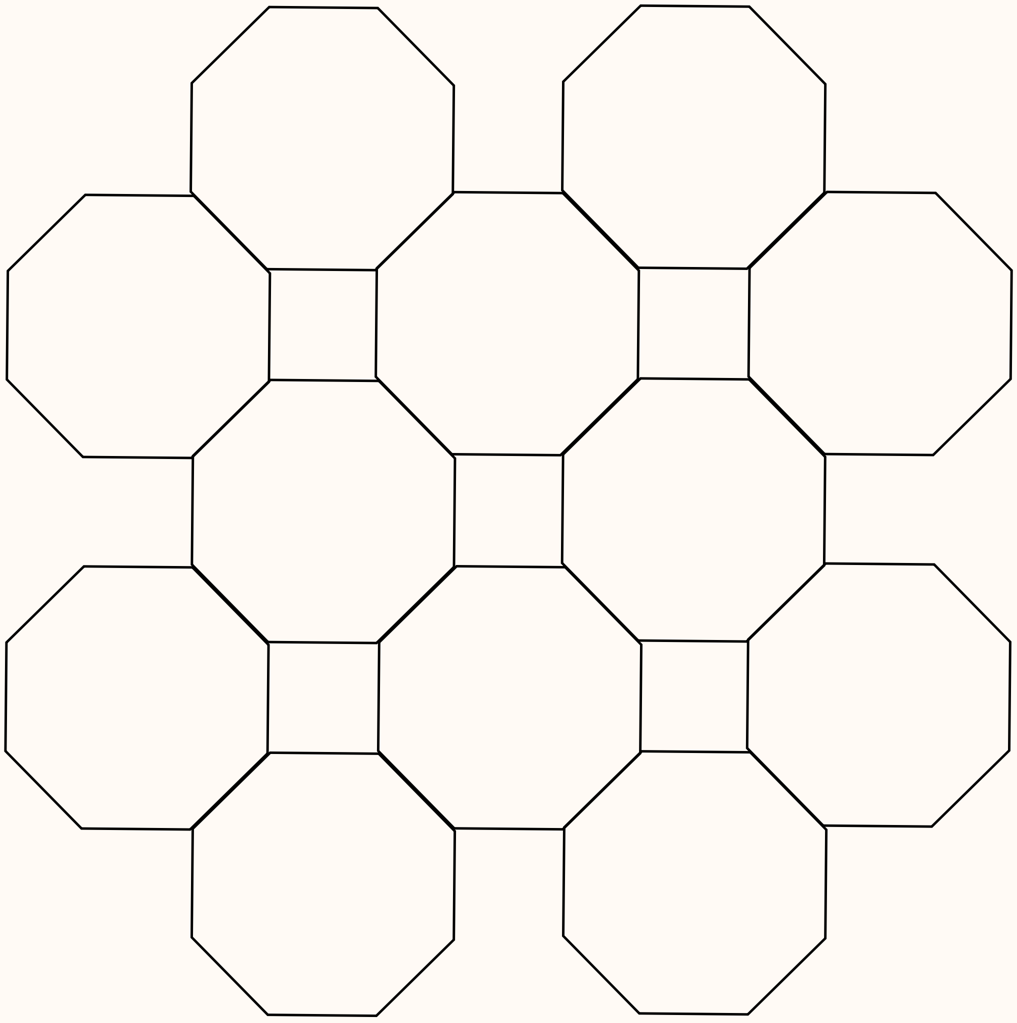




$$m_{01} = 6$$

$$m_{12} = 3$$

Example Delaney/Dress symbol



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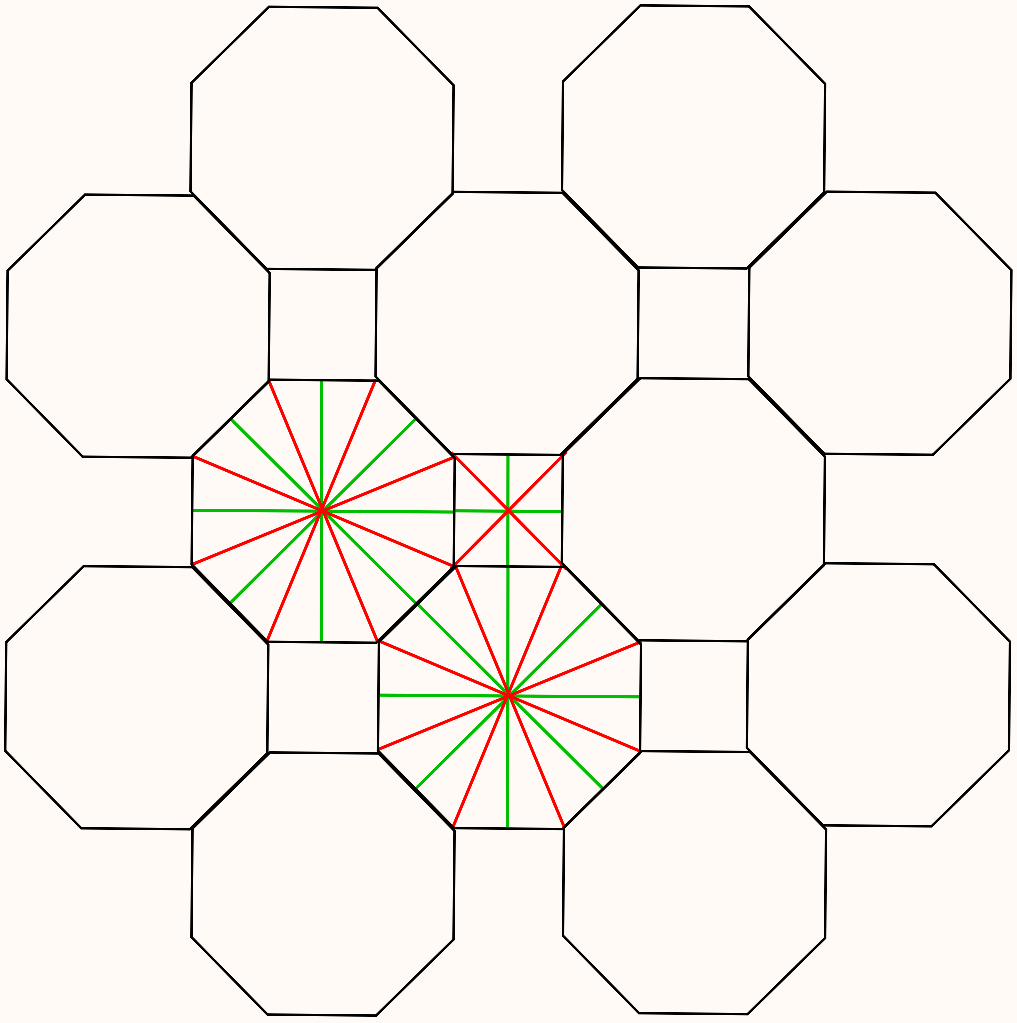

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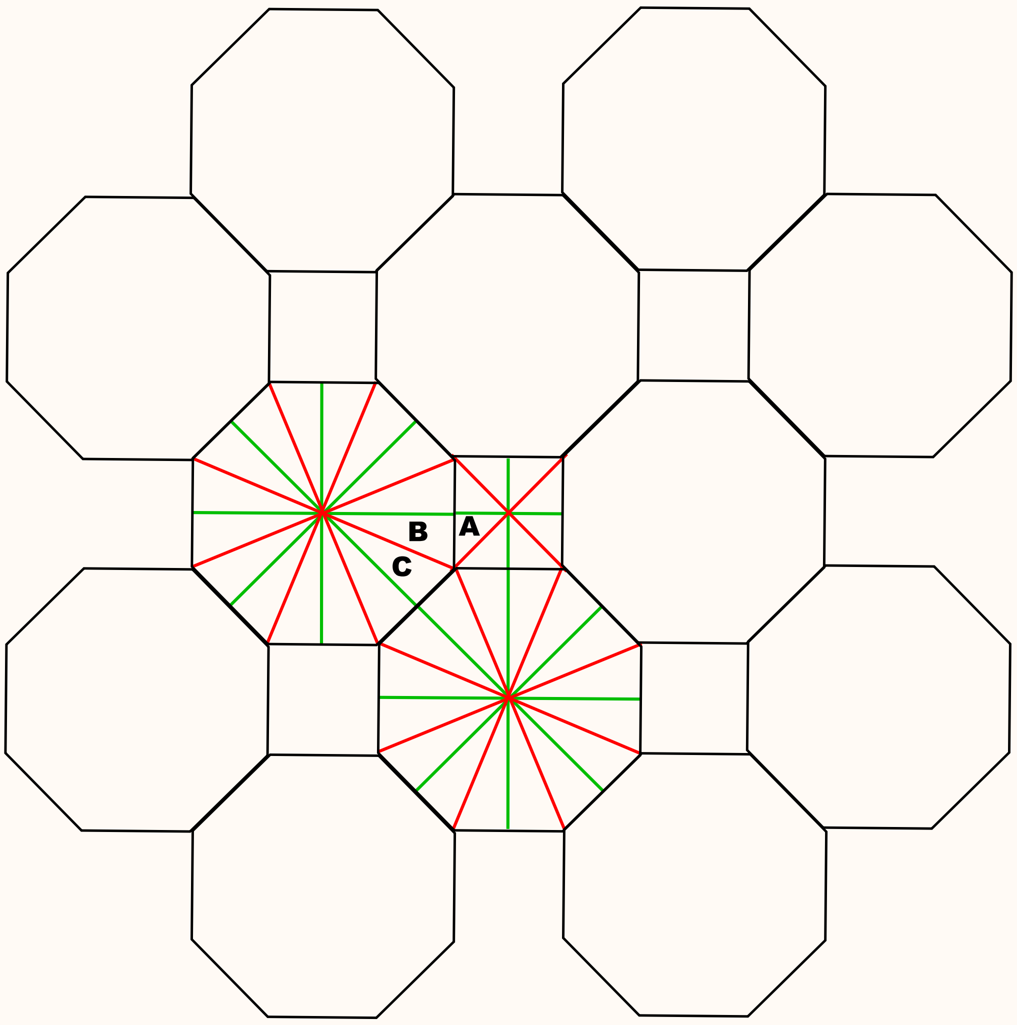

