

On Symmetries of Benzenoid Systems

Jurij Kovič,^{a,e} Tomaž Pisanski,^{d,e}

Alexandru T. Balaban^b, Patrick W. Fowler^c

^aUniversity of Ljubljana, IMFM, Jadranska 19, 1000 Ljubljana, Slovenia

jurij.kovic@siol.net

^bTexas A&M University at Galveston, 5007 Avenue U, Galveston, Texas 77551, USA

balabana@tamug.edu

^cDepartment of Chemistry, Sheffield, S3 7HF, UK

p.w.fowler@sheffield.ac.uk

^dUniversity of Ljubljana, FMF, Jadranska 19, 1000 Ljubljana, Slovenia

Tomaz.Pisanski@fmf.uni-lj.si

^eInstitute Andrej Marušič, University of Primorska, Muzejski trg 1, 6000 Koper, Slovenia

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Dedicated to the memory of Ante Graovac

Abstract. We use flag graphs to describe benzenoid and coronoid systems. Factoring out symmetries, we obtain a *symmetry-type graph*, which may be interpreted as a surface with boundary plus an additional combinatorial structure, which is then used to partition benzenoids into 14 classes, thereby re-interpreting in a purely combinatorial way the classification proposed by Gutman and Cyvin. Formulations in terms of automorphism groups or point groups (which are exactly twice as large for benzenoids) are equivalent. A boundary-edges code is used to describe benzenoids: combinatorial properties, including assignment to the 14 classes, can be recovered from this code.

1 Introduction

Benzenoid hydrocarbons are important from both practical and theoretical chemical viewpoints [5,11–13,15,21,24,25,30]. Many of their properties can be understood, at least qualitatively, using simple models which take into account little more than the symmetry and combinatorial structure, as embodied in the molecular graph (the graph of the hydrogen-depleted molecule, i.e., the carbon skeleton). In the present paper we take some ideas from the mathematical theory of maps on surfaces and describe their application to

benzenoids (and coronoids), where they can be used to give a combinatorial description of the possible symmetries of these systems in terms of properties of the *flag graph*. The flag graph itself contains all information necessary to reconstruct the underlying benzenoid/coronoid system, allowing reconstruction of the adjacency matrix, vertices, edges, faces and holes (if any). The flag-graph description also allows us generalise beyond purely chemical examples.

We will find it useful to distinguish between chemical and mathematical approaches to symmetry, which give rise to two different but equally natural labelling schemes that hinge on the difference between point groups and automorphism groups. This potentially confusing difference of language is discussed in detail below.

To keep the treatment reasonably self-contained, we repeat here some necessary definitions and notation, following as far as possible the presentation by Gutman and Cyvin in their *Introduction to the Theory of Benzenoid Hydrocarbons* [21]. The basic concept is of the *benzenoid system* \mathfrak{B} (a mathematical model for a polycyclic benzenoid hydrocarbon molecule in which the graph induced by the carbon skeleton is retained and hydrogen atoms are suppressed) [13]. Several definitions and naming systems for these objects are current, and we present below two of the several definitions given by these authors ([21] pp.11-15).

1.1 Definition of benzenoid and coronoid systems

An intuitive description of a *benzenoid system* \mathfrak{B} is given by Definition A ([21], p.11): ‘A benzenoid system is a connected geometric figure obtained by arranging congruent regular hexagons in a plane so that two hexagons are either disjoint or have a common edge. This figure divides the plane into one infinite (external) region and a number of finite (internal) regions. All internal regions must be regular hexagons.’¹ A supplementary definition D ([21], p.15) describes isomorphism in this context: two benzenoid systems belonging to the plane σ are isomorphic if they can be brought into coincidence by any combination of translations in σ , rotations in σ and a reflection in a plane perpendicular to σ . This is effectively a statement of the types of symmetry operation that are to be

¹Note that this definition excludes *helicenes*, where the graph is planar, but cannot be drawn without overlap on the tessellation of the plane with congruent hexagons. Helicenes and benzenoids taken together constitute the class of *fusenens* [8, 20].

considered in the construction of the groups. Here we note that this is a more restricted set than those considered by chemists in treatments of symmetry of benzenoid *molecules* (e.g. [16]). Benzenoid systems in the mathematical sense are 2D objects. In 2D, reflection in the plane σ has the same effect as the identity operation. In contrast, the molecule, even if rigorously planar at equilibrium geometry, is seen in chemistry as an intrinsically 3D object, with nuclei that may move out of plane during the course of vibrations and with a three-dimensional electron cloud surrounding those nuclei; in these circumstances it is appropriate to extend the symmetry group by reflections in the plane σ , and the *point group* of the molecule will therefore be twice as large as the *automorphism group* of the corresponding benzenoid system \mathfrak{B} , as the point group will be the direct product of the automorphism group with the abstract group of order two.

Other definitions of benzenoid exist. One uses *dualists*, defined as a collection of vertices placed in the centre of each hexagonal benzenoid ring, plus edges connecting vertices of rings sharing a CC bond; angles of dualists matter, unlike in normal graphs. Benzenoids are called *cata-condensed* when the dualist is acyclic, *peri-condensed* when the dualist contains three-membered rings, and *corona-condensed* when the dualist contains larger rings that are not perimeters of fused triangles; for cata-condensed benzenoids, dualists allow a simple notation based on digits 0 and 1 [2,4].

One remark about the figures in the present paper, and the way that molecular graphs are typically drawn, is that graph-theoretical diagrams generally use single lines for edges, ignoring the presence of alternating single and double bonds in the usual chemical Kekulé formulas for benzenoids. In both, hydrogen atoms are suppressed.

Molecules similar to benzenoids, but with internal holes, have also been synthesised [15,30]. These are described as ‘coronoids’ [5,11,12,21]. A benzenoid system can be defined with respect to cycles on the hexagonal lattice (definition C, [21], p.13): given such a cycle, \mathfrak{B} is formed by the vertices and edges lying on the cycle and in its interior. This definition is easily adapted for coronoids. *Single coronoid systems* have exactly one hole, and can be defined by assuming two cycles on the hexagonal lattice, C' and C'' , with C'' ‘completely embraced’ by C' [21, p.119]: the single-coronoid system \mathfrak{C} consists of the vertices and edges on C' and C'' , together with those in the interior of C' , but outside C'' . This idea can be extended to systems with more holes by adding curves C''' , ... Clearly, if \mathfrak{C} is to describe a molecule, C' , C'' , ... must have size greater than 6, to form inner

perimeters where some vertices are have degree 2, corresponding to CH groups in the molecule, and considerations of steric strain imply that holes should be even bigger. The mathematical definition of a *coronoid system* \mathcal{C} does not require these restrictions (although holes of size 6 are explicitly forbidden in [21]).

