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ORIGINAL PAPER

Flag graphs and their applications in mathematical chemistry for benzenoids

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Abstract Flag graphs have been used in the past for describing maps on closed surfaces. In this paper we use them for the first time in mathematical chemistry for describing benzenoids and some other similar structures. Examples include catacondensed and pericondensed benzenoids. Several theorems are included. Symmetries of benzenoid systems, flag graphs, and symmetry type graphs are briefly discussed.

Keywords Benzenoid · Flag graph · Symmetry type graph

1 Introduction

Flag graphs are a useful tool in topological graph theory and related fields. For instance, they can be used for description of maps, i.e. graphs embedded in closed surfaces with faces being open 2-cells, i.e. homeomorphic to discs. In this paper we use this concept with slight modifications in order to describe certain molecules that have "faces", i.e. special rings that can be found, for instance, in fullerenes or benzenoid systems. Such systems correspond to maps on surfaces with boundary.

2 Flag graphs or flag systems

For a map on a surface, we obtain flags from baricentric subdivison of the map. Each k-sided face or ring in a system is therefore subdivided into 2k right triangles. Each

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flag can thus be viewed as a right triangle, with its three vertices corresponding to the vertex-, center of an edge, and center of a face of the original map. In a map of a closed surface, each flag triangle is adjacent to three triangles and the adjacencies can be viewed as reflections with respect to the three sides of the flag triangle. On a closed surface, there are four flags along each edge, hence the total number of flags is four times the number of edges [1–6].

Example 2.1 Let us take for example the maps of a four-sided pyramid with the vertices of the square base denoted by abcd and the apex denoted by e. The vertex set is V = {a,b,c,d,e}, the edges are E = {ab,bc,cd,da,ea,eb,ec,ed}, and the five faces are F = {abe,bce,cde,dae,abcd}. There are $4|E| = 4 \times 8 = 32$ flags in this system.

If we take the dual of the baricentric subdivision, the flag triangles are represented as flag vertices. Each flag has three semi-edges, indicated by three different colors: 0, 1 and 2. Assigning numbers as colors has a strong mnemonic advantage over arbitrary colors. Namely, color 0 means that that adjacency comes with the respect to the side edge-face of the flag triangle. In this case we move from a flag triangle to the adjacent triangle by keeping the edge and face but changing the vertex (dimension 0). In a similar way the semi-edges of colors 1 and 2 can be described. In our paper we denote 0 by green, 1 by red and 2 by blue. In a closed map the semi-edges of adjacent flags of the same color are glued into an edge in such a way that no pendant edges remain.

3 Benzenoid systems

We think of benzenoid systems (or benzenoids for brevity; π-electrons are ignored) not only as graphs composed of vertices and edges, but also consider rings as faces. Hence such systems can be described by flag graphs, too. However, in benzenoid systems, the situation is different in that flags lying at the peripheral edges of rings have no neighbours, and some blue semi-edges (dimension 2) remain pendant. Along each C–C bond (black lines) we get a green edge (dimension 0) and along each angle spanned by two incident edges we get a red edge (dimension 1).

In the dual approach, where the flags are vertices and not triangles, we may describe a flag system in a purely combinatorial way.

We start with a finite collection of flags Φ and three involutions s_0, s_1, s_2 defined on Φ. There are two axioms:

a) The group $< s_0, s_1, s_2 >$ acts transitively on Φ.
b) $s_0 s_2 = s_2 s_0$

The first axiom ensures that the flag system (Φ; s_0, s_1, s_2) is connected. The second axiom is related to the edges of the structure described by the flag system. We may view a flag system to be the flag graph with a given 3-edge-coloring. A flag system is described by three involutions. Since each involution is a permutation, it can be described in a tabular form or as product of disjoint cycles. In the latter case each cycle is of length 2 or 1. Cycles of length 2 correspond to edges, while cycles of length 1 correspond to pendant edges.