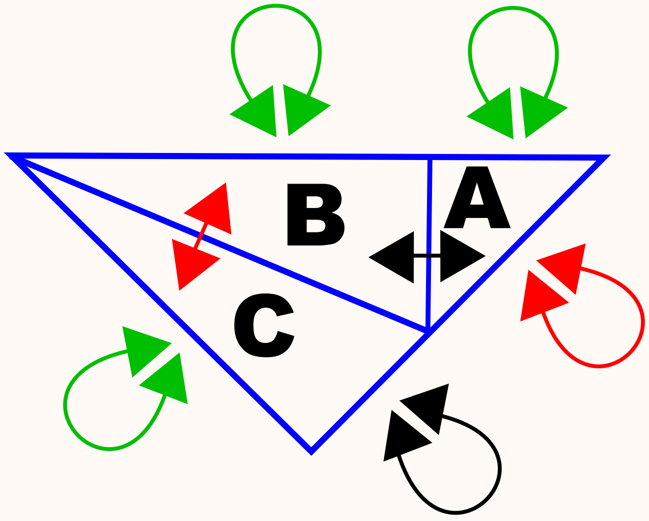

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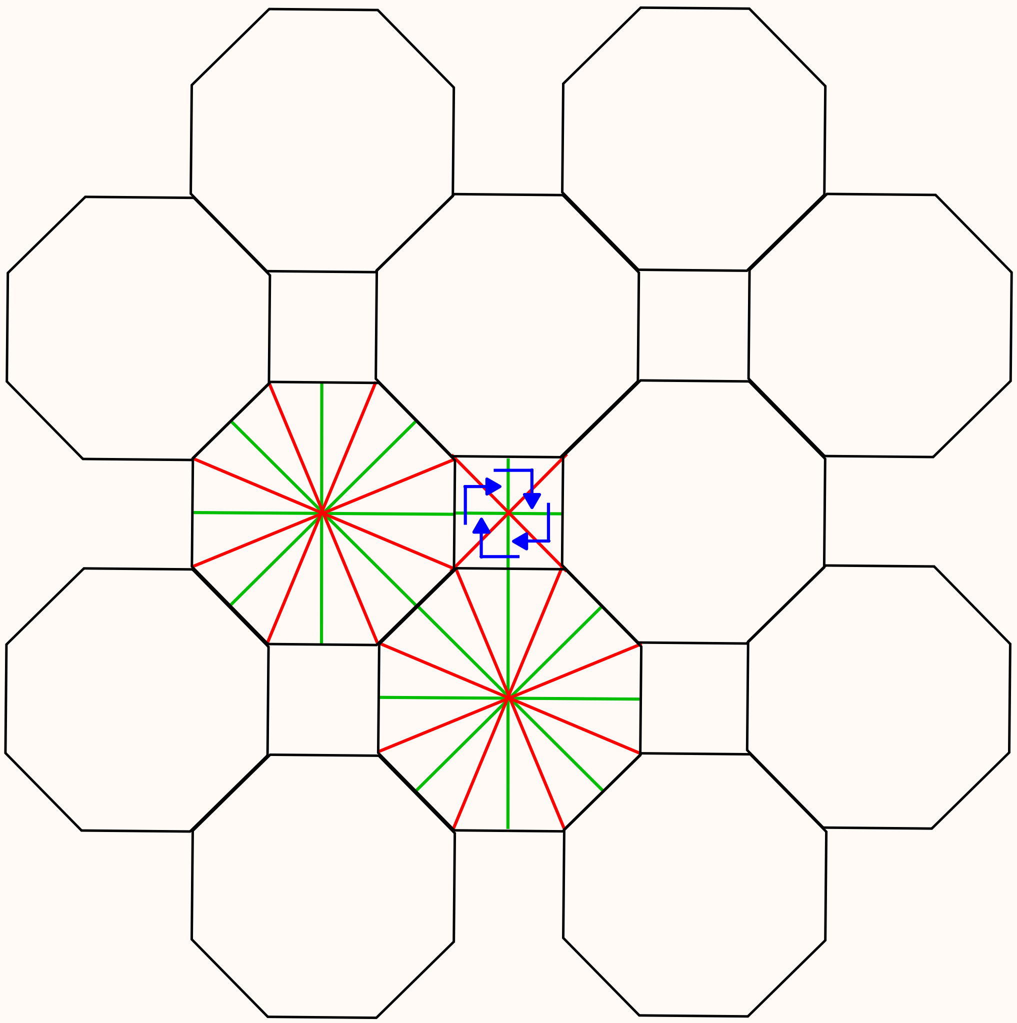

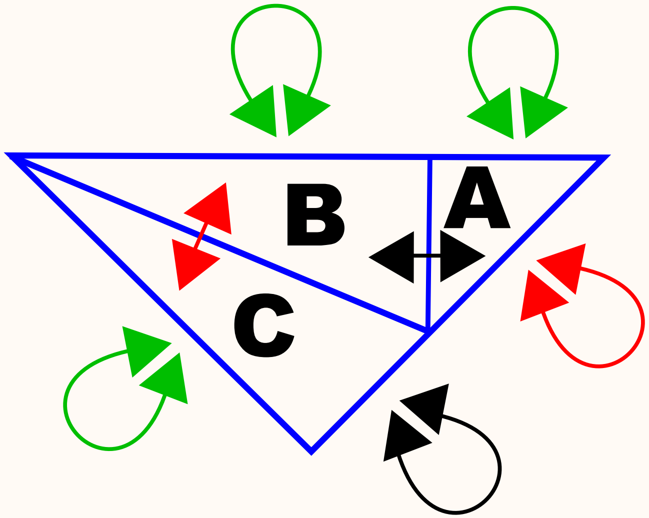

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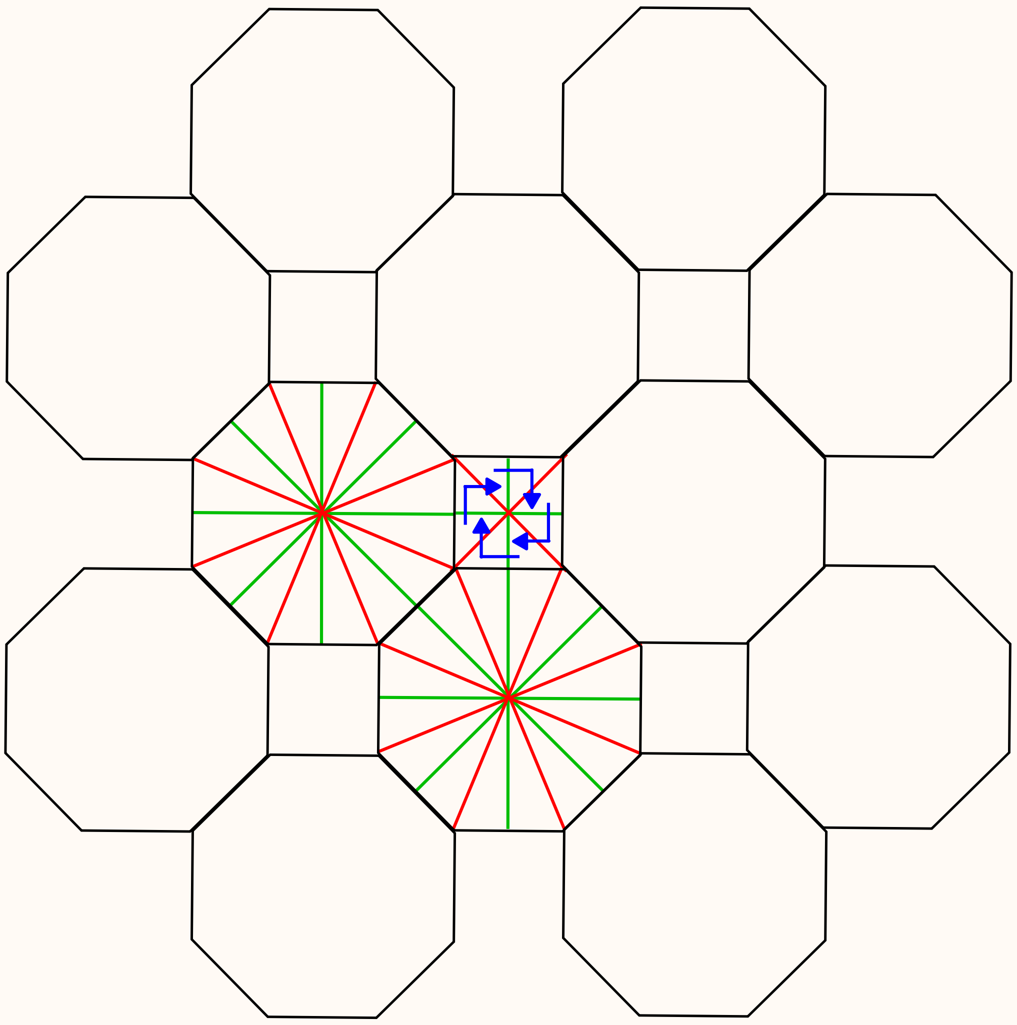
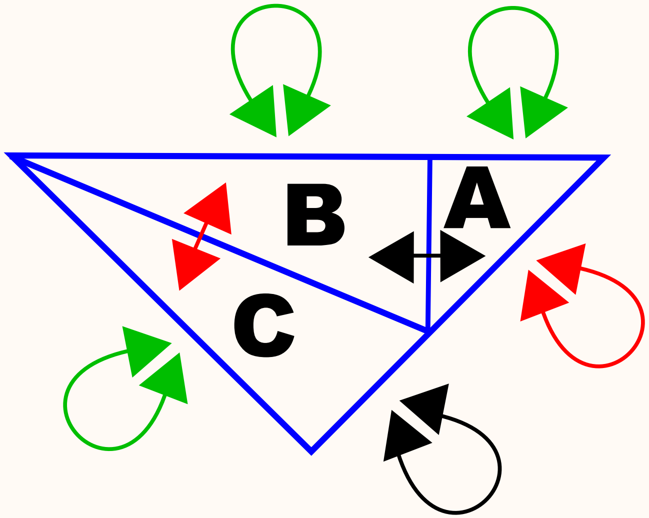
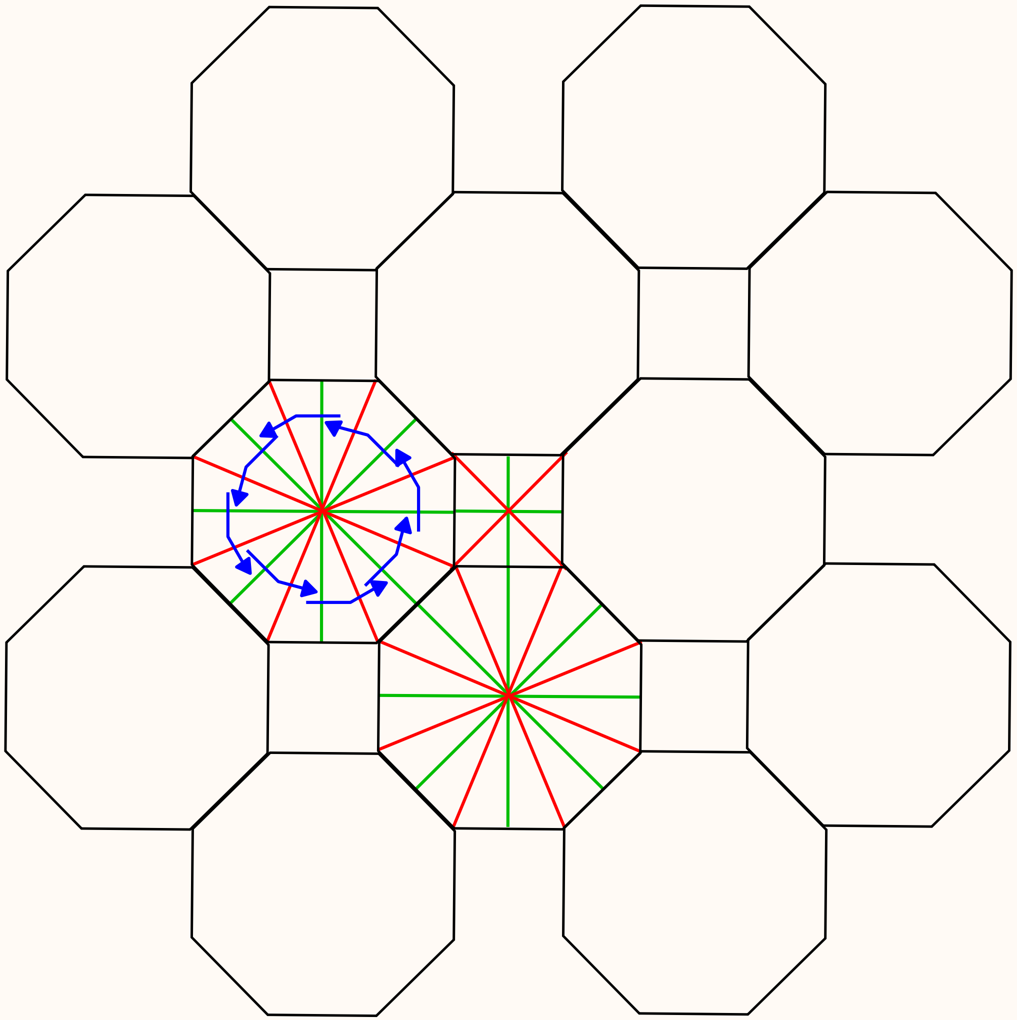
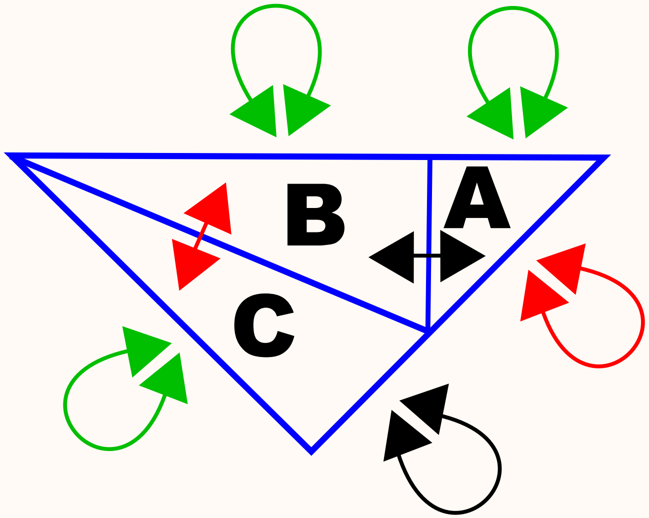