A *primitive coronoid system* consists of a single chain of hexagons in a macro-cyclic arrangement. Every coronoid system with $h+1$ hexagons is either a primitive coronoid or is constructed from a coronoid system with h hexagons by adding a hexagon on the outer (or if possible, inner) perimeter ([21], p.119).

The number of *internal* vertices of a benzenoid or coronoid system (incident with three hexagonal faces) is denoted n_i . A benzenoid system is either *cata-condensed* (if $n_i = 0$) or *peri-condensed* (if $n_i \geq 1$.) Primitive coronoids with holes of size greater than 6 correspond to the *cycloarenes* [30], i.e., molecules in which catacondensed rings form a macrocyclic system with a cavity into which carbon-hydrogen bonds project.

The synthesis of kekulene, a coronoid with an internal hole having a periphery of 18 carbon atoms was achieved by Diederich and Staab in 1978 [15] and later improved by Staab and coworkers, as recounted in the book on coronoids by Cyvin, Brunvoll and Cyvin [11, p.5]. A generalization of aromatic systems [6] with a central conjugated n -membered ring surrounded by benzenoid rings (as in coronene, which has a benzenoid ring in the centre) is the concept of $[n]$ circulenes [24]; for instance, with a central five-membered ring ($n = 5$), the bowl-shaped molecule of corannulene has been thoroughly investigated.

Benzenoids could of course be considered as the limiting case of the coronoids, as ‘coronoids with zero holes’, but it is useful from both chemical and mathematical points of view to preserve the distinction implied by the use of separate symbols \mathfrak{B} and \mathcal{C} .

1.2 A *topological* distinction between benzenoid and coronoid systems

A fundamental topological distinction between benzenoids and coronoids can be seen clearly using the *first homotopy group*, also known as the *fundamental group*, $\pi_1(S,P)$, which can be defined for any surface S (orientable or non-orientable, with or without boundary) as follows: starting at an arbitrary point P we may draw different oriented loops beginning and ending in P . If two loops can be transformed one into another via continuous transformation, they are *homotopic*. For the classes of homotopic loops a

natural group operation can be defined [19]: for representative loops a_1 and a_2 of homotopic classes, we find a representative loop $b = a_1a_2$ of the *product homotopy class* by joining the end of a_1 with the beginning of a_2 (after detaching them from the point P), as shown in Figure 1 (left), whereas the representative of the *inverse homotopy class* is a_1^{-1} , the same curve as a_1 but with opposite orientation.

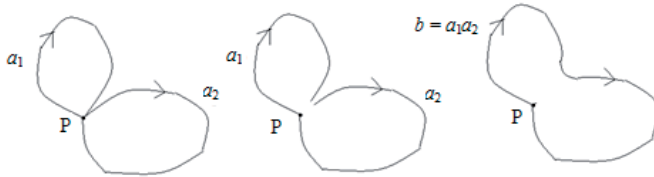


Figure 1: The process of forming the product $b = a_1a_2$ of loops a_1 and a_2 on any surface S .

Thus we obtain a *free group* – a group without relations between its generators, in which each generator has an infinite order (see [19], pp.65-66) – known as the *first homotopy group* or *fundamental group* $\pi_1(S,P)$. Generators of this group are in one-to-one correspondence with ‘holes’ in the surface. Given a surface with boundary, there is a unique way to complete it to a surface without boundary by patching disks to boundary ‘holes’. We restrict attention to surfaces that can be obtained from a sphere or a plane by excising a finite number of topological disks. In benzenoid systems all loops may be contracted via continuous transformation to a point, but in coronoids this is not the case (see Figure 1). Two coronoids have the same number of holes if and only if their fundamental groups are isomorphic.

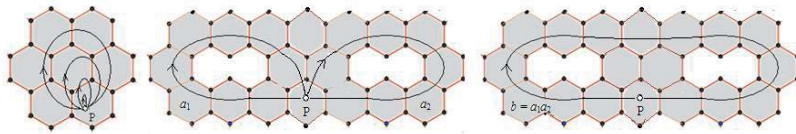


Figure 2: Loops in benzenoids and coronoids: (left) any loop in a benzenoid can be contracted to a point; (middle and right) the product of representative loops a_1 and a_2 (middle) is $b = a_1a_2$ (right), which is a representative of the homotopy class of a_1a_2 .

Figure 2 shows an important topological distinction between benzenoids and coronoids. In a benzenoid, all loops are contractible to a point but in a coronoid, loops surrounding the holes cannot be contracted. In [21] only those coronoids with a single hole

are considered. These *single coronoid systems* are characterized by the fact that the fundamental group $\pi_1(S,P)$ is generated by a single element and hence isomorphic to the group of integers under addition.

1.3 A combinatorial distinction between benzenoid and coronoid systems

Benzenoid system \mathfrak{B} and coronoid system \mathfrak{C} contain *vertices* and *edges*. Pisanski and Balaban [28] introduced the idea of studying their hexagonal *faces*, each of which is divided into 12 right triangles called *flags*. One of the first appearances of flags in connection with graphs on surfaces was around 1980, in a paper by Lins [26]. Flags may be viewed as vertices of a *flag graph* $F(\mathfrak{B})$ or $F(\mathfrak{C})$. The theory of flag graphs for closed surfaces [7,27] has been adapted for surfaces with boundary, such as \mathfrak{B} and \mathfrak{C} , in [28].

