Staggered benzenoid pairs as potential spin coupling systems

D. Babic[1], D. J. Klein[2] and D. M. Smith[1]

[1] Institute "Ruđer Bošković", Bijenička 54, HR-10002 Zagreb, Croatia (dbabic@irb.hr, dsmith@irb.hr)

[2] Texas A&M University at Galveston, Galveston, TX 77553-1675, USA (kleind@tamug.edu)

Abstract

Staggered benzenoids are a novel class of benzenoid systems with a potential to manifest intermolecular spin coupling, as in the prototypical case of the phenalenyl radicals. To define this new class, benzenoids are represented by pi-network graphs, with vertices coloured or uncoloured such that each edge is between a coloured and an uncoloured vertex. Two benzenoids, **B** & **B'**, not necessarily different, are said to be *staggered* if they satisfy three conditions. By the first condition, their geometries, represented as fragments of the hexagonal lattice, should be superimposable so that the coloured vertices of B each perfectly overlaps an uncoloured vertex of **B'**. By the second condition the uncoloured vertices of B must be at staggered positions, avoiding overlap to vertices of **B'**. By the third condition, two overlapping vertices have a common neighbour either in both graphs or in none.

We present an overview of this class of staggered benzenoids in terms of their trigonal graph representation, regarding specific structural features and nullities of the Hückel π-molecular spectra. Possible applications are briefly discussed and phenalenyl tilings are pointed out as the particularly interesting subclass.

Keywords: phenalenyl radical, staggered benzenoids, spin coupling, antiferromagnetically coupled dimer

1. Introduction

It has been found [1] that the phenalenyl radical (precisely, its *t*-butyl derivative) in the crystal structure forms dimers with an antiferromagnetically signed coupling (Figure 1). The dimerization occurs also in solution at room temperature [2], thus pointing to a relatively strong interaction between monomers. Quantum-chemical calculations indicate [3] that the antiferromagnetic interaction arises from an overlap of the semioccupied π-molecular orbitals (SOMOs) of the two dimerized radicals. This feature has been recognized as the decisive factor for packing of planar radicals in the solid state and possibly for the very existence of spin coupling, and formulated as the *maximin principle* [4]. According to this principle, the packing geometry is determined by the maximum overlap of atoms participating in the radical SOMO and simultaneous maximum avoidance of all other atoms. The geometry of the phenalenyl dimer provides an illustrative example of this principle – the two radical monomers are superimposed so that the central atom and its next-nearest neighbours in one monomer perfectly overlap with the same kind of atoms in the second monomer (Fig. 1), while all other atoms avoid each other as much as the molecular structures allow. From (a slightly extended) Hückel molecular orbital (HMO) theory it can be easily derived that only the overlapping atoms have nonzero contributions in the SOMO, and this is to a large extent confirmed by the *ab initio* calculations of electronic structure.
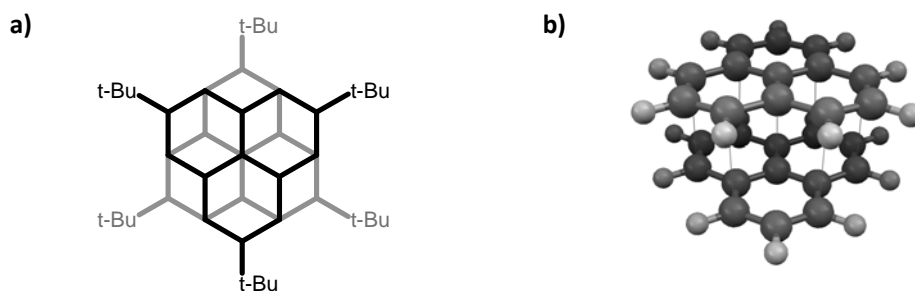

Figure 1. Phenalenyl dimer: a) orthogonal view at the overlapping molecules of the t-Bu derivative; the bottom molecule is in grey, b) perspective view of the plain phenalenyl dimer; the overlapping atoms are connected by thin lines.

Naturally, one is prompted to look for other molecules that could exhibit a similar manner of spin couplings. Open shell graphene fragments related to phenalenyl radicals are recognized as a rich source of potential quantum electronic devices [5]. Note that in the phenalenyl example, the molecular features required for the spin coupling are: (i) a molecular structure which conforms to the maximin principle; and (ii) planar molecular geometry, needed for close approach of one molecule to another. Here we outline a novel class of molecules, termed *staggered benzenoids*, in

which these two conditions are ideally fulfilled for many of its members. We examine their distinct characteristics to provide a basis for the systematic generation and classification. Finally, interesting possibilities for their utilization are pointed out and the smallest members of the class are listed in the Appendix.