	m_{01}	m_{12}
A	4	
B		
C		

Example Delaney/Dress symbol





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

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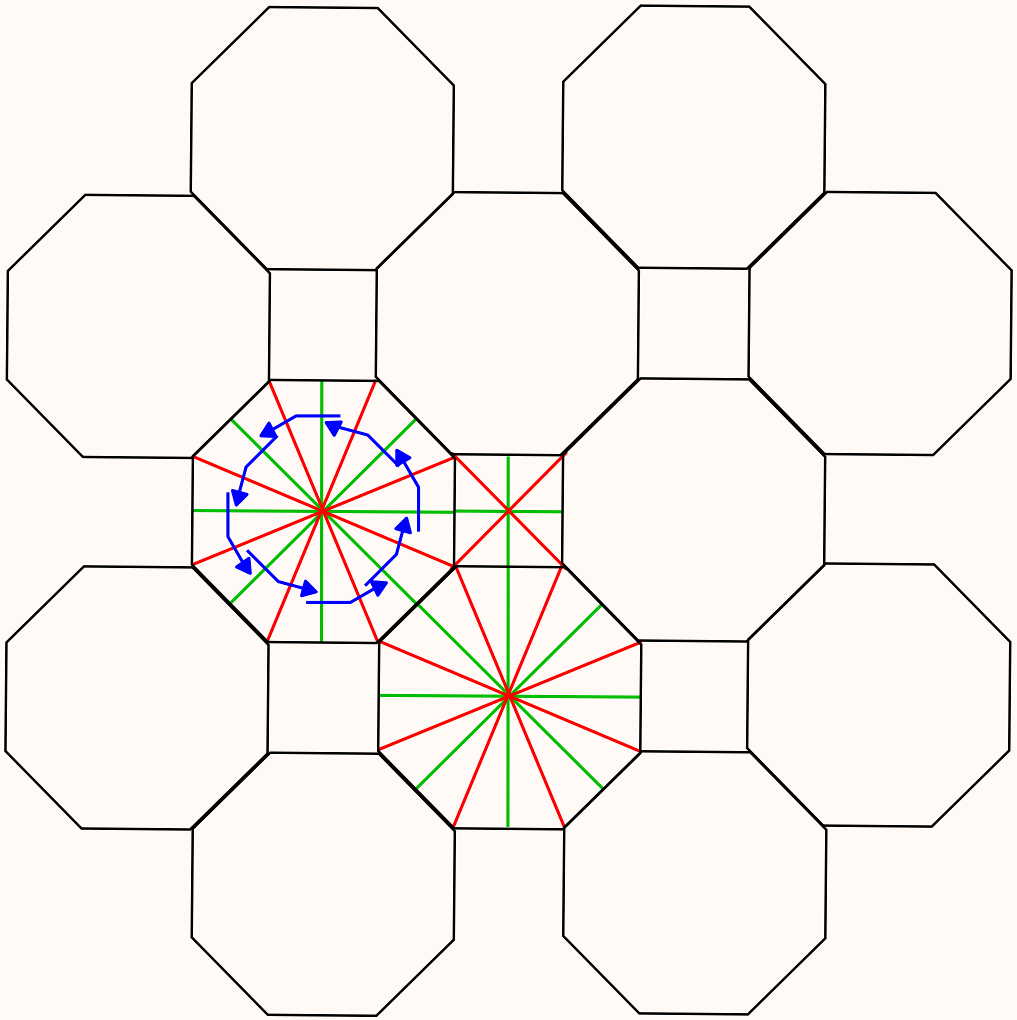
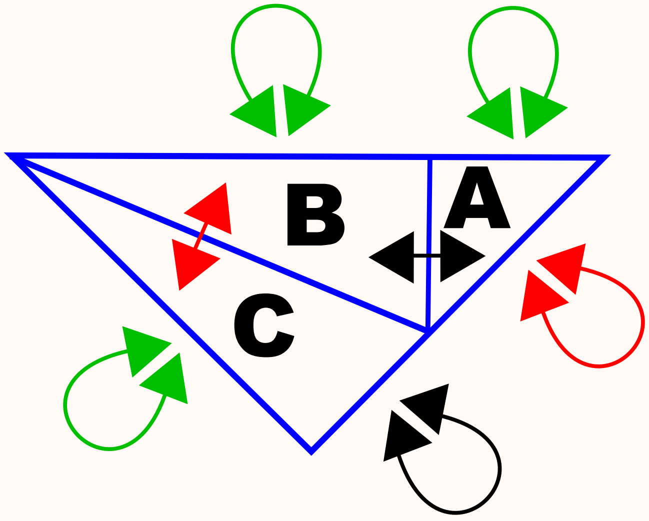
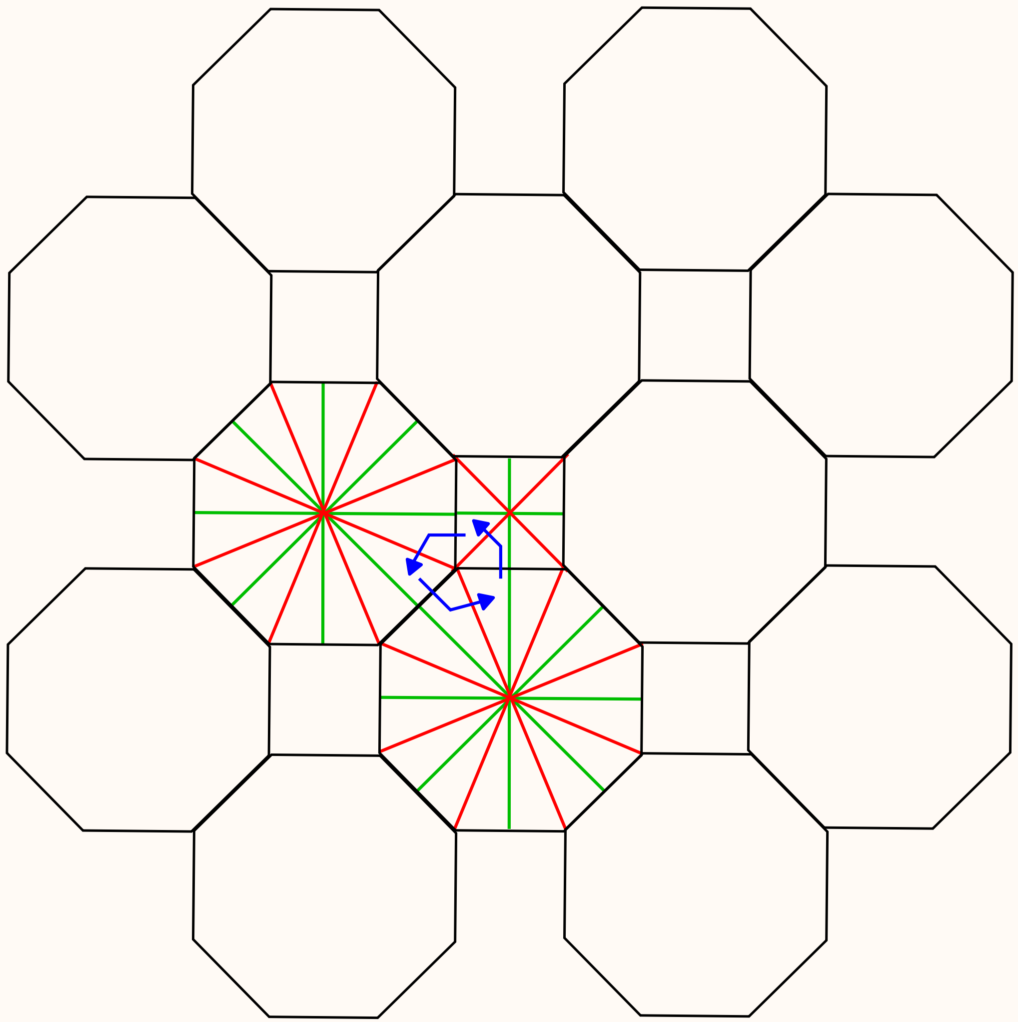
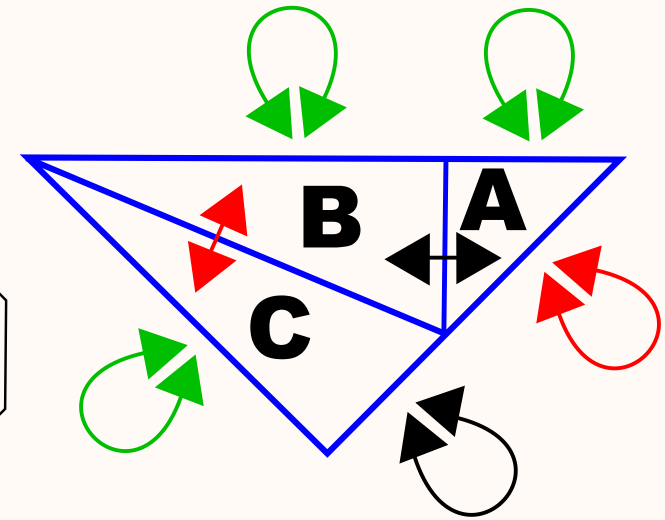