In the present paper we depart in one respect from the approach to flag graphs taken in [28]. There it was required that all vertices of the flag graph have degree 3, and semi-edges leading across the boundary were therefore introduced. In the present description, the flag graphs are not required to be 3-regular, and no semi-edges are needed. Specifically, the vertices of a flag graph $F(G)$ derived from an embedded graph G correspond to the flags of G . A flag is defined by a triple (v, e, f) consisting of a vertex v of G , an edge e of G that is incident on v , and a face f of G that is incident with both. Edges of the flag graph are defined by adjacency of the flags. Two flags are adjacent if they share two members of the triple. Colours are assigned to the edges of the flag graph according to the prescription: if the adjacent flags differ in v , the colour is 0, if they differ in e , the colour is 1 and if they differ in f , the colour is 2. If G is embedded in a surface without boundary, $F(G)$ is cubic, and removal of all edges of colour 1 gives a subgraph consisting of a disjoint union of 4-cycles, each corresponding to an edge of G . Removal of all edges coloured 0 from $F(G)$ gives a subgraph consisting of a disjoint union of cycles in one-to-one correspondence with the vertices of G , and each of size equal to twice the degree of the corresponding vertex of G . Likewise, removal of all edges of colour 2 breaks $F(G)$ into cycles corresponding to faces of G . All vertex, edge and face information from the original graph is thus encoded in $F(G)$.

For \mathfrak{B} and \mathfrak{C} , the embedding surface has one (\mathfrak{B}) or more (\mathfrak{C}) boundaries. In the latter case, the flag graph contains some vertices of degree two, corresponding to flags whose triples contain vertices and edges in the boundary. If in such a case we remove those

edges of $F(G)$ that are coloured 0 and belong to a 0,2 four-cycle, the resulting graph will be composed of a disjoint union of cycles in which the two-coloured cycles (coloured alternately 1 and 2) correspond to internal vertices, and of the remaining $k+1$ cycles, one corresponds to the outside boundary, and (if $k > 0$) k are in one-to-one correspondence with the internal perimeters, i.e., with the holes. In the case that G has no boundary, deletion of the edges with 0 colour gives *only* the (1,2) two-coloured cycles, corresponding to *all* vertices of G .

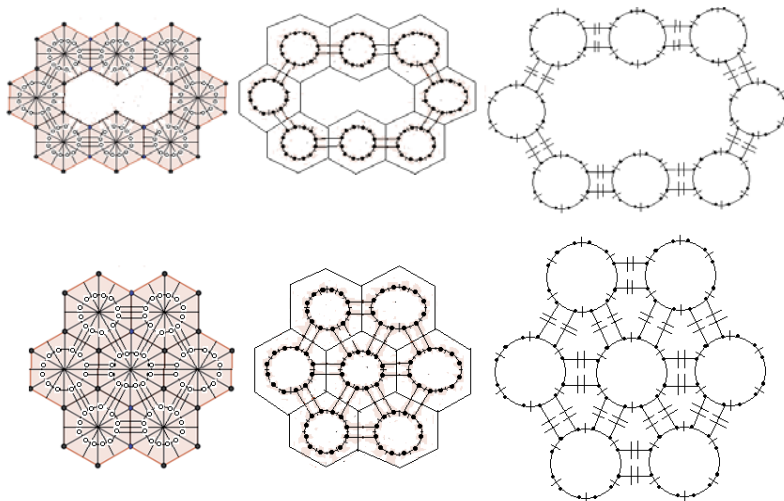


Figure 3: Flag graphs obtained as duals of a benzenoid (top) and a coronoid (bottom). Flags are represented as congruent right triangles in the barycentric subdivision of faces. Circles correspond to 0-1 cycles of edges with alternating numbers 0 and 1; the parallel pairs of edges linking the circles correspond to 2-edges.

As an easy concrete example, the flag graph of benzene consists of 12 vertices arranged in the 12-cycle with edges alternately coloured 0-1. Figure 3 shows examples of the construction and analysis of flag graphs for larger benzenoid and coronoid systems.

Using flag-graphs we may make a mathematical distinction between two systems, both formally derived from the coronene molecule: a benzenoid in which a central hexagon is present and a coronoid in which the central hexagon is absent (Figure 4). Note that no chemical significance in terms of molecular structure can be given to the absence of the

central hexagon if the vertices around the hole are still intended to represent carbon atoms trigonally bonded to carbon neighbours only.

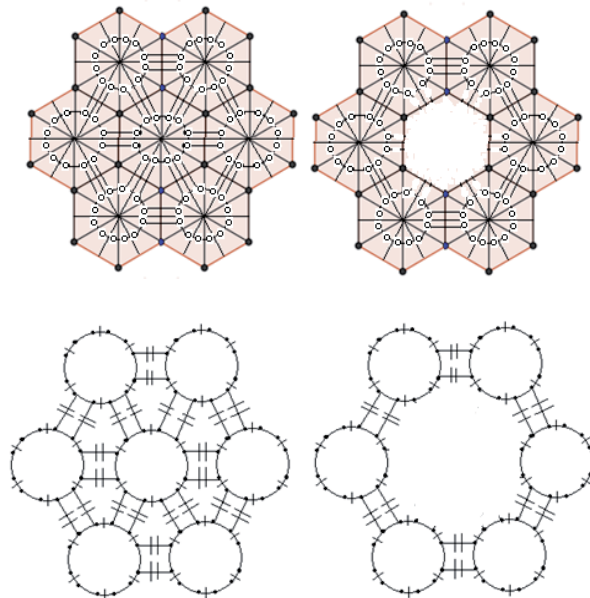


Figure 4: Flag graphs of a benzenoid and a coronoid with the same graph and boundary cycle.

Flag graphs can be used to obtain the symmetry information for the benzenoid as follows. The group A of edge-color preserving automorphisms of $F(G)$ acts regularly on G in the sense that for each pair of vertices u, v of $F(G)$ there is at most one automorphism mapping u to v . This fact has interesting consequences. Namely, each orbit of A has the same size in $F(G)$, both in edges and vertices. In particular, each orbit has $|A|$ elements. This implies that the order of the group A divides n , the number of vertices of $F(G)$. The quotient graph $F(G)/A$ is denoted by $T(G)$ and is the *symmetry-type graph* of G . The projection that maps each vertex or edge to the corresponding orbit is a regular covering projection (see [27]). The symmetry-type graph may have semi-edges that result from mirror symmetries. For example, the symmetry-type graph of benzene (Figure 5) consists of a single vertex with two semi-edges, one labelled 0 and the other labelled 1.