2. Definition and representation of staggered benzenoids

We use graph-theoretical terms [6] as the most appropriate for describing the relevant structural relations, with electronic structure aspects referenced to the HMO model [7]. A benzenoid molecule is represented by subgraph **G** from the honeycomb lattice with (conjugated) C atoms corresponding to vertices such that **G** consists of whole hexagons. The vertices are connected by edges whenever they represent σ-bonded atoms. The graph is to be embedded in Euclidean space, with the geometric arrangement taken to correspond to the arrangement in a perfect honeycomb lattice (as a first good approximation). Graph relations to be considered are easily visualized and understood in this way. We limit our consideration to pure benzenoid graphs – those without any terminal vertices, bridges, or holes other than hexagonal rings.

Evidently, each member of a simple neutral spin-coupled pair should ideally have an odd number of electrons. In neutral hydrocarbons, the parity of the number of electrons is equal to the parity of the number H of hydrogens since each carbon atom contributes an even number of electrons. That is, one sees that the number of σ-bonds between C conjugated carbon centers is $(3C\text{-}H)/2$, whence since the quotient must be equal to an integer, the number of hydrogens and the number of π-centers have equal parities. Then such a neutral benzenoid has an odd number of π-electrons and should be a radical (even somewhat beyond the context of the HMO model). In odd-sized benzenoid graphs a single semioccupied π-orbital has zero coefficients on the „minority" centers, which are simply determined by the structure [8], thus providing a direct relation with the maximin principle. (The last statement has some exceptions pointed out in Section 5). Yet, our consideration is not immediately limited to the odd-sized benzenoids because, e.g., diradicals could be also considered as potential spin-coupled systems or radicals produced by charging the even electronic system.

In working toward our notion of *staggered benzenoid graphs*, recall that benzenoids are *bipartite* graphs (also called *alternant*), which means that the vertices can be divided in two subsets so that no two adjacent vertices are in the same subset. The vertices in one such subset are here designated as *coloured* while the others are chosen as *uncoloured*. A pair of such benzenoid graphs, **B** & **B'**, is

termed a *staggered benzenoid* if they satisfy three structural conditions. First, they allow a superposition such that there is a 1-to-1 overlap between the coloured vertices of **B** and the uncoloured vertices of **B'**. Second, the uncoloured vertices of **B** avoid overlap with any vertex of **B'**, and the coloured vertices of B' avoid overlap with vertices of B. In slightly different words (for these first two conditions), each coloured vertex of **B** associates with an uncoloured vertex of **B'**, while every uncoloured vertex of **B** avoids association with any vertices of **B'**. An example is provided by both **B** and **B'** being phenalenyl radicals, with the central vertex of the first (**B**) being coloured (& the other vertices labeled consistently), and the opposite for the second phenalenyl (**B'**). More examples are given in Figure 2. Note that two staggered benzenoid graphs can be equal.
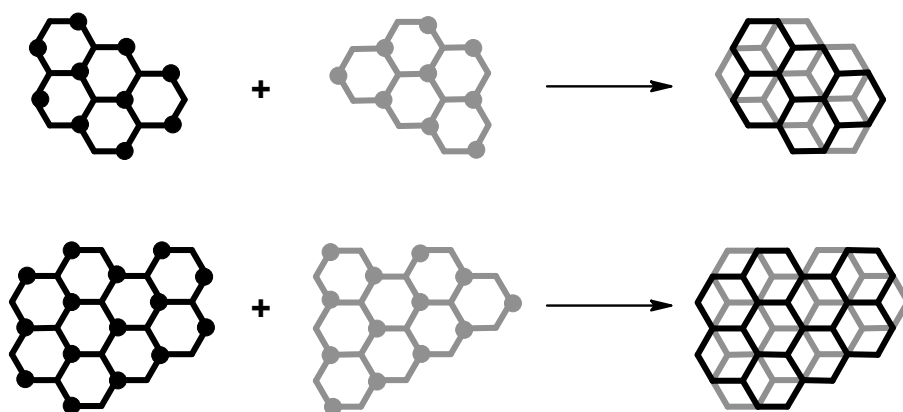

Figure 2. Two examples of staggered benzenoid pairs. The benzenoids in the pair are drawn separately on the left side, with the coloured vertices outlined in bold, and the overlapped arrangement is on the right side. The pair in the top row has equal members.