	m_{01}	m_{12}
A	4	
B	8	
C	8	

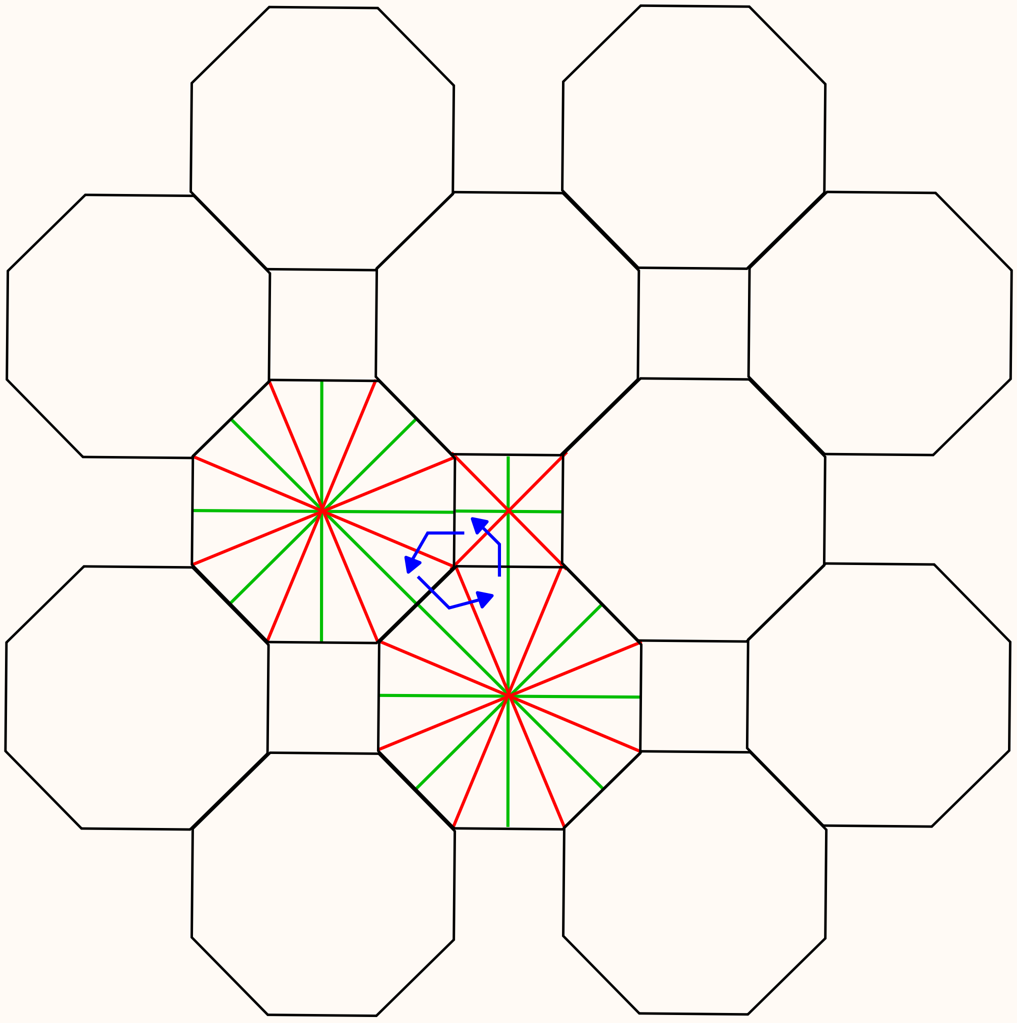
Example Delaney/Dress symbol

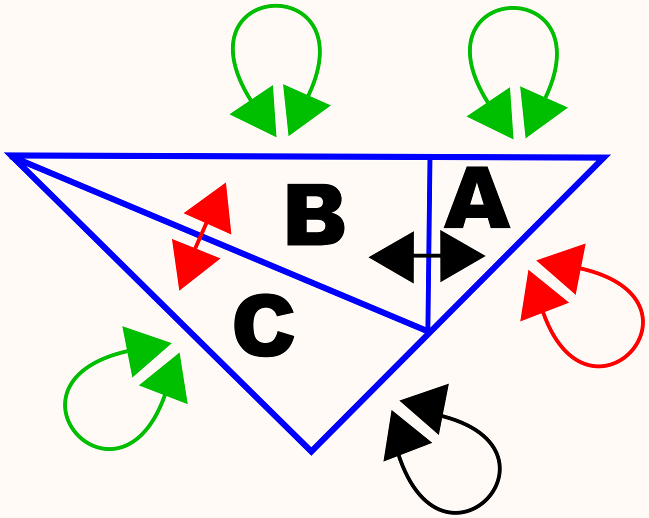




	m_{01}	m_{12}
A	4	
B	8	
C	8	

Example Delaney/Dress symbol





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

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Delaney/Dress symbol

$(\mathcal{D}; m_{01}, m_{12})$ is the Delaney/Dress symbol of a periodic tiling 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. $\forall d \in \mathcal{D} : d(\sigma_0\sigma_2)^2 = d$

Delaney/Dress symbol

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

1. $K(\mathcal{D}) < 0$
2. $K(\mathcal{D}) = 0$
3. $K(\mathcal{D}) > 0$

Delaney/Dress symbol

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

1. $K(\mathcal{D}) < 0 \rightarrow$ hyperbolic plane
2. $K(\mathcal{D}) = 0$
3. $K(\mathcal{D}) > 0$

Delaney/Dress symbol

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

1. $K(\mathcal{D}) < 0 \rightarrow$ hyperbolic plane
2. $K(\mathcal{D}) = 0 \rightarrow$ euclidean plane
3. $K(\mathcal{D}) > 0$

Delaney/Dress symbol

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

1. $K(\mathcal{D}) < 0 \rightarrow$ hyperbolic plane
2. $K(\mathcal{D}) = 0 \rightarrow$ euclidean plane
3. $K(\mathcal{D}) > 0 \rightarrow$ sphere iff. $\dfrac{4}{K(\mathcal{D})} \in \mathbb{N}$

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Representation

	σ_0	σ_1	σ_2	m_{01}	m_{12}
1	$\sigma_0(1)$	$\sigma_1(1)$	$\sigma_2(1)$	$m_{01}(1)$	$m_{12}(1)$
2	$\sigma_0(2)$	$\sigma_1(2)$	$\sigma_2(2)$	$m_{01}(2)$	$m_{12}(2)$
3	$\sigma_0(3)$	$\sigma_1(3)$	$\sigma_2(3)$	$m_{01}(3)$	$m_{12}(3)$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
N	$\sigma_0(N)$	$\sigma_1(N)$	$\sigma_2(N)$	$m_{01}(N)$	$m_{12}(N)$