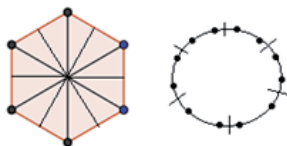


Figure 5: Flag graph $F(G)$ (right) and symmetry-type graph $T(G)$ (left) for the molecular graph G corresponding to the benzene molecule.

The symmetry type graph can be obtained from the flag graph in a purely combinatorial way. Namely, each automorphism preserves edge-colors. Hence, for each pair of vertices of the flag graph there exists at most one automorphism mapping one to another. On the other hand, the symmetry type graph is *connected*. Thus, vertices of the symmetry type graph are found by breath-first search: they are those vertices close to a root vertex of the flag graph that are not in the same orbit as the root. For benzenoids, this mechanical procedure is often replaced by simple observation of geometric symmetries and hand calculation of the quotient graph.

For instance, the flag-graph F of naphthalene has 24 flags (Figure 6). Subgraphs $F_{0,1}$, $F_{1,2}$ and $F_{0,2}$ recover the numbers of faces, edges and vertices, respectively. As the flag graph has 4 automorphisms, its symmetry-type graph T has six vertices. Since the 0-1 subgraph $T_{0,1}$ is connected, naphthalene is face-transitive, and as the 0-2 subgraph $T_{0,2}$ has four components, naphthalene has 4 edge-orbits. Finally, since the 1-2 subgraph $T_{1,2}$ has three components, naphthalene has three vertex-orbits. A similar analysis could be carried out for any of the benzenoids or coronoids.

1.4 A Boundary Edges Code for benzenoid systems

A simple code for describing a benzenoid \mathfrak{B} by its shape has been used in several places in the literature. After Hansen and coworkers [20,22], we call it the Boundary Edges Code (BEC), but for benzenoids it is identical to perimeter code $PC-2$ of Herndon and Bruce [23] (see also Balaban [2]). The idea is to count the consecutive edges of \mathfrak{B} in the boundary cycle belonging to consecutive hexagons. We start with any hexagon at the boundary of \mathfrak{B} and travel around the boundary clockwise, i.e., such that we always have the interior of \mathfrak{B} on our right.

Definition 1. *Boundary Edges Code:* Let $e(\mathfrak{B}) = (k_1, k_2, \dots, k_r)$ be a cyclical sequence of numbers 1, 2, 3, 4, 5, 6 counting the numbers of the consecutive boundary edges of a given

benzenoid \mathfrak{B} belonging to the same hexagon, travelling clockwise along the boundary. Shift of a cyclic sequence does not change it: $e^+(\mathfrak{B}) = (k_2, \dots, k_r, k_1) = e(\mathfrak{B})$, and the reversed sequence $e^{-1}(\mathfrak{B}) = (k_r, \dots, k_2, k_1)$ are considered to be the same cyclic sequence, describing the same benzenoid system (reflected in the plane of the hexagonal net – see Definition D of Gutman and Cyvin [21]).

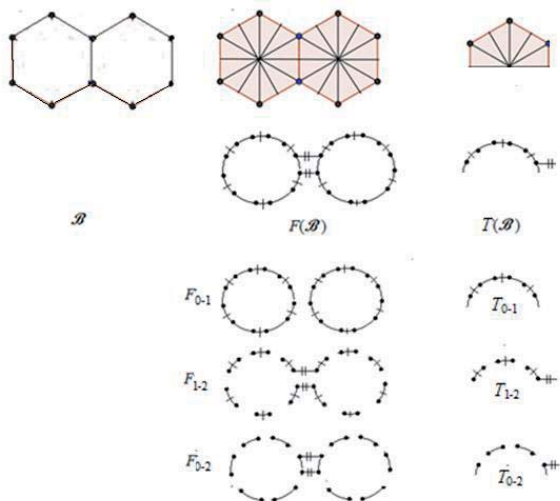


Figure 6: Molecular graph \mathfrak{B} = naphthalene, flag graph $F(\mathfrak{B})$, symmetry-type graph $T(\mathfrak{B})$, spanning subgraphs F_{0-1} , F_{1-2} , F_{0-2} of the flag graph, and connected components of spanning subgraphs T_{0-1} , T_{1-2} , T_{0-2} , corresponding to orbits of faces, vertices and edges of \mathfrak{B} .

In the present work, benzenoids are drawn in a standard orientation, such that every hexagon has two vertical edges. If the initial hexagon of the boundary edge code is chosen as the leftmost element in the bottom row of a *standard drawing* of a benzenoid, we call the code a *standard code*. The choice of a standard code is useful, since it is uniquely determined by the drawing and it is not hard to check that there are at most 12 standard boundary-edges codes. In fact, a benzenoid with s symmetries (i.e., with automorphism group of order s) has exactly $12/s$ standard codes, i.e., $12/s$ different initial positions in the hexagonal net.

2 Classification of symmetry-types of benzenoid systems

The starting point for the study of symmetry-types of benzenoid systems is the well known classification of benzenoid systems into eight possible point symmetry groups D_{6h} , C_{6h} , D_{3h} , C_{3h} , D_{2h} , C_{2h} , C_{2v} and C_s (e.g. [21], p.31). The same groups apply to coronoids.

Automorphism group	D_6	C_6	D_3	C_3	D_2	C_2	C_s	C_1
Order	12	6	6	3	4	2	2	1
Point group	D_{6h}	C_{6h}	D_{3h}	C_{3h}	D_{2h}	C_{2h}	C_{2v}	C_s
Order	24	12	12	6	8	4	4	2

Allowing for the different settings of the point groups, there is a further subdivision into 14 symmetry types of benzenoid system (Figure 7, and Tables 1 and 2 in the next section). We can give an alternative description in terms of the corresponding 14 *symmetry schemes* of the hexagonal net, as shown in Figure 8 (see [28], Theorem 6.1). To derive this, we introduce the *symmetry scheme*, a concept having its origin in the theory of covering graphs and quotient spaces; the idea of the fundamental domain is taken from Coxeter and Moser ([10], p.37).

Definition 3. Let σ be a plane in which all benzenoid systems are embedded. The *fundamental domain* $FD(G) = \sigma / G$ of a given planar group G with respect to the hexagonal net H is a part of the plane, subdivided by this net, whose ‘copies’ obtained by the action of the group G cover the whole plane. The *symmetry scheme* of the given (planar) group G with respect to the hexagonal net H is the fundamental domain of this group together with marked positions of the reflection axes and the pole and the angle of the corresponding rotation. The corresponding *quotient net* is denoted H/G .