Φ	1	2	3	4	5	6	7	8	9	10	11	12
s_0	2	1	4	3	6	5	8	7	10	9	12	11
s_1	12	3	2	5	4	7	6	9	8	11	10	1
s_2	1	2	3	4	5	6	7	8	9	10	11	12

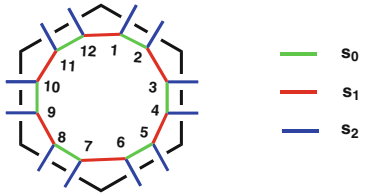


Fig. 1 The flag graph of benzene (*colors*) superimposed on benzene (*black*) (color figure online)

Φ	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
s_0	2	1	4	3	6	5	8	7	10	9	12	11	14	13	16	15	18	17	20	19	22	21	24	23
s_1	12	3	2	5	4	7	6	9	8	11	10	1	24	15	14	17	16	19	18	21	20	23	22	13
s_2	14	13	3	4	5	6	7	8	9	10	11	12	2	1	15	16	17	18	19	20	21	22	23	24

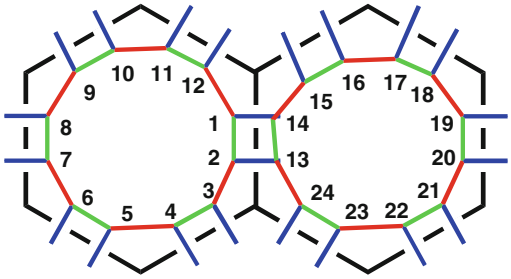


Fig. 2 Flag graph of naphthalene (*colors*) superimposed on naphthalene (*black*) (color figure online)

Example 3.1 Let us consider the two smallest benzenoids: benezene and naphthalene, represented by their hydrogen-depleted graphs, and ignoring the π-electrons.

Here is a possible description of benzene by a flag system. For benzene we have 12 flags, as shown in Fig. 1.

Instead of using table or edge-colored graph, we may use the product of cycles to represent the three involutions:

$$s_0 = (1\ 2)(3\ 4)(5\ 6)(7\ 8)(9\ 10)(11\ 12)$$
$$s_1 = (2\ 3)(4\ 5)(6\ 7)(8\ 9)(10\ 11)(12\ 1)$$
$$s_2 = (1)(2)(3)(4)(5)(6)(7)(8)(9)(10)(11)(12)$$

For naphthalene we have 24 flags, as shown in Fig. 2.

Anthracene

Φ	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
s_0	2	1	4	3	6	5	8	7	10	9	12	11	14	13	16	15	18	17
s_1	12	3	2	5	4	7	6	9	8	11	10	1	24	15	14	17	16	19
s_2	14	13	3	4	5	6	7	8	9	10	11	12	2	1	15	16	17	18

Φ	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
s_0	20	19	22	21	24	23	26	25	28	27	30	29	32	31	34	33	36	35
s_1	18	21	20	23	22	13	36	27	26	29	28	31	30	33	32	35	34	25
s_2	26	25	21	22	23	24	20	19	27	28	29	30	31	32	33	34	35	36

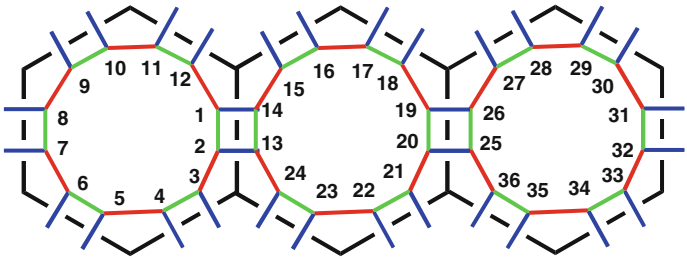


Fig. 3 Flag graph of anthracene

Example 3.2 For the isomeric catafusenes anthracene and phenanthrene we have 36 flags in each case, as shown in Figs. 3 and 4, respectively.