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Canonical form

Canonical form

based on index priority depth-first traversal of graph

Canonical form

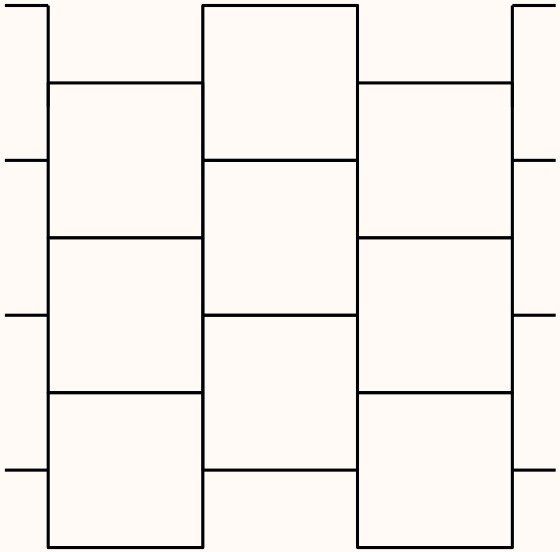
based on index priority depth-first traversal of graph

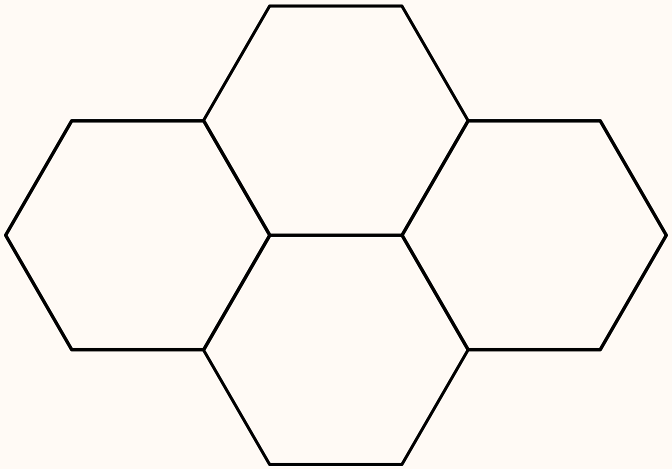
canonical relabelling when

$$m_{01}(1)\ldots m_{12}(1)\ldots \sigma_0(1)\ldots \sigma_1(1)\ldots \sigma_2(1)\ldots$$

is lexicographically smallest.

Minimal symbol





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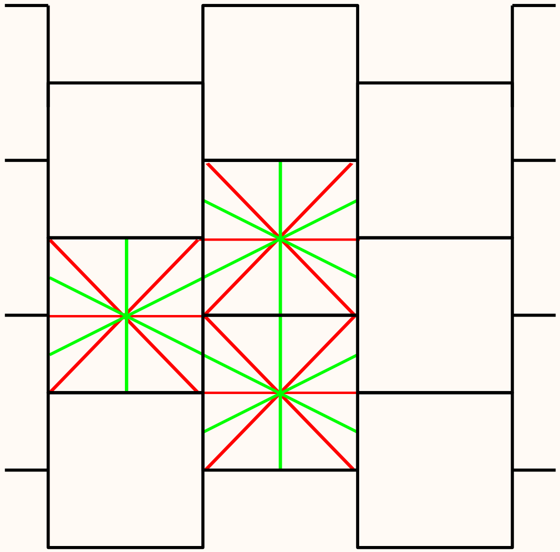

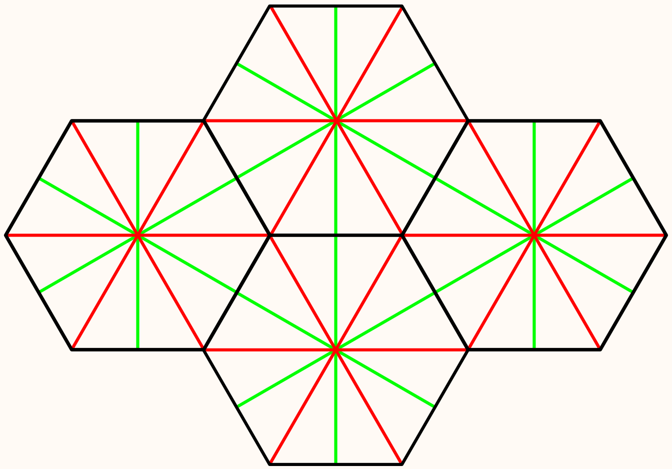

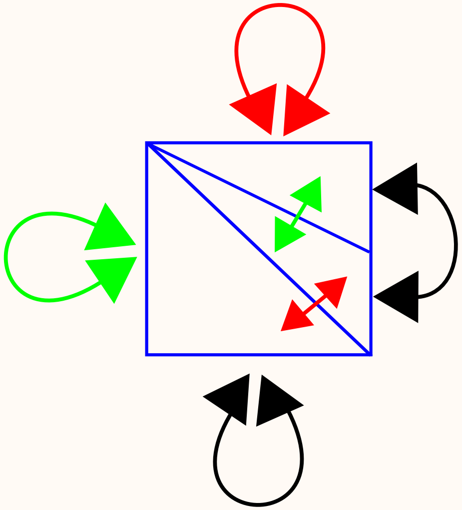

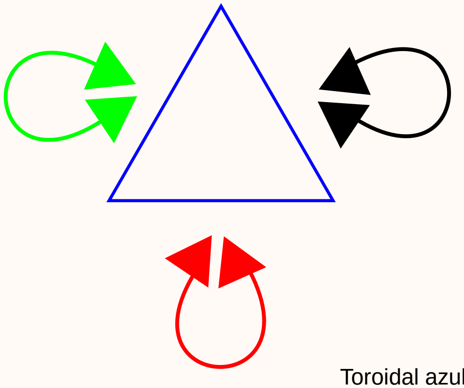

Minimal symbol

add symmetry

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add symmetry $\Rightarrow$ map orbits onto each other

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- Choose two orbits c and d

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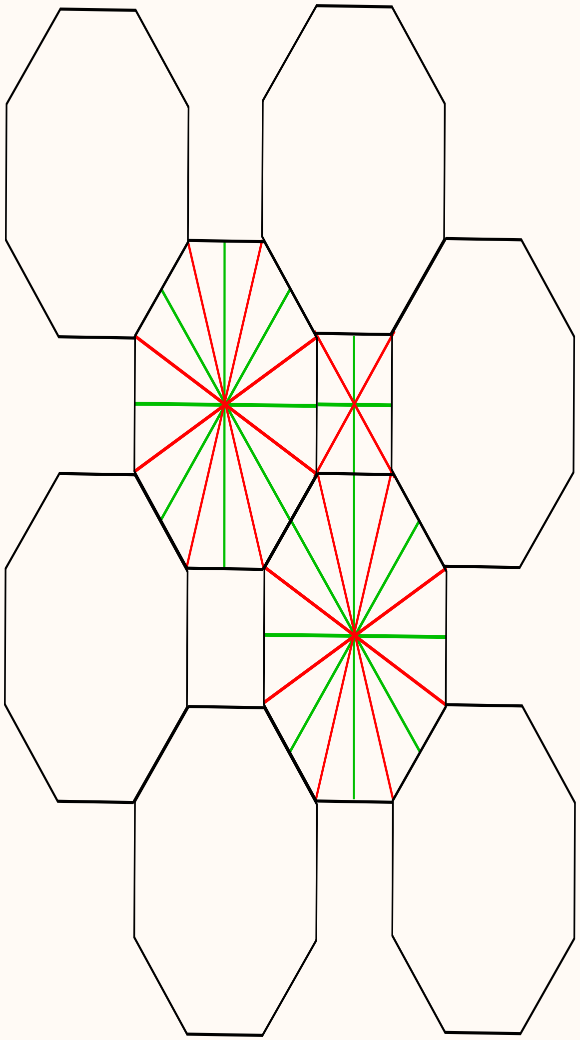
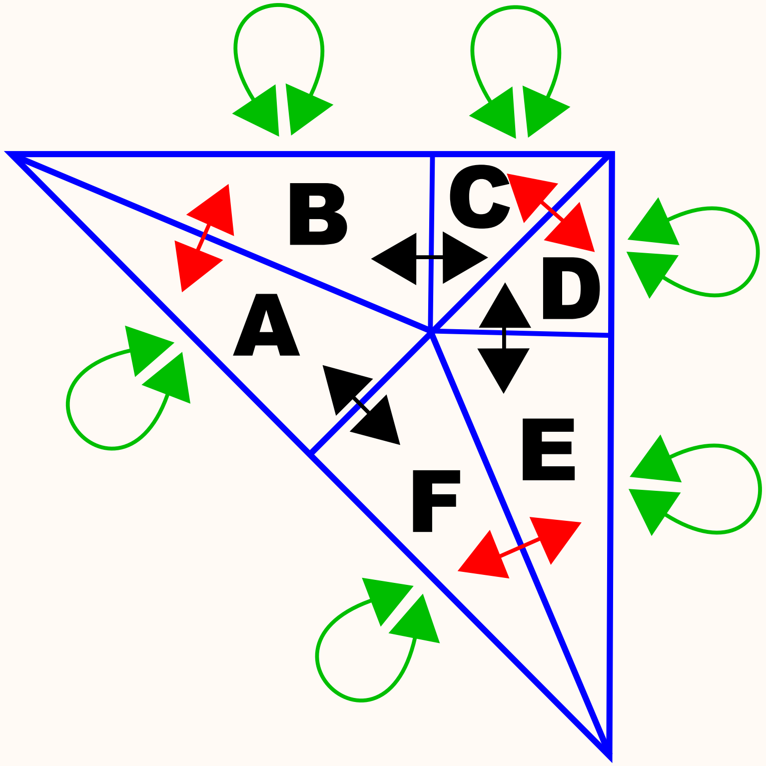
$\sigma_i(c)$ maps onto $\sigma_i(d)$

$m_{ij}(\cdot) = m_{ij}(\cdot)$?