Theorem 1. *There are 14 different symmetry schemes of a planar hexagonal net and hence of benzenoid and coronoid systems embedded into this net.*

Proof. This follows immediately from the classification made by Gutman and Cyvin; the hierarchical arrangement of symmetry schemes (our Figures 7 and 8) unifies separate tables of Pisanski and Balaban (Figures 8, 9, and 10 in [28]) which show the same hierarchical description in terms of subgroups of automorphism groups D_6 , D_3 and D_2 .

Of the four definitions given in [21], Definition C characterises a benzenoid by its boundary cycle on the hexagonal lattice. This definition can now be used with our 14 fundamental domains to obtain benzenoids with prescribed symmetry:

Theorem 2. *Using the 14 symmetry schemes (Theorem 1) we obtain a benzenoid system with prescribed symmetry group simply by choosing some cycle (sequence of edges) containing the centre of the quotient net) in the symmetry scheme. Any such cycle describes the boundary of a benzenoid system.*

Proof. Let H denote the original planar hexagonal net. The fundamental schemes having rotation symmetries in the centre of a hexagon can be represented on a conic surface (obtained by identifying two boundary half-lines of the fundamental domain) and then projected back onto the whole plane again; thus we get a ‘rotational quotient’ net on the plane with respect to a given rotational group G , and any cycle in this quotient net, denoted H/G , defines a ‘quotient molecule’ \mathfrak{B}/G . This quotient molecule has, in addition to the hexagons, one face with $6/r$ edges, where $r = 1, 2, 3, 6$. Vertices, edges and faces of the quotient molecule correspond with one exception to rotational orbits of vertices, edges and faces of \mathfrak{B} . The exception is the ‘degenerate’ central face $6/r$, representing the quotient of the original central hexagon, which is not a hexagonal face and does not correspond to any rotational orbit of faces of the original central hexagon.

If reflection symmetries are present, then any quotient molecule is defined by a path (ending at a reflection line). In the example shown below in Figure 9, there is a branching point (corresponding to a pole of the rotation) in the centre of the hexagon. In the two cases $D_{3h}(ii)$ and $C_{3h}(ii)$ there is a vertex at the centre of rotational symmetry, and there is a branching point at this vertex. In the two cases, $D_{2h}(ii)$ and $C_{2h}(ii)$, there is an edge centre at the centre of the rotation at an edge centre, and a branching point at this edge centre.

To obtain \mathfrak{B} from \mathfrak{B}/G it suffices to reverse the process: H is the covering space of H/G with respect to the group G and any cycle of edges in H/G containing the branching point lifts to a cycle in H . (For the theory of covering spaces, see Gross and Tucker [18].) This cycle is the boundary of \mathfrak{B} and uniquely determines \mathfrak{B} . If the cycle in H/G does not contain the branching point in its boundary, its ‘lift’ contains r congruent cycles.

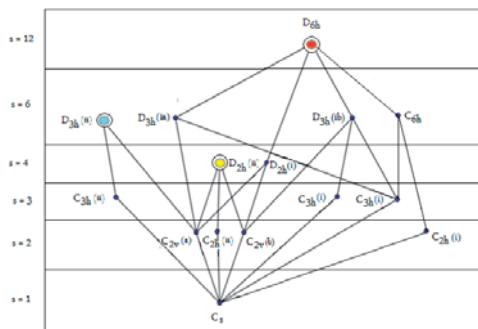


Figure 7. Subgroup relations amongst the point groups and settings for benzenoid systems. The order of the point group is denoted by s . The large circles indicate the three symmetry schemes that are not obtained by descent from any other.

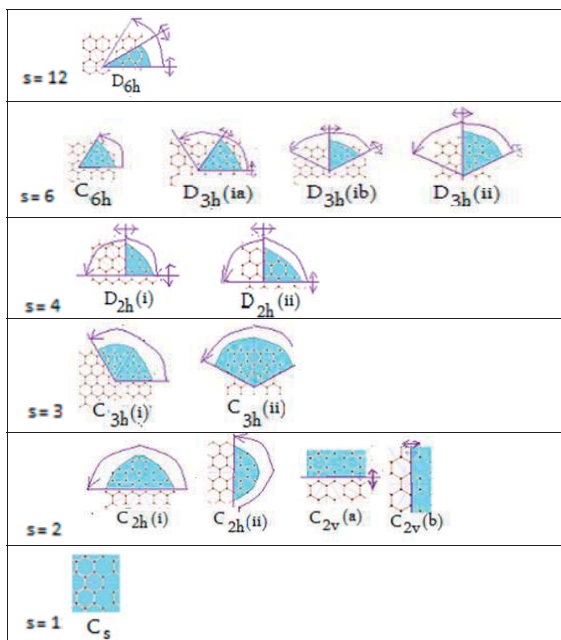


Figure 8. The 14 symmetry schemes of the hexagonal net, corresponding to the subgroups and settings shown in Figure 7. Face-, edge- and vertex-centred point groups are subgroups of D_{6h} , $D_{2h}(ii)$ and $D_{3h}(ii)$, respectively. The 14 symmetry schemes of the hexagonal net are graphical representations (with the indicated generators and centres of rotation) of the 14 point groups and settings of benzenoid systems.

An example of the relationship between symmetry scheme and quotient is shown in Figure 9. Note that there is a branching point (corresponding to a pole of the C_2 rotation) in the centre of the central hexagon. The central hexagon is thereby reduced to a triangle in the quotient.

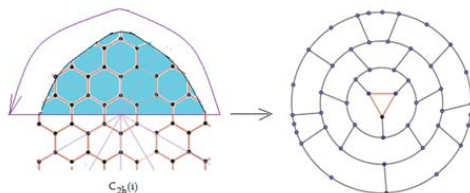






Figure 9: The symmetry scheme and corresponding quotient net H/G for group $G = C_{2h}(i)$.

2.1 The smallest benzenoids with a given symmetry scheme

The smallest benzenoid systems (by hexagon count) for each symmetry scheme are given in Table 1. These examples give a good ‘visualisation’ of the groups. Each is shown in its *canonical position*, corresponding to the *canonical code* (see Appendix for definitions.).