Example 3.3 A last example is for the flag graph of a perifusene, namely pyrene, with 48 flags, as seen in Fig. 5.

Each flag system can be described as a trivalent pre-graph. The vertices are the flags and the edges are involutions. Different involutions correspond to different colors: s_0, s_1, s_2. Pendant edges in the flag graph for involution s_2 represent boundary vertices (and edges).

4 Some properties of flag graphs

Here we list some properties of flag graphs.

1. Orbits of $< s_0, s_1 >$ correspond to faces (or rings) of the original.
2. Orbits of $< s_0, s_2 >$ correspond to edges (or C–C bonds) of the original, and
3. Orbits of $< s_1, s_2 >$ correspond to vertices (or carbon atoms) of the original.
4. We easily distinguish between interior edges (shared by two rings) and boundary edges. Namely, the edge is a boundary edge if and only if the 0–2 (alias green-blue) component in the flag graph is a path (with blue pendant edges at both ends.)

Phenanthrene:

Φ	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
s_0	2	1	4	3	6	5	8	7	10	9	12	11	14	13	16	15	18	17
s_1	12	3	2	5	4	7	6	9	8	11	10	1	24	15	14	17	16	19
s_2	14	13	3	4	5	6	7	8	9	10	11	12	2	1	15	16	17	18

Φ	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
s_0	20	19	22	21	24	23	26	25	28	27	30	29	32	31	34	33	36	35
s_1	18	21	20	23	22	13	36	27	26	29	28	31	30	33	32	35	34	25
s_2	19	20	26	25	23	24	22	21	27	28	29	30	31	32	33	34	35	36

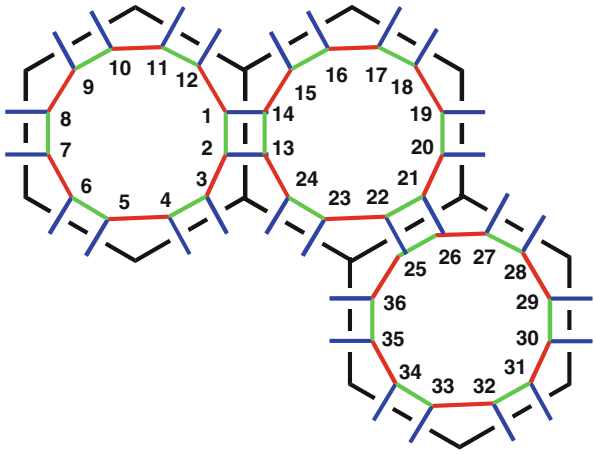


Fig. 4 Flag graph of phenanthrene

5. In a similar way we may distinguish between an interior and a boundary vertex, except that, for the latter, we consider 1–2 (red-blue) components.
6. In a similar way we may distinguish between a face with open boundary from the usual face that is bounded by a cycle in graph. Such "semi-faces" appear, for instance in the process of factoring a system with respect to its symmetry (See, for instance Figs. 6, 7).

Theorem 4.1 *A flag system* $(\Phi; s_0, s_1, s_2)$ *describes a catacondensed system if and only if all vertices are boundary vertices, i.e. if and only if each component* $< s_1, s_2 >$ *is a path.*

We illustrate these properties by a system composed of a hexagon and a square representing the carbon skeleton of benzocyclobutadiene.

F	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
s_0	2	1	4	3	6	5	8	7	10	9	12	11	14	13	16	15	18	17	20	19	22	21	24	23
s_1	12	3	2	5	4	7	6	9	8	11	10	1	24	15	14	17	16	19	18	21	20	23	22	13
s_2	14	13	3	4	5	6	7	8	9	10	11	12	2	1	15	16	17	18	19	20	21	22	23	24

F	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48
s_0	26	25	28	27	30	29	32	31	34	33	36	35	38	37	40	39	42	41	44	43	46	45	48	47
s_1	36	27	26	29	28	31	30	33	32	35	34	25	48	39	38	41	40	43	42	45	44	47	46	37
s_2	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48