Example minimal symbol





Example minimal symbol

	σ_0	σ_1	σ_2	m_{01}	m_{12}	
A	A	B	F	8	3	A
B	B	A	C	8	3	B
C	C	D	B	4	3	C
D	D	C	E	4	3	D
E	E	F	D	8	3	E
F	F	E	A	8	3	F

C **D**

caagt

Example minimal symbol

	σ_0	σ_1	σ_2	m_{01}	m_{12}	
A	A	B	F	8	3	A
B	B	A	C	8	3	B
C	C	D	B	4	3	a
D	D	C	E	4	3	a
E	E	F	D	8	3	E
F	F	E	A	8	3	F

C D

Example minimal symbol

	σ_0	σ_1	σ_2	m_{01}	m_{12}	
A	A	B	F	8	3	A
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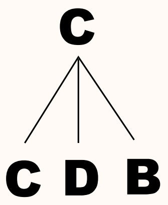
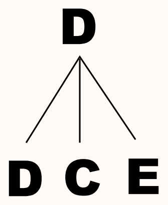
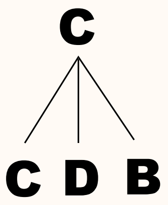
E	E	F	D	8	3	E
F	F	E	A	8	3	F

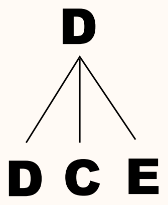




Example minimal symbol

	σ_0	σ_1	σ_2	m_{01}	m_{12}	
A	A	B	F	8	3	A
B	B	A	C	8	3	b
C	C	D	B	4	3	a
D	D	C	E	4	3	a
E	E	F	D	8	3	b
F	F	E	A	8	3	F





Example minimal symbol

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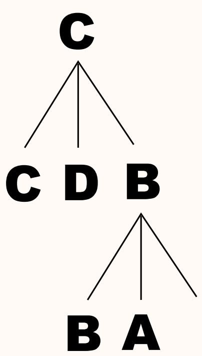
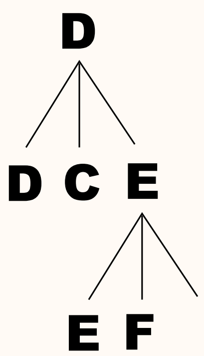
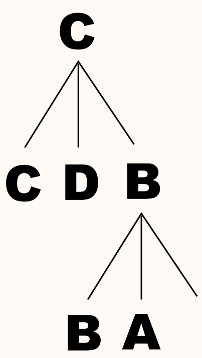
D	D	C	E	4	3	a
E	E	F	D	8	3	b
F	F	E	A	8	3	F

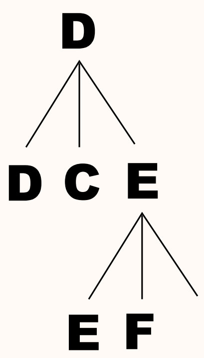




Example minimal symbol

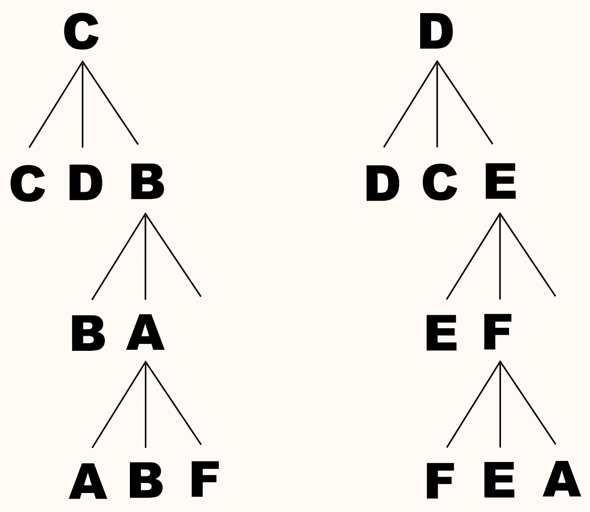
	σ_0	σ_1	σ_2	m_{01}	m_{12}	
A	A	B	F	8	3	c
B	B	A	C	8	3	b
C	C	D	B	4	3	a
D	D	C	E	4	3	a
E	E	F	D	8	3	b
F	F	E	A	8	3	c





Example minimal symbol

	σ_0	σ_1	σ_2	m_{01}	m_{12}	
A	A	B	F	8	3	c
B	B	A	C	8	3	b
C	C	D	B	4	3	a
D	D	C	E	4	3	a
E	E	F	D	8	3	b
F	F	E	A	8	3	c



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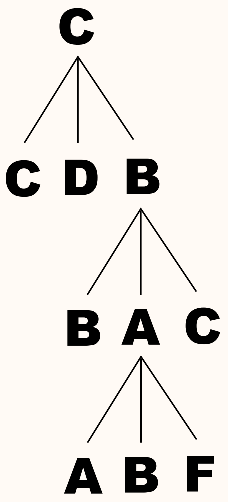
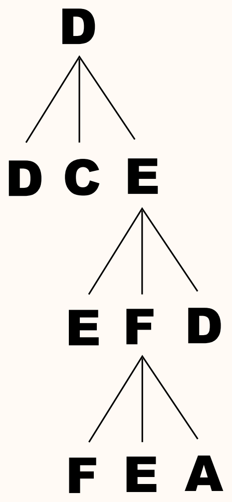
D	D	C	E	4	3	a
E	E	F	D	8	3	b
F	F	E	A	8	3	c





Example minimal symbol

	σ_0	σ_1	σ_2	m_{01}	m_{12}
a	a	a	b	4	3
b	b	c	a	8	3
c	c	a	b	8	3

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 orbit of azulenes?

Translation

Restrictions azulenoid:

- 1 orbit of azulenes
- every atom part of exactly one azulene

Translation

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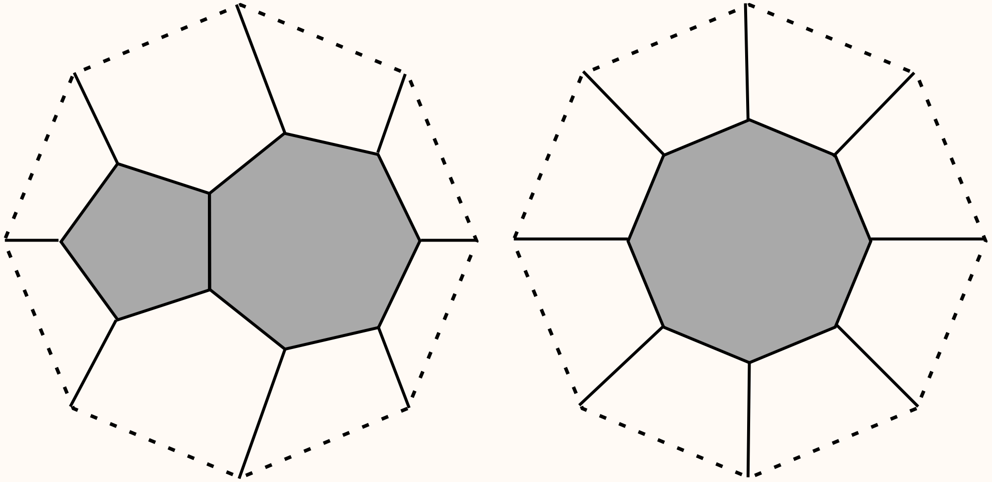
Restrictions Delaney/Dress symbol:

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



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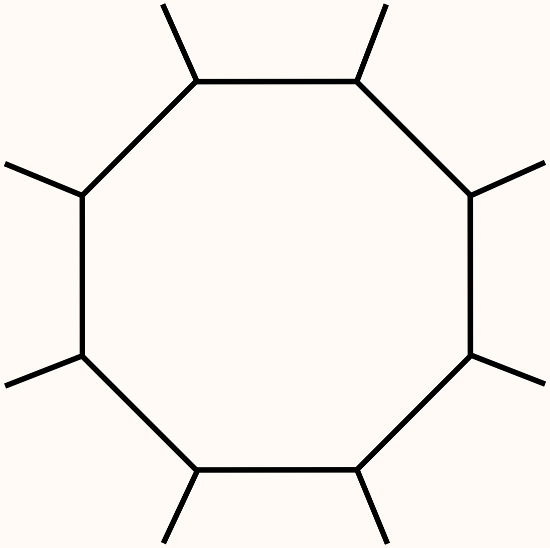
- $\forall \sigma_1\sigma_2$ orbit $V : r_{12}(V) = 3$
- $\sum_{d\in\mathcal{D}} (\frac{1}{m_{01}(d)} + \frac{1}{m_{12}(d)} - \frac{1}{2}) = 0$

Method

- Octagon and the different vertex orbits



Method

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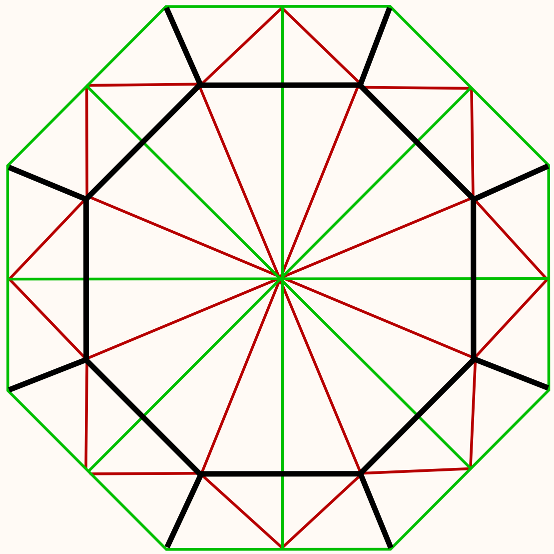
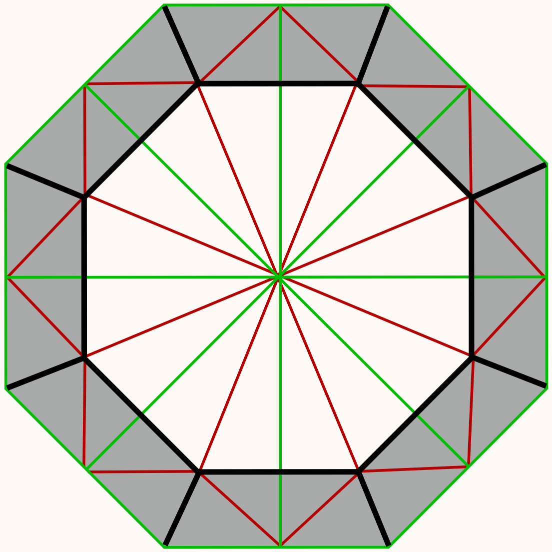