Table 1: Boundary-edges codes of smallest benzenoids in the 14 symmetry schemes

Symmetry scheme	Smallest benzenoid	Formula	BEC
1: D_{6h}		C_6H_6	(6)
2: C_{6h}		$C_{72}H_{36}$	$(51113)^6$
3: $D_{3h}(ia)$		$C_{18}H_{12}$	$(51)^3$
4: $D_{3h}(ib)$		$C_{33}H_{15}$	$(422)^3$
5: $D_{3h}(ii)$		$C_{13}H_9$	$(4)^3$
6: $C_{3h}(i)$		$C_{30}H_{18}$	$(5113)^3$
7: $C_{3h}(ii)$		$C_{25}H_{15}$	$(512)^3$
8: $D_{2h}(i)$		$C_{20}H_{12}$	$(414)^2$
9: $D_{2h}(ii)$		$C_{10}H_8$	$(5)^2$
10: $C_{2h}(i)$		$C_{22}H_{14}$	$(5123)^2$

11: $C_{2h}(ii)$		$C_{18}H_{12}$	$(513)^2$
12: $C_{2v}(a)$		$C_{14}H_{10}$	(3515)
13: $C_{2v}(b)$		$C_{18}H_{12}$	(351153)
14: C_s		$C_{18}H_{12}$	(325215)

Hansen *et al.* [22] give details of how the BEC can be used to detect symmetry elements in both simply and multiply connected benzenoids. In the case of benzenoids, the whole group can be reconstructed, as follows.

Theorem 3. *Let $c(\mathfrak{B}) = (k_1, k_2, \dots, k_r)$ be a cyclic sequence of numbers 1, 2, 3, 4, 5, 6 counting the numbers of the consecutive boundary edges in a given benzenoid \mathfrak{B} belonging to the same hexagon. Then \mathfrak{B} is uniquely defined by $c(\mathfrak{B})$ and the symmetry group of $G(\mathfrak{B})$ is also uniquely determined by symmetries of $c(\mathfrak{B})$.*

Proof. For the smallest benzenoid \mathfrak{B}_1 , consisting of just one hexagon, and $c(\mathfrak{B}_1) = (6)$. Now we proceed by induction. By definition B ([21], 11-12) any benzenoid system \mathfrak{B}_{h+1} with $h+1$ hexagons can be obtained by adding just one hexagon \mathfrak{B}_1 to some benzenoid system \mathfrak{B}_h with h hexagons. After choosing the common edges of \mathfrak{B}_1 and \mathfrak{B}_h , the boundary cycles of \mathfrak{B}_1 and \mathfrak{B}_h merge into one uniquely determined cycle.

To see that the rotational symmetry group $G_R(\mathfrak{B})$ of \mathfrak{B} is uniquely determined by $c(\mathfrak{B})$, it suffices to realize that no boundary edge is fixed by a rotational symmetry. Thus, \mathfrak{B} has a rotation $2\pi/r$ if and only if $c(\mathfrak{B})$ can be written as a periodic cyclic sequence composed of r equal sub-sequences. For example, if $c(\mathfrak{B}) = (3,3,3,3,3,3) = (3^6)$, then the corresponding \mathfrak{B} (coronene) has a rotation by $2\pi/6$ and the quotient system has the boundary cycle (3). Likewise, we see that \mathfrak{B} has a reflection symmetry if and only if $c(\mathfrak{B})$ is a centrosymmetric sequence. For example (5,5) (naphthalene) must have reflection symmetry in \mathfrak{B} .

In general, from the boundary of \mathfrak{B} we can determine the symmetry scheme corresponding to \mathfrak{B} (Table 2).

Table 2: The 14 possible symmetry schemes corresponding to the 8 possible groups for benzenoids. w^R denotes the reverse of the string w .

Case	Group	Centre of rotation			Line of reflection		BEC
		vert ex	edge	face	horizontal	vertical	
1 D_{6h}	$D_{6h} = Z_2 \times D_6$	NO	NO	YES	YES	YES	$w^6, w = w^R$
2 C_{6h}	$C_{6h} = Z_2 \times C_6$	NO	NO	YES	NO	NO	$w^6, not w = w^R$
3 $D_{3h}(ia)$	$D_{3h} = Z_2 \times D_3$	NO	NO	YES	YES	NO	$w^3, w = w^R$
4 $D_{3h}(ib)$		NO	NO	YES	NO	YES	
5 $D_{3h}(ii)$		YES	NO	NO	NO	YES	
6 $C_{3h}(i)$	$C_{3h} = Z_2 \times C_3$	NO	NO	YES	YES	YES	$w^3, not w = w^R$
7 $C_{3h}(ii)$		YES	NO	NO	NO	NO	
8 $D_{2h}(i)$	$D_{2h} = Z_2 \times D_2$	NO	NO	YES	YES	YES	$w^2, w = w^R$
9 $D_{2h}(ii)$		NO	YES	NO	YES	YES	
10 $C_{2h}(i)$	$C_{2h} = Z_2 \times C_2$	NO	NO	YES	NO	NO	$w^2, not w = w^R$
11 $C_{2h}(ii)$		NO	YES	NO	NO	NO	
12 $C_{2v}(a)$	$C_{2v} = Z_2 \times D_1$	NO	NO	YES	YES	NO	ww^R
13 $C_{2v}(b)$		NO	YES	NO	NO	YES	
14 C_s	$C_s = Z_2 \times C_1$	NO	NO	NO	NO	NO	$not w = w^R$

2.2 The concept of a quotient benzenoid (or coronoid) system

The concept of *symmetry scheme* introduced above is very similar to the concept of *orbifold* (a topological space that is a quotient space of a Euclidean space under the linear action of a finite group) which appears under various names in the literature. For example, Coxeter and Moser used a similar concept that they called the *fundamental region* [10]. However, the symmetry scheme is a little more than a quotient space; essential parts of a symmetry scheme are also the positions of poles of rotation, and orders of rotation and positions of mirror planes, from which the original hexagonal net (or a benzenoid system embedded into it) can be reconstructed. A part of the hexagonal net containing exactly one representative flag of each orbit of flags of a benzenoid system \mathfrak{B} (or coronoid system \mathfrak{C}) exactly corresponds to the *symmetry-type graph* $T(\mathfrak{B})$ of \mathfrak{B} . This symmetry-type graph is really a quotient graph of the flag graph $F(G)$ under the action of the group $G(\mathfrak{B})$ of those automorphisms of hexagonal net B that preserve B (see Figure 10, lower row, left) . We

could go one step further and define also the *quotient system* $\mathfrak{B}/G(\mathfrak{B})$ whose vertices are orbits of vertices of \mathfrak{B} and whose edges are orbits of edges of \mathfrak{B} (see example in Figure 10, lower row, right). A quotient benzenoid (or coronoid) system is the ‘seed’ from which the whole molecular graph can be reproduced, if we also know the corresponding symmetry scheme.