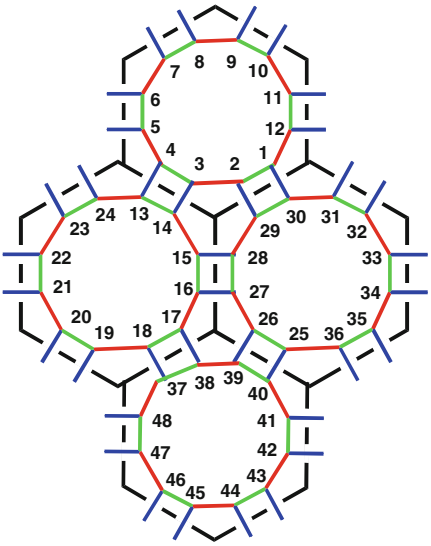


Fig. 5 Flag graph of pyrene

5 The symmetry type graph

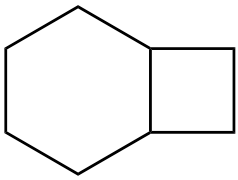
As for flag graphs of maps we may also define more general type graphs.

Let $(\Phi; s_0, s_1, s_2)$ be a flag system. A permutation f: $\Phi \to \Phi$ that preserves all colors, i.e.: $fs_0 = s_0f$, $fs_1 = s_1f$, $fs_2 = s_2f$ is called an *automorphism* of F (that preserves edge-colors). Automorhpisms form a group Aut Φ. The quotient Φ /Aut $\Phi = T(\Phi)$ is the *symmetry type graph* of Φ.

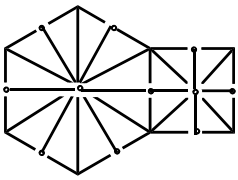
Theorem 5.1 *If a benzene system has m automorphisms and n flags, then m must divide n and the number of vertices in its symmetry type graph is n/m.*

Example 3.1, revisited:

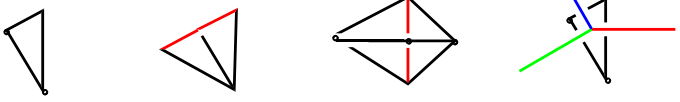
Now the flags are labeled by lower-case letters and each permutation is described by a product of disjoint cycles. For instance, the type graph of benzene has only one vertex.



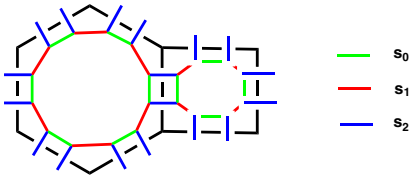
A graph with 8 vertices, 9 edges (8 boundary, 1 internal) and 2 faces



The set of flags Φ has 20 flags ($8 \times 2 + 4 \times 1 = 20$)



A flag ϕ | Two flags at each boundary edge | Four flags at each internal edge | Dual of flag, ψ colored lines



Dual of the set of flags

Fig. 6 Flag graph for benzocyclobutadiene

T(benzene):

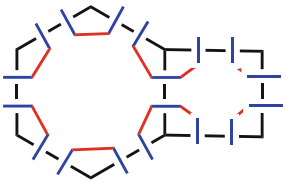
$$s_0 = (a)$$
$$s_1 = (a)$$
$$s_2 = (a)$$

The symmetry type graph of the naphthalene has 6 vertices. Vertices of the type graph correspond to flag orbits under the group of automorphisms.

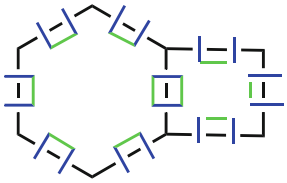
T(naphthalene):

$$s_0 = (a\ b)\ (c\ d)\ (e\ f)$$
$$s_1 = (a)\ (b\ c)\ (d\ e)\ (f)$$
$$s_2 = (a)\ (b)\ (c)\ (d)\ (e)\ (f)$$

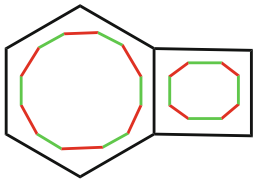
In the same way we could describe symmetry type graphs of other examples.