Method

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



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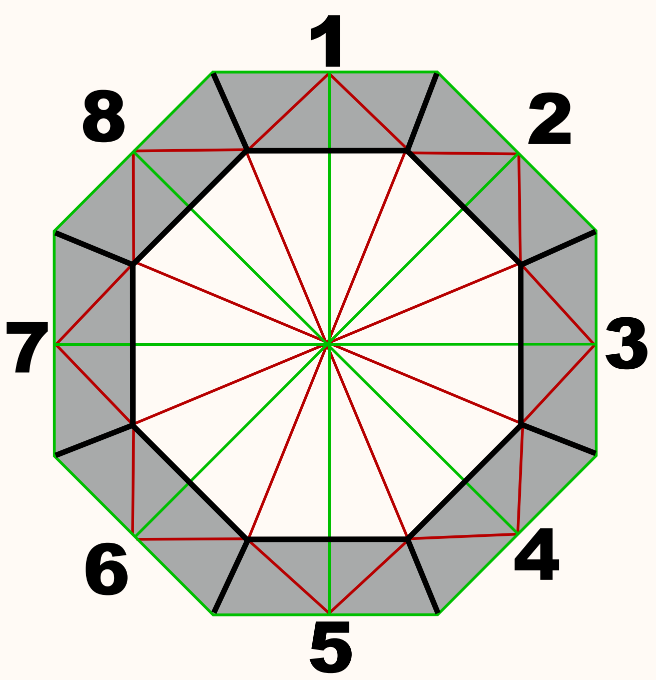
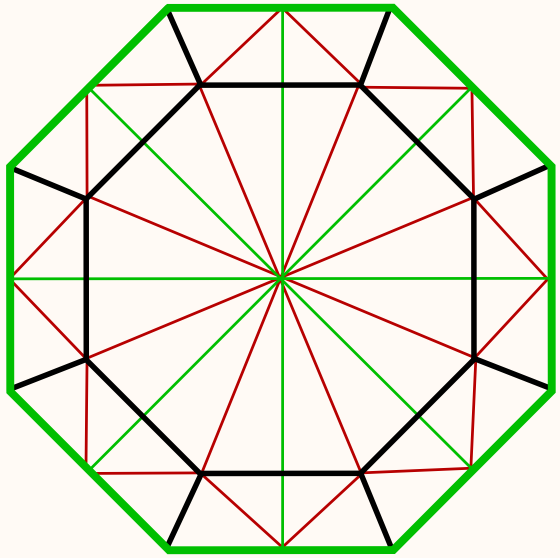


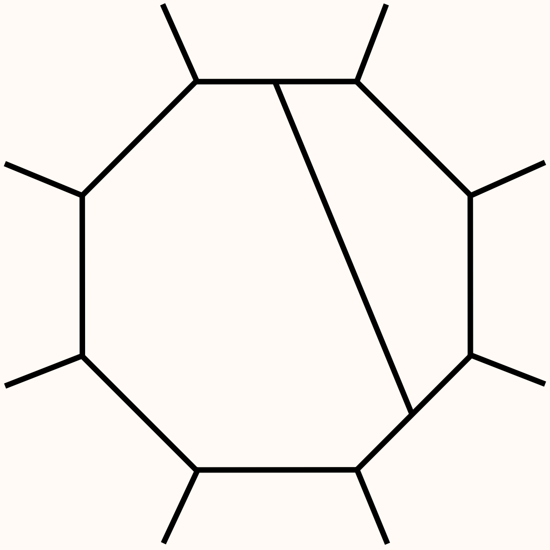
Method

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



Method

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



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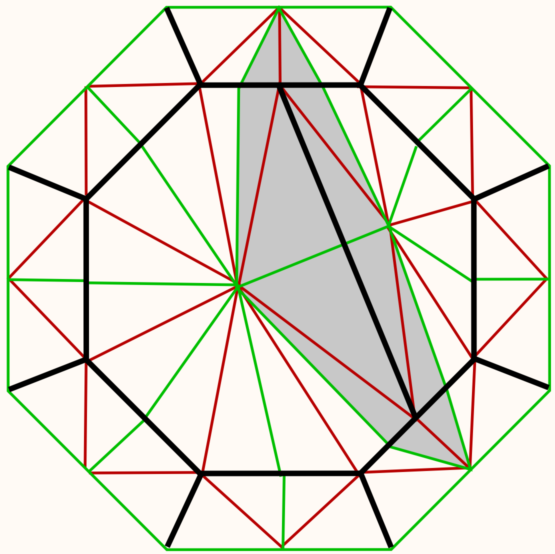

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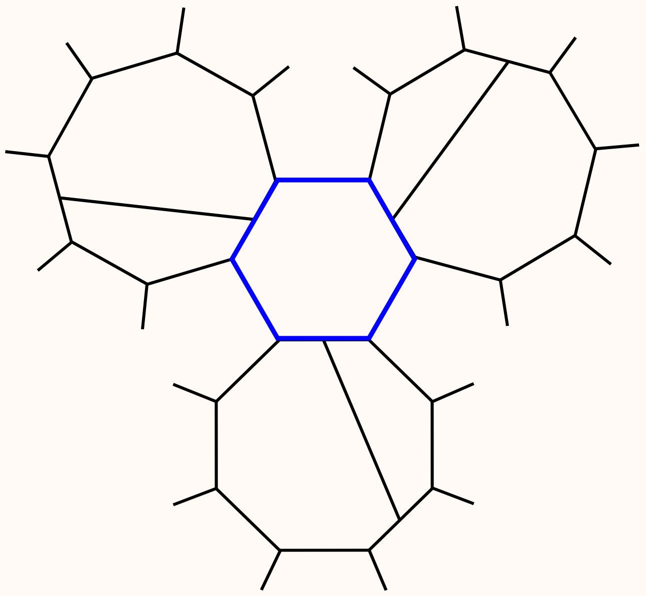

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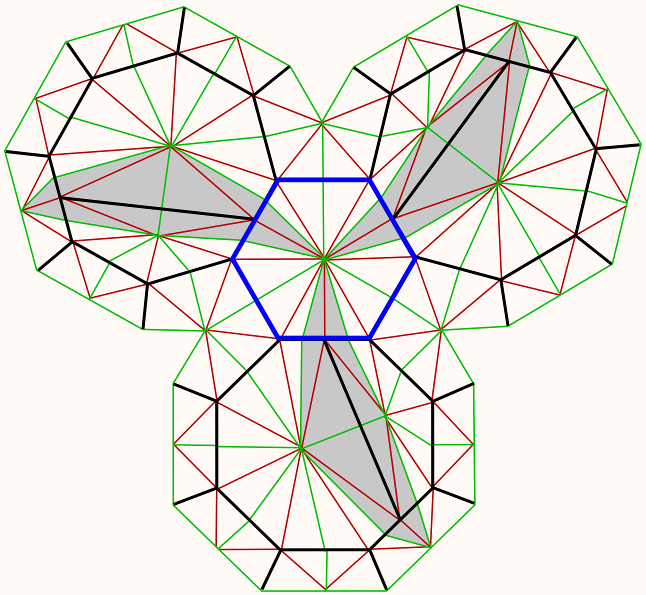
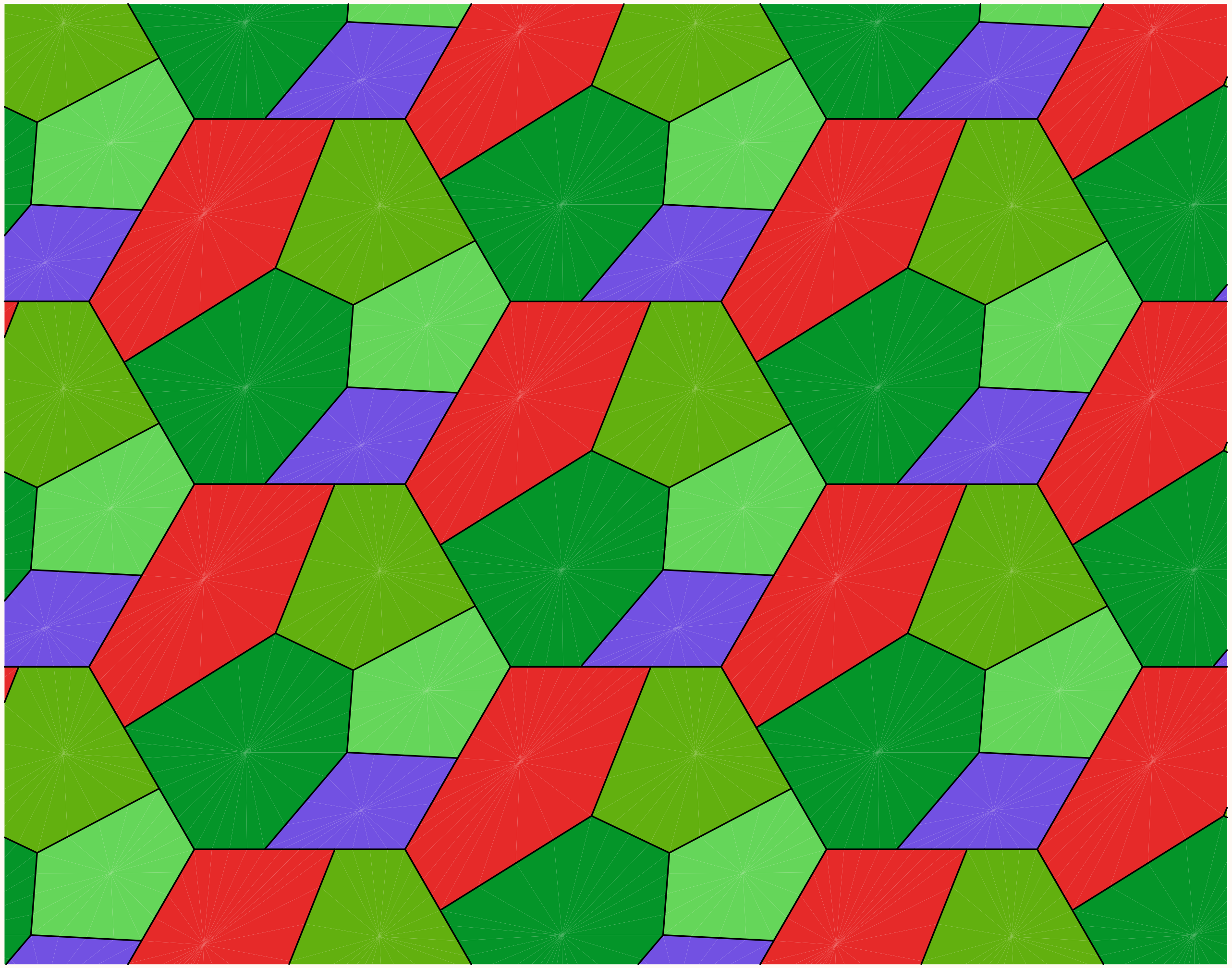
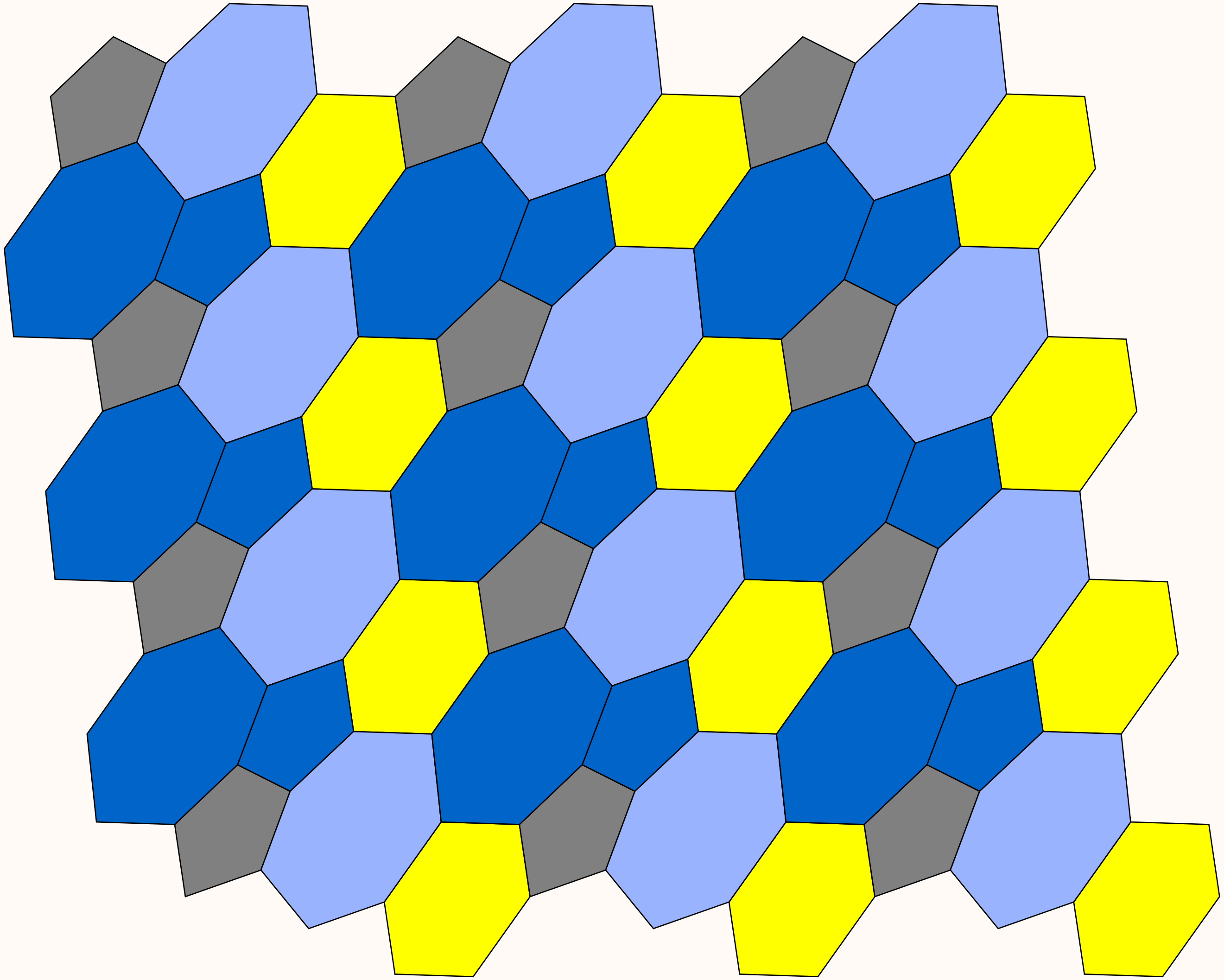