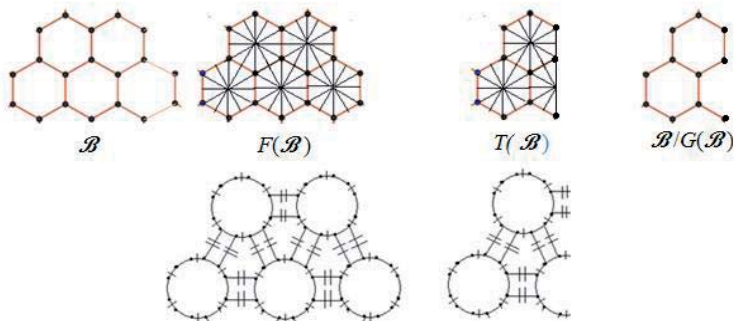


Figure 10: Example of a benzenoid system \mathfrak{B} , its flag graph $F(\mathfrak{B})$, its symmetry-type graph $T(\mathfrak{B})$ and the quotient ‘kernel’ or ‘seed’ $\mathfrak{B}/G(\mathfrak{B})$.

3 Calculation of invariants from the boundary edges code of a benzenoid

Many relations connect the counts for structural components of benzenoids. (See [21].) The counts can be determined by manipulation of the boundary edges code $c(\mathfrak{B}) = (k_1, \dots, k_r)$ of a benzenoid system \mathfrak{B} , as now briefly discussed. Trivially, we can obtain the number of boundary edges, e_b , from

$$e_b = k_1 + \dots + k_r$$

and the number of boundary vertices as $v_b = e_b$. Boundary edges have 2 incident flags, whereas inner edges have 4. The number of boundary vertices of degree 3 is $v_{2b} = r$. Boundary vertices have degree 2 or 3, and therefore

$$v_{3b} = v_b - v_{2b} = k_1 + \dots + k_r - r.$$

Inner vertices have degree 3. Therefore inner vertices have 6 incident flags, boundary vertices of degree 3 have 4, and boundary vertices of degree 2 have 2.

The motivation for finding the number of hexagons is that if we know $h(\mathfrak{B})$, then we can distinguish between benzenoids with various kinds of rotational symmetry, for example, if the centre of 3-fold rotation is at a vertex, then $h(\mathfrak{B}) \equiv 0 \pmod{3}$; if the centre of 3-fold rotation is in the face, then $h(\mathfrak{B}) \equiv 1 \pmod{3}$.

In the past several algorithms have been used to obtain the hexagon count. We propose one based on the recursive formulation:

$$h(\mathfrak{B}) = h(\mathfrak{B}') + 1,$$

where \mathfrak{B}' is a benzenoid system obtained from \mathfrak{B} by taking one hexagon away. To obtain $h(\mathfrak{B})$ it suffices to be able to obtain the boundary code $c(\mathfrak{B}) = c(\mathfrak{B}')$. The idea for this is as follows. First, the procedure is initialised with

$$h(6) = 1 \text{ and } h(55) = 2$$

and repeated use is made of

$$h(\dots, a, 5, b, \dots) = h(\dots, a+1+b, \dots) + 1 \text{ and } h(\dots, a, 4, b, \dots) = h(\dots, a+1, b+1, \dots) + 1$$

(by which we can consecutively eliminate numbers 5 and then 4 from the code). We assume $a < 5$ and $b < 5$. Then, with one proviso, we can use

$$h(\dots, a, 3, b, \dots) = h(\dots, a+1, 1, b+1, \dots) + 1$$

for consecutive elimination of numbers 3 in the boundary code. The snag is that care must be taken at this stage to avoid attempting to remove a bridging hexagon, which would invalidate this last reduction formula (see Figure 11). Although the details of how to select a non-problematic hexagon with entry 3 in the code become somewhat complicated (and will be given elsewhere [Kovič and Pisanski [29)]), it is always possible to make a suitable choice, since:

Lemma 1. If a benzenoid \mathfrak{B} has only numbers 3, 2, 1 in the boundary edges code $c(\mathfrak{B})$, then there is at least one hexagon H corresponding to number 3, such that $\mathfrak{B}' - H$ is still a connected region (and a benzenoid).

Proof. If all the hexagons 3 are ‘bridges’, then we have a contradiction. We simply use the induction argument: after removing the bridge we obtain at least two non-problematic

boundary hexagons with number 3 in the boundary code, even if we do not make the assumption that there are only entries 3, 2, 1 in $c(\mathfrak{B})$.

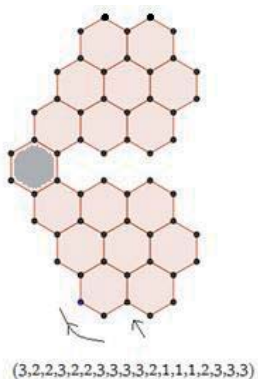


Figure 11: A benzenoid that includes a bridging hexagon with entries 3 and 1 in the code.

Once we have $h = h(\mathfrak{B})$, we can deduce the remaining invariants by counting up the flags present in the benzenoid in two ways

$$2e_b + 4e_i = 12h = 2v_{2b} + 4v_{3b} + 6v_i$$

$$v_{2b} + 3v_{3b} + 3v_i = 2e = 2e_b + 2e_i$$

and invoking Euler's formula for benzenoids.

$$(v_{2b} + v_{3b} + v_i) - (e_b + e_i) + h = 1.$$

from which

$$e_i = 3h - e_b/2, \quad v_i = 2h - v_{2b}/3 + 2v_{3b}/3, \text{ and } e = e_i + e_b.$$

4 Conclusions

We have introduced some techniques which may be useful in studying the structure and symmetry properties of benzenoid and coronoid systems. We have described the symmetries of benzenoid systems in terms of their symmetry schemes and described their shapes with the established boundary edges code, which consists of cyclic sequences of numbers 1, 2, 3, 4, 5, 6. From these sequences, the symmetries of the system and its quotient may be easily deduced.