Deletion of the green edges (s_0): each blue-red-blue component corresponds to a vertex in the original graph, i. e. 8 vertices



Deletion of the red edges (s_1): each blue-green-blue component corresponds to an edge in the original graph, i. e. 9 edges



Deletion of the blue edges (s_2): each green + red component corresponds to a face in the original graph, i. e. 2 faces

Fig. 7 Results of deleting various types of edges in the flag graph of naphthalene

6 Symmetry of benzenoid systems, flag graphs, and symmetry type graphs

The symmetry of graphene, the infinite hexagonal tiling of the Euclidean plane, has a well-known group of isometries that can be described via **p6m**, one of the 17 wallpaper groups. For finite benzenoids, each symmetry group must fix either a vertex, or center of an edge or center of a face. If a vertex is fixed, the largest group is $S_3 = D_3$ on 6 elements that permutes the set of neighbors of a vertex. If the center of an edge is fixed, the largest group is $Z_2 \times Z_2$. If the center of a face is fixed, the largest group is D_6, the dihedral group of order 12 (Figs. 8, 9, 10).

In particular this gives the following result.

Theorem 6.1 *Let B be a simply connected benzenoid system with non-trivial automorphism group of order m. Then exactly one of the following three cases can occur:*

Its automorphism group is a subgroup of a dihedral group D_6 and

0. *fixes a vertex (t0) and m = 2, 3, or 6 (a subgroup of D_3)*
1. *a center of an edge (t1) and m = 2 or 4, (a subgroup of $Z_2 \times Z_2$) or*
2. *a center of a ring (t2) and m = 2, 3, 4, 6, or 12 (a subgroup of D_6).*

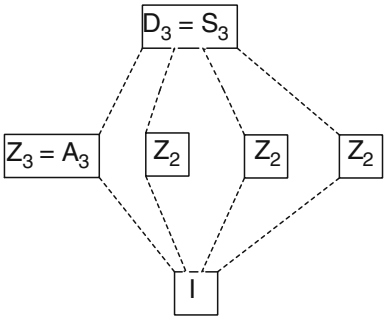


Fig. 8 (t0) Vertex-centered symmetry. The dihedral group D_3 of order 6 and the lattice of its subgroups. There are 6 subgroups in total, however, only 2 of them are proper and pairwise non-isomorphic. These are all possible symmetries of a benzenoid system that fix a vertex

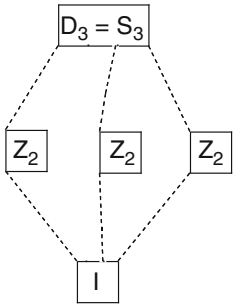


Fig. 9 (t1) Edge-centered symmetry. The Klein four-group $Z_2 \times Z_2$ of order 4 and the lattice of its subgroups. There are 5 subgroups in total, however, only 1 of them is proper (up to isomorphism). These are all possible symmetries of a benzenoid system that fix a vertex

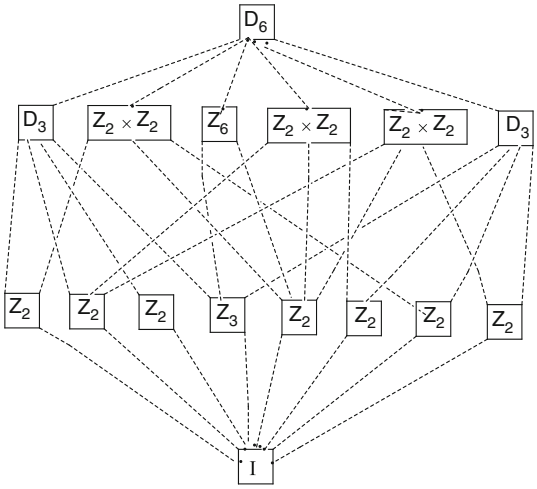


Fig. 10 (t2) Face-centred symmetry. The dihedral group D_6 of order 12 and the lattice of its subgroups. There are 16 subgroups in total, however, only 5 of them are proper and pairwise non-isomorphic. These are all possible symmetries of a benzenoid system that fix a center of a benzene ring