The first condition is related to the maximin principle by the fact that in bipartite graphs the SOMO has zero coefficients either on the coloured or the uncoloured vertices [8]. The maximin principle is fulfilled when the zero coefficients are on the non-overlapping vertices of the both members in the staggered pair. However, it remains to examine whether this happens with staggered benzenoids and when. As will be shown shortly, staggered benzenoids include also polyradicals or those which are not radicals at all in the neutral state. They still deserve consideration since in a charged state they could act as radicals.

Our third condition relates to planarity of the two benzenoid molecules. Whenever two coloured vertices of **B** (overlapping with vertices of **B'**) have a common neighbour, we require that the two associated vertices of **B'** also have a common neighbour. Namely, in a benzenoid **B** with bond lengths a, two vertices connected to the same vertex are at a distance $a\sqrt{3}$. If atoms at this

distance (of $a\sqrt{3}$) in an embedded benzenoid graph do not have a common neighbour, they must be on the perimeter, carrying H atoms which strongly sterically hinder and induce deviation from planarity, as illustrated in Figure 3. It should be noted that the third condition is only necessary but not sufficient for planarity as shown later in Section 4.
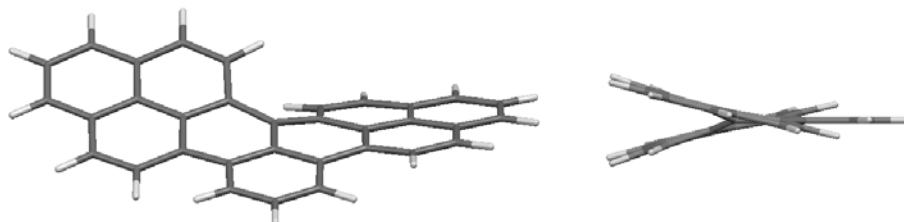

Figure 3. Optimized geometry (UB3LYP/6-31G(d,p)) of the benzenoid molecule with the *cove* on the perimeter. On the right is sideview showing the extent of an out of plane deformation.

The overlapping of two molecules of a dimer is dependent on their real geometries. As a first approximation we assume that the carbon skeleton geometries perfectly fit into the graphene lattice so that the atoms corresponding to the coloured vertices of **B** perfectly overlap the uncoloured ones of **B'**. Although the real molecules may deviate from this assumption, it is not significant for our present analysis.

Our three conditions define the staggered benzenoids, being introduced primarily as a reference class that can be specified in simple terms. Many but not all of its members are suitable for intermolecular spin coupling. Among the benzenoid molecules which are not included because they do not satisfy the three conditions completely – for example, with defective vertices that miss the overlapping partner – might be capable for spin coupling, and be interesting research subjects. Yet, based on the discussion in Section 6, it is reasonably expected that the staggered benzenoids include the most prominent candidates. To get a little ahead of our discussion: the first condition guarantees the overall alternancy of the pair **B** & **B'** including the intermolecular interactions from coloured vertices of **B** to uncoloured ones of **B'**, and the second condition, having to do with the nonalignment of the uncoloured vertices of **B** with coloured ones of **B'**, avoids 4-membered rings induced between the two molecules. The third condition helps provide a simple assurance of the matching of the numbers of starred & unstarred sites for the overall pair, with the consequent indication of a singlet ground state for the pair.

One may wonder if the staggering superposition of two given benzenoids **B** & **B'** can be realized in more than one way – by overlapping different subsets of vertices. It is shown later (in Section 5) that

this is not possible, so long as we use a maximal overlapping encompassing all the coloured vertices of **B** & all the uncoloured ones of **B'**, whence the staggering relation between two benzenoids is unique. Then, the overlapping vertices can be used for the single graph representation of both members in the staggered pair, as we next explain.
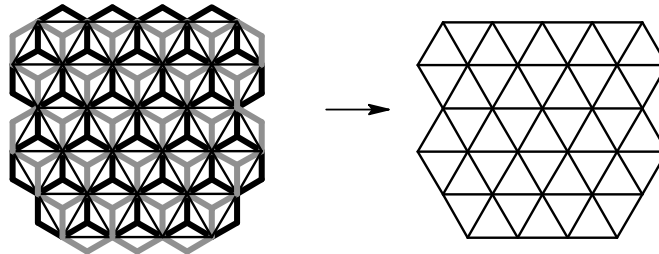

Figure 4. Trigonal representation (on the right) obtained from the overlapping vertices of the two staggered hexagonal lattices (in bold black and grey).

3. Concise „trigonal" representation of staggered benzenoids

Our condensed trigonal representation is produced in three steps. First the two constituent benzenoids **B** & **B'** are superposed so that the overlapping vertices become single new vertices. Second, whenever such condensed new vertices have a common neighbour in either **B** or **B'** they are connected by a new edge. Third, all the avoiding vertices and their incident edges are deleted. The resulting graph is a *trigonal* representation as it consists of fused triangles and is embeddable in the trigonal lattice. See, e.g., Figure 4.