We have concentrated in this paper on the simple boundary-edges code (BEC), but we note that other definitions of a canonical code are often used. Often, instead of standard

codes, all codes describing a given benzenoid are generated, and the lexicographical minimum or maximum (depending on the authors) is selected. Many codes have been studied and several have been used for enumeration of benzenoids (e.g., [1,9,14,17,21,22,25]). Even our canonical code may correspond to more than one embedding of the figure in the planar hexagonal net (if we draw benzenoids on the hexagonal lattice in the convention that every hexagon has two vertical edges). Figure 12 presents examples.

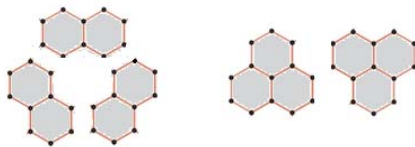


Figure12: Three embeddings of the benzenoid (5,5) and two of the benzenoid (4,4,4).

In fact, it is easy to show that:

Theorem 4. *The number $emb(\mathcal{B})$ of different embeddings of a planar benzenoid \mathcal{B} into a hexagonal net is $emb(\mathcal{B}) = 12/s$, where s is the number of automorphisms of the benzenoid.*

In connection with the extension of BEC codes to non-planar analogues of the benzenoids, we just mention that there exist non-isomorphic (non-planar) benzenoids with the same boundary (See [9], p. 28, and the detailed study by Graver [17]).

Finally, we note that the two faces of a planar benzenoid are physically distinct in complexes where one face coordinates to a metal atom. The benzenoid then ‘lives’ in 3D, with implications for point group symmetry. Stereoisomerism can involve enantiomers or diastereomers, and is relevant beyond benzenoids: in photosynthetic light-harvesting systems, chlorophyllous pigments have diastereotopic faces, as the central magnesium is coordinated by the protein matrix (usually a His residue) preferentially from one side [31]. Extensions of flag-graph techniques may be able to include these extra features.

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Appendix: Canonical boundary edges code

Definition 1 is useful when we want to deduce symmetries of \mathfrak{B} (as in the proof of Theorem 1). However, for enumeration purposes it is desirable to have a unique, canonical code. One such code can be defined as follows:

Definition 2. The canonical boundary-edges code $c(\mathfrak{B}) = (k_1, k_2, \dots, k_r)$ is lexicographically smallest among all standard codes for a benzenoid system \mathfrak{B} .

To the twelve different positions of \mathfrak{B} in a hexagonal net correspond an equal number of boundary codes $e(\mathfrak{B})$, all candidates for the canonical code. Figure A1 shows them for an example, which also illustrates the various possible topographical features that can arise in a benzenoid. Gutman and Cyvin ([21], p.21), define typical shapes, i.e., *fissures*, *bays*, *caves* and *fjords* on the boundary of a benzenoid system. With the boundary-edges code we can easily recognize such structures as: fjord $\leftrightarrow (\dots a, 1, 1, b, \dots)$, cave $\leftrightarrow (\dots, a, 1, 1, b, \dots)$, bay $\leftrightarrow (\dots, a, 1, b, \dots)$, fissure $\leftrightarrow (\dots a, b, \dots)$ where a, b both differ from 1.

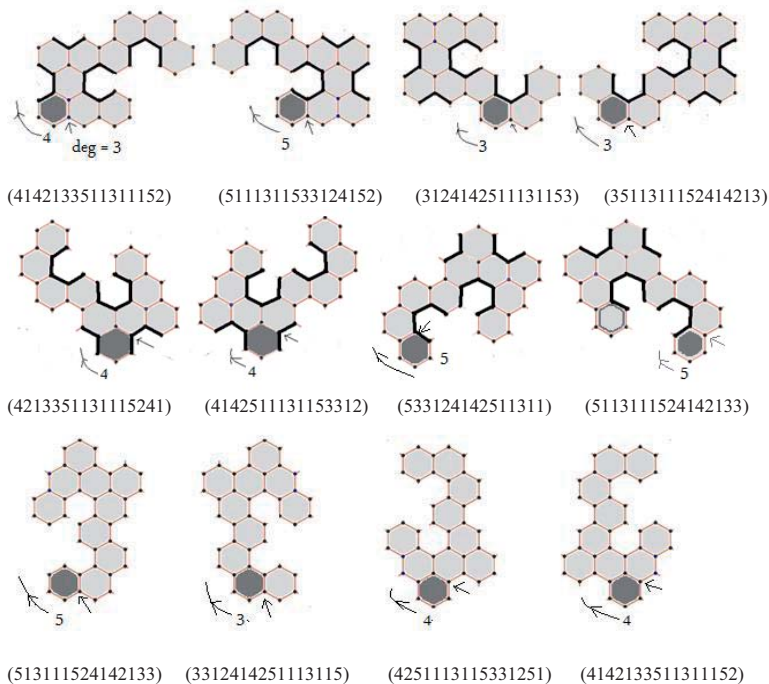


Figure A1: The canonical code for a benzenoid. In this example, the lexicographically smallest boundary-edge sequence is $c(\mathfrak{B}) = (3124142511131153)$.

Examples of benzenoids \mathfrak{B} for which the canonical code of Hansen, Lebatteux and Zheng [22] is different from all of our standard codes are shown in Figure A2: all twelve start with the gray hexagon, which cannot be in the bottom row of hexagons, no matter how the molecule is embedded into the hexagonal net.

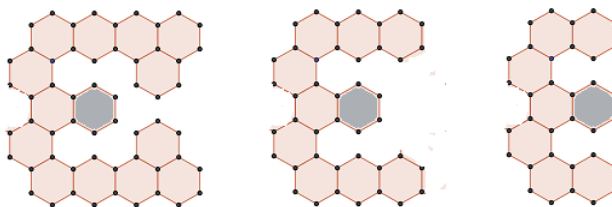


Figure A2: Three examples where the canonical code of Hansen, Lebatteux and Zheng [22] is different from all twelve of our standard codes.