Note that the theorem holds also for benzenoid systems that are not simply connected (have holes) but in this case the center of symmetry may reside in such a hole. We will explore this phenomenon in a sequel paper.

Example 6.1 Triphenylene and coronene, shown in Fig. 11.

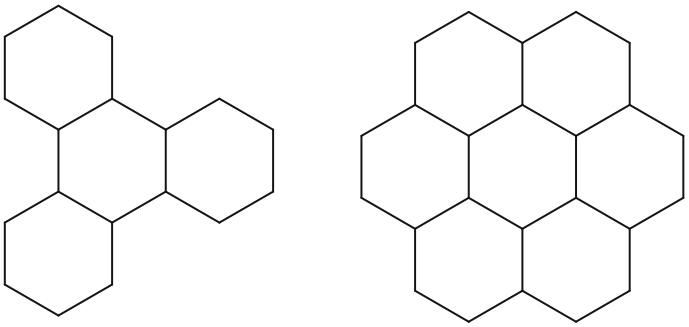


Fig. 11 Both triphenylene and coronene are of type (t2). The former has a symmetry group D_3 while the latter has symmetry group D_6. T(triphenylene) has $(4 \times 3 + 2 \times 18)/6 = 8$ vertices (= flag orbits), T(coronene) has $(4 \times 12 + 2 \times 18)/12 = 7$ vertices (= flag orbits)

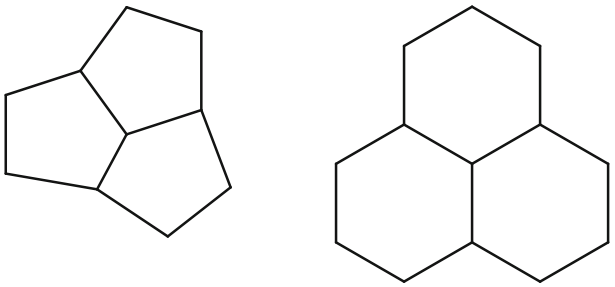


Fig. 12 Both graphs have (t0) symmetry and the group is D_3

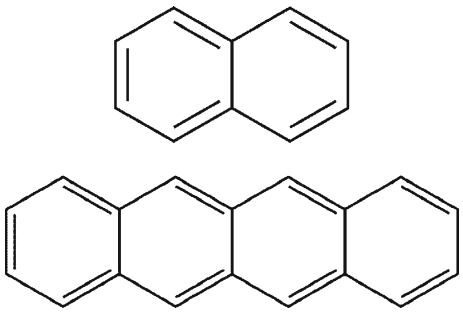


Fig. 13 Both graphs have (t1) symmetry and the group is $Z_2 \times Z_2$. The delocalized π-electrons may be ignored

Example 6.2 Hexahydrotriquinacene $(CH)_{10}$ or acepentalene $C_{10}H_6$, and perinaphthenyl free radical $C_{13}H_9$ (Fig. 12).

Example 6.3 Naphthtalene and tetracene have type (t1) (Fig. 13).

7 Conclusion

In this paper we developed the basics of the theory of flag graphs and symmetry type graphs for benzenoid systems. When considering groups, we restricted our attention to

the abstract groups and not to their geometric actions as point groups. In our sense only the following groups may appear as symmetry groups of benzenoids: D_6, D_3, Z_6, $Z_2 \times Z_2$, Z_3, Z_2 and I, where I denotes the trivial group. Note that they are all subgroups of the D_6.

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