In order to recover a staggered benzenoid pair from its trigonal representation, the triangles are divided in two disjoint groups, such that no edge is shared by the triangles in the same group (similar to the labelling of vertices in bipartite graphs). A simple way to do this is to divide the triangles according to whether they point upwards or downwards (assuming that the triangle graph is oriented with one set of parallel edges lying horizontally). In the example on the left side of Figure 5,
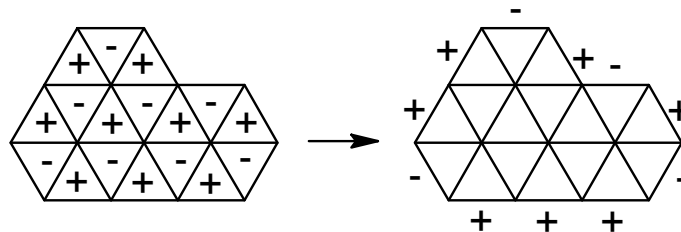

Figure 5. On the left side: a trigonal graph with upward and downward pointing triangles denoted by (+) and (−) signs, respectively. On the right side: the edges of the perimeter are signed by the signs of the nearby triangles.

one group is denoted by (+) and the other by (–) signs. The subsequent construction of the staggered benzenoid pair proceeds: first, by *capping* all the triangles in the (+) group while adding a bridge to the outer side of every perimeter edge belonging to a (–) triangle, thereby identifying **B**; and second, by doing the same for the (–) triangles, to identify **B'**. (*Capping* is the graph transformation in which a new vertex is inserted into a ring and connected to the ring vertices [9]). Two examples of the procedure are shown in Figure 6. The staggered benzenoid pair {**B,B'**} is uniquely determined after removing all the edges of the trigonal representation.

a)

b)

22 vertices
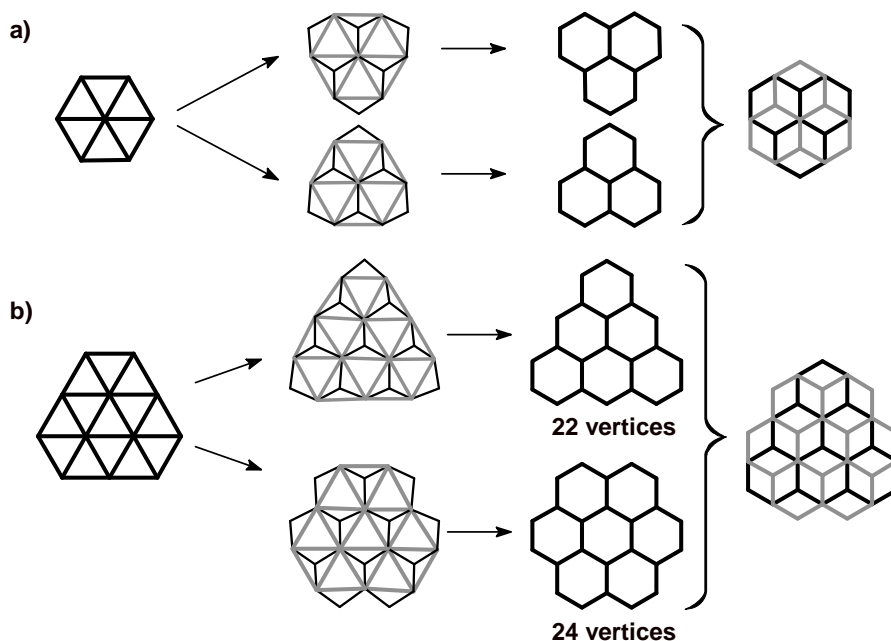
24 vertices

Figure 6. Construction of the staggered benzenoid pair from the trigonal graph. These are the smallest cases which produce a) equal benzenoids (phenalenyl dimer), b) different benzenoids (even with different numbers of vertices: 22 and 24). Their staggered superpositions are in the rightmost column.