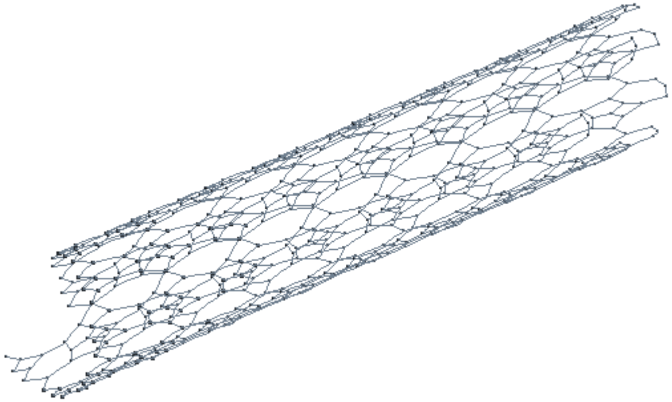
Visualisation

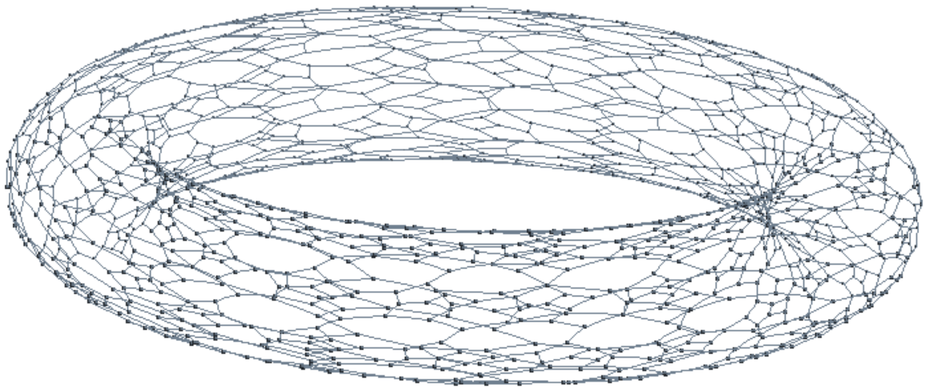


Visualisation



Visualisation





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

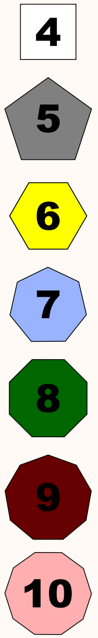
Translation only

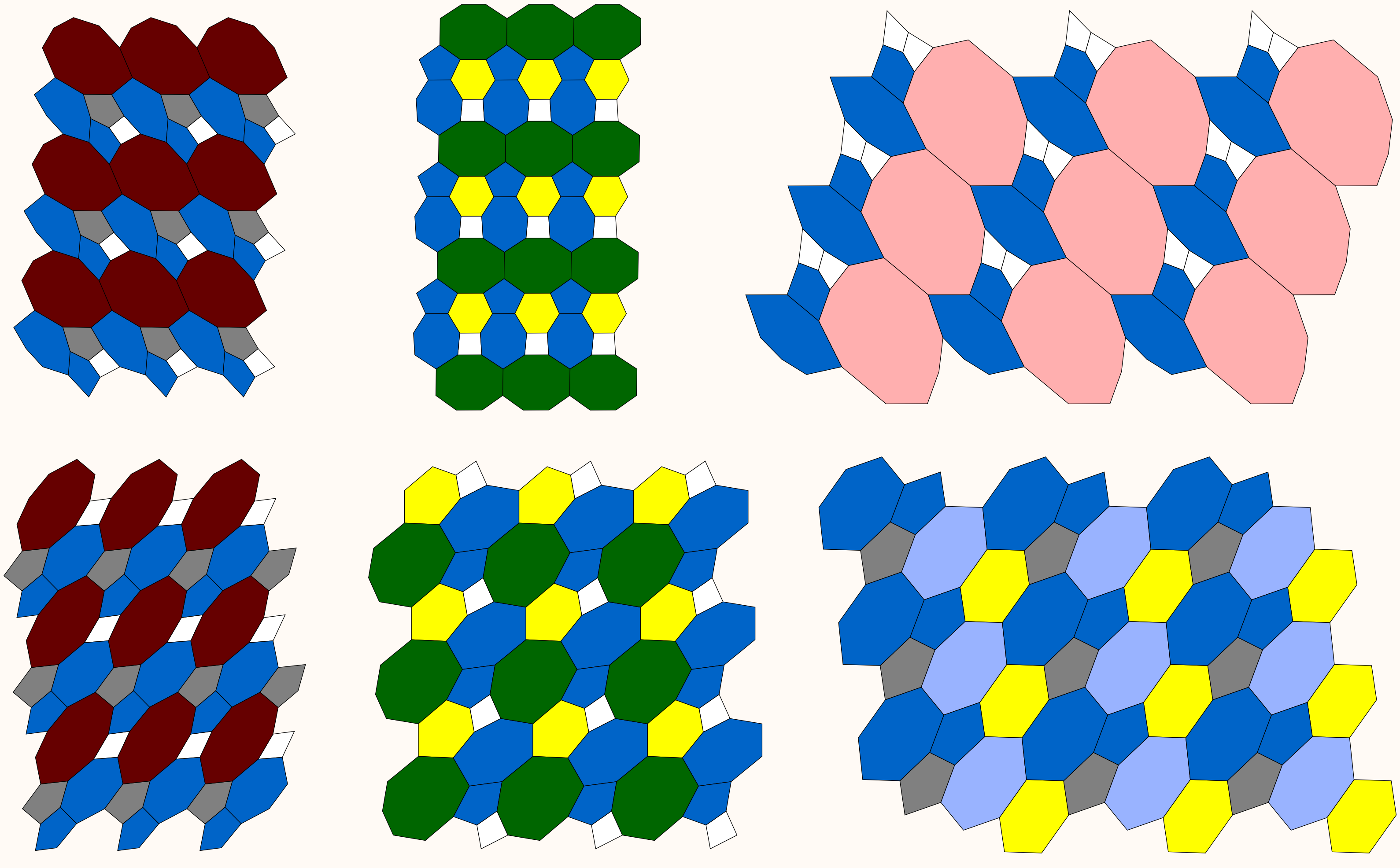
one orbit of azulenes under the subgroup of translations

or

all the azulenes have the same orientation

Translation only





End

Thanks for your attention!