Since the staggered benzenoid pair yields only one trigonal graph, it follows that the trigonal representation is faithful. The properties of staggered benzenoids as well as their comprehensive generation can be conveniently discussed in terms of their trigonal representations. It may be noted that a single benzenoid graph by itself, does not fully determine the staggered benzenoid pair, as demonstrated by the example in Figure 7 in which the same benzenoid graph participates in two different pairs. The overlapping vertices within the common member of these two pairs are complementary.
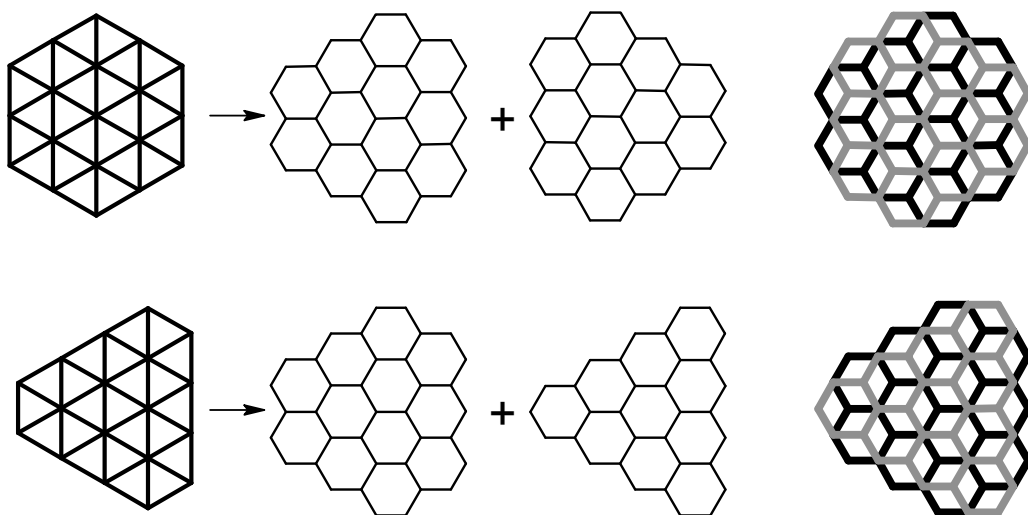
Figure 7. Two pairs of staggered benzenoids with a common member. On the left are trigonal graphs representing staggered benzenoid pairs in the middle. On the right are their superpositions. Note that the first benzenoid graph is present in both rows; in the top row it is paired with itself, and in the bottom row with a different benzenoid.

The question arises as to just which connected subgraphs of the triangular lattice may be inverted to give a staggered benzenoid. First, it is clear that the triangular-net subgraph must have every face a triangle (which is to say no holes are to be cut in the net). Next it is noted that only vertices of degrees 3, 4 or 5 might occur on the perimeter. For the case of a degree 2 vertex, Figure 8a shows that this would lead to a terminal vertex in one of the two benzenoids, whence vertices of degree 2 are not allowed (if a staggered benzenoid is to be obtained). A perimeter degree 6 is not allowed as such a vertex results either with a nonbenzenoid graph or with a pair of benzenoid graphs that violate the third condition a staggered pair has to fulfill. Note that according to the recipe for construction of the benzenoids from trigonal representation, the bridge vertices should be added beside both incident perimeter edges at the degree 6. One way to do this is by adding a separate vertex beside each edge (as everywhere else). However, the result would not be a benzenoid graph, as it would have the degree 4 on the vertex which had degree 6 in the trigonal representation (Fig 8b - upper branch). For this reason one could try to add these two vertices by merging them into a single one (Fig. 8b - lower branch). But in this case the new vertex would connect a pair of overlapping vertices (marked in Fig. 8b) which do not have a common neighbour in the staggered partner, and thus in opposition to the third condition. The perimeter should be a closed path without a crossing point, as one such case implies a bridge in the benzenoid graph, while the other cases, all shown in Fig. 8c, include sharp angle on the outer side of the perimeter - a feature shared with the degree 6 on the perimeter and for the same reason dismissed. All the above conditions are

equivalent to a demand that the perimeter be a closed (noncrossing) path on the trigonal lattice such that the incoming and outgoing edges at every vertex never belong to the same triangle of the triangular lattice. Systematic generation of staggered pairs reduces to producing all such cycles.
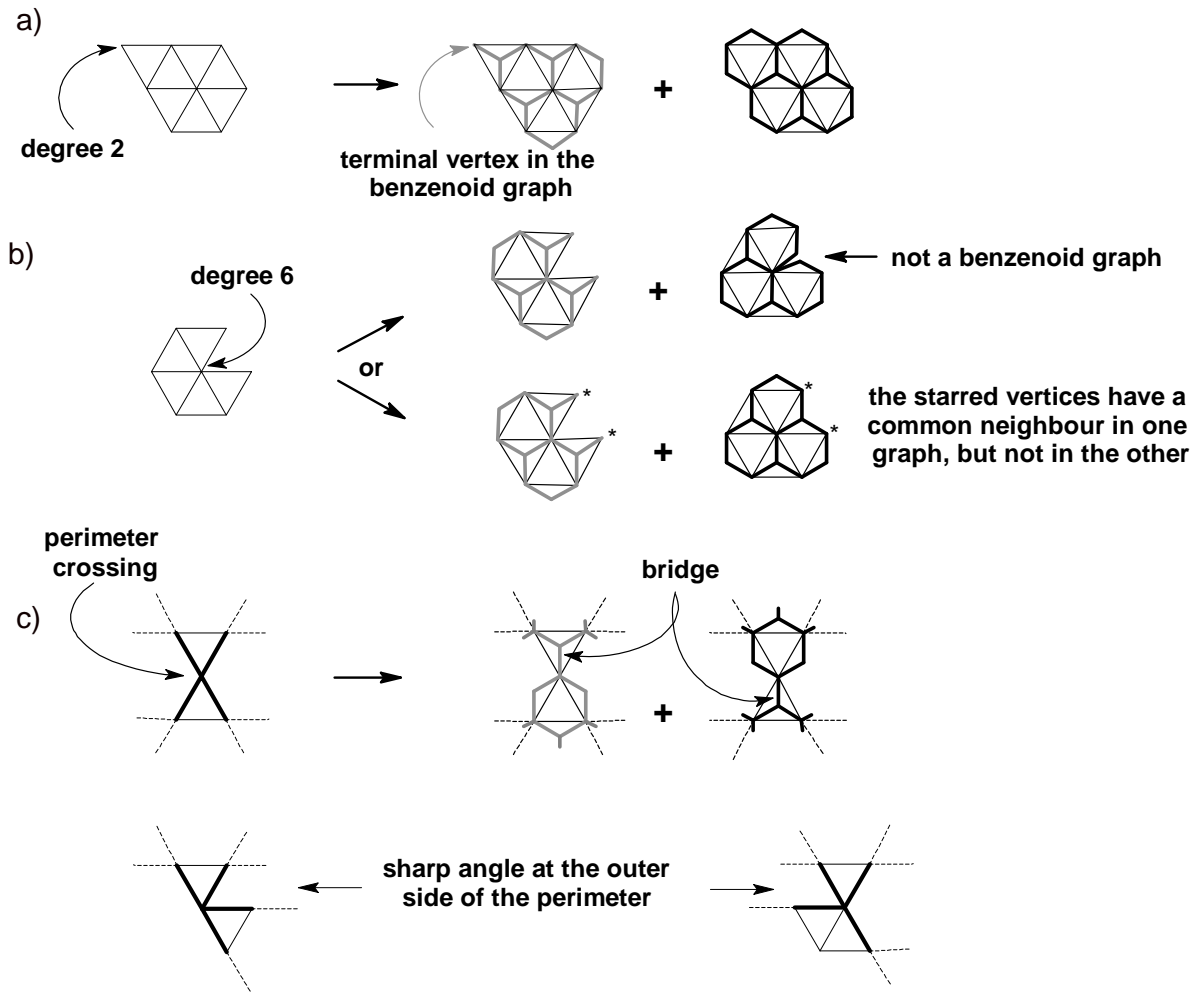

Figure 8. Forbidden details on the perimeter of the trigonal representation: a) a vertex of the degree 2 leads to a hexagonal graph with terminal vertex; b) a vertex of the degree 6 results in a nonbenzenoid graph or violates the third condition for staggering benzenoids; c) crossing of the perimeter leads to a bridge in the hexagonal graph, or involves a sharp angle with the same consequences as with the degree 6.

4. Perimeter of the trigonal representation

In this section we analyze a relation between the perimeter of the trigonal representation and the characteristics of the corresponding staggered benzenoid graphs. This is important because the generation procedure is completely reduced to consideration of a perimeter. Then it is useful to

know which properties of the represented benzenoid graphs can be deduced directly from the perimeter so that unwanted results can be avoided or removed. For example, if we are interested in neutral radicals, we may want only staggered benzenoid graphs with an odd number of vertices, and avoid those even-sized like the example in Fig. 6b.

Let n, m and t, respectively denote the numbers of vertices, edges and triangles in the trigonal graph. The triangles are divided in two disjoint groups labelled by (+) and (−) signs (as in Fig. 5, left) with t_+ and t_- denoting the numbers of triangles in these two groups, respectively. Further, let p be the number of perimeter vertices, and let p_+ and p_- be the number of perimeter edges belonging to (+) and (−) triangles, respectively. Also, let N_+ and N_- denote the numbers of vertices in the two hexagonal graphs **B** & **B'** produced after capping the (+) and (−) triangles, respectively. By the construction of the staggered benzenoid pair from the trigonal representation, it follows:

$$N_+ = n + t_+ + p_- \tag{1a}$$

$$N_- = n + t_- + p_+ \tag{1b}$$

Basic relations in a trigonal representation give:

$$m = 3t_+ + p_- = 3t_- + p_+ \tag{2}$$

By expressing p_+ and p_- from (2) and by substitution into (1a,b), one obtains:

$$N_+ = n + m - 2t_+ \tag{3a}$$

$$N_- = n + m - 2t_- \tag{3b}$$

and then by the subtraction (3a)-(3b):

$$N_+ - N_- = 2(t_- - t_+) \tag{4}$$

From (3a,b) it follows that N_+ and N_- have equal parities, determined by $(n+m)$. By using $t = t_+ + t_-$ and $p = p_+ + p_-$, it follows from (2):

$$2m = 3t + p \tag{5}$$

The Euler relation between the numbers of vertices, edges and faces in a planar graph gives:

$$t + n - m = 1 \tag{6}$$

and by summing (5) and (6) one gets:

$$n + m = 2t + p + 1 \qquad (7)$$

The above relation shows that $(n+m)$ and p have the opposite parities, and that the parity of N_+ (and N_-) is opposite to the parity of p. To obtain the staggered benzenoids with an odd number of vertices, one should generate trigonal graphs with an even perimeter length, and vice versa. The result could be expected since the construction transforms each perimeter edge of the trigonal graph into a pair of incident edges on the perimeter of the benzenoid graph, resulting with the perimeter length of the benzenoid equal to $2p$. The relation to parity of $N_{+/-}$ follows by recalling that the number of vertices enclosed by cycles of length $4k$ ($4k+2$) in the hexagonal lattice is odd (even) [10].

According to (6), t and $(n+m)$ have opposite parities. Hence, whenever N_+ and N_- are even, implying that $(n+m)$ is even too, t is odd, and t_+ and t_- are unequal. From (3a,b) it follows that the staggered benzenoid graphs with even numbers of vertices may not be equally sized. This further implies that only the staggered benzenoid graphs with an odd number of vertices can be equal (isomorphic).

From the perimeter one may easily determine $|t_+ - t_-|$, which is by (4) simply related to the difference between sizes of the staggered benzenoids . From (2) it follows:

$$3(t_+ - t_-) = p_+ - p_- \qquad (8)$$

The sign of the triangles containing the perimeter edges switches whenever the perimeter changes direction, and only then (Fig. 5, right). Note that this holds only for the trigonal graphs without degrees 2 and 6 on the perimeter since the perimeter would change direction at such vertices, but the sign of the perimeter triangle would remain the same. To obtain $|t_+ - t_-|$, one may trace the perimeter and sum the perimeter edges with switching the summation sign whenever the direction of the perimeter changes. The summation may start at any perimeter edge, beginning either with (+) or (−) sign, proceeding until the perimeter cycle is closed. By (8), the absolute value of the sum divided by 3 equals to $|t_+ - t_-|$.

The perimeter of the trigonal graph provides information about possible sterical obstruction from closely spaced hydrogen atoms. Apart from the sterical hindrance which is prevented by the very definition of the staggered benzenoids, a similar detail on the benzenoid perimeter occurs whenever the trigonal perimeter contains vertices of degree 5 in succession. The atoms with close hydrogens now correspond to the avoiding vertices of the staggered benzenoid pair, in contrast to the

overlapping vertices referred in the definition. An example is given in Figure 12a, with the later discussed phenalenyl tilings. Staggered benzenoids without this feature can still have too close hydrogens as shown by the example in Figure 9. Such situations are not related to some local perimeter details, but they can still be easily recognized in systematic generation and filtered out.

By writing down the vertex degrees along the perimeter. one obtains a compact linear code of the trigonal representation. The code is straightforwardly turned to the trigonal graph because the degrees 3, 4 and 5, correspond respectively to turning right, going straight or turning left in the clockwise tracing of the perimeter. In general many different codes of the same trigonal graph can be obtained since the perimeter tracing can start at any of its vertices, in two possible directions. Then some distinct one, for example the smallest lexicographically, can be chosen to uniquely identify the trigonal graph. It makes a basis for recognition of duplicates that comprehensive generation normally produces.
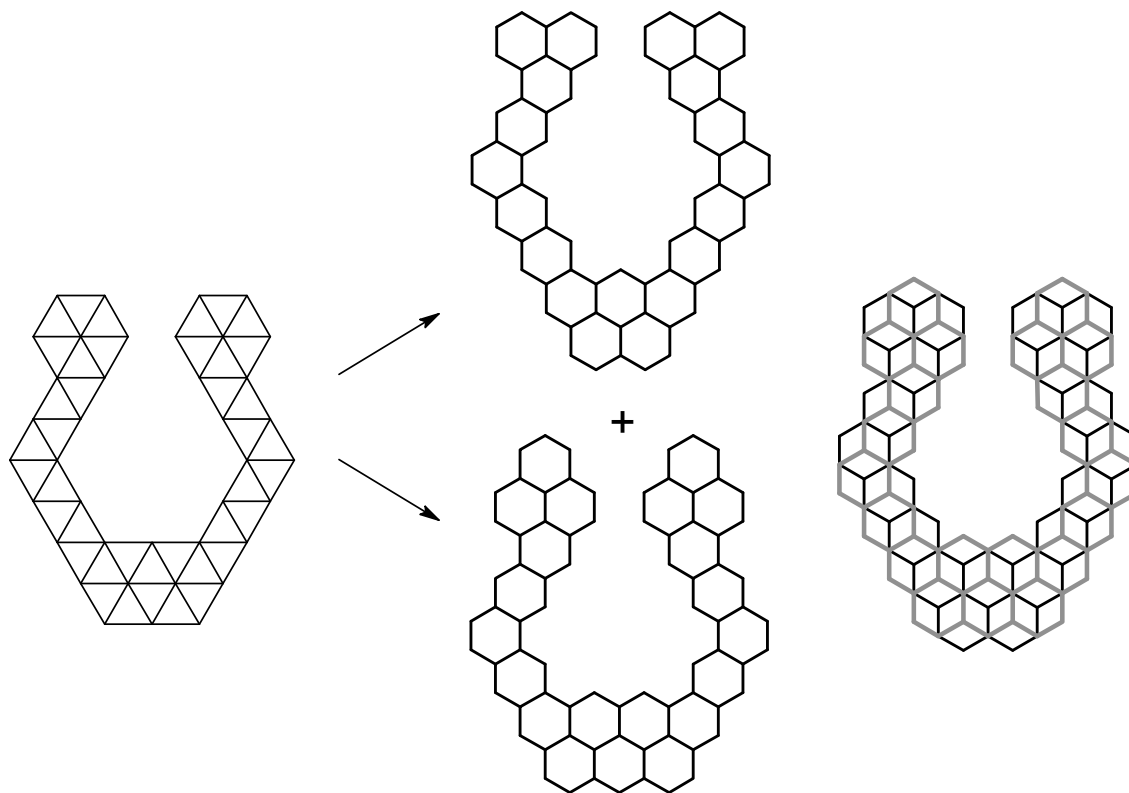
Figure 9. An example of staggered benzenoid pair with closely spaced hydrogens due to nonlocal features. The top benzenoid have 73 vertices and the bottom one 77 vertices.

From the perimeter code one can conclude about the symmetry of the trigonal graph. This is important, for example, when one needs to recognize the isomorphic pairs of staggered benzenoids.

It is clear from the construction that the staggered benzenoids are isomorphic if and only if there is a symmetry operation of the trigonal representation that exchanges (+) and (−) triangles. It can be the reflection in the plane passing through two perimeter vertices of degrees 3 or 5, or the twofold rotation around the axis perpendicular to the graph plane (because of planarity, this rotation is equivalent to the inversion through the center). Relation to the perimeter code becomes clear by considering effect of the symmetry operation on the perimeter. The reflection switches between two perimeter codes going in the opposite directions from the vertex lying in the mirror plane. The existence of a vertex with degree 3 or 5, from which equal perimeter codes are produced in the opposite directions, implies automorphic mapping which exchanges (+) and (−) triangles and consequently the isomorphism of staggered benzenoids. The twofold rotation symmetry implies equal perimeter codes started in the same direction at any two vertices at the distance $p/2$. In reverse, the perimeter symmetric upon the $p/2$ shift of the starting vertex implies twofold rotation symmetry around the axis perpendicular to the molecular plane. Clearly, the twofold rotation exchanges (+) and (−) triangles because it maps the upside pointing triangles into those pointing downside. By looking for these perimeter symmetries it is easy to recognize those corresponding to isomorphic pairs of staggered benzenoids.

5. Nullity of staggered benzenoids

Semioccupied molecular orbital, as the populated orbital with the highest energy and unpaired spin, influences molecular properties to a great extent. In the alternant conjugated system, within HMO, these molecular orbitals have eigenvalue zero and their number is called the nullity of graph [11]. The lower limit to this number is equal to the absolute difference between the numbers of coloured and uncoloured vertices [11]. The difference is called the *colour excess* [8]. For the (+) and (−) staggered benzenoid graphs, the respective colour excesses D_+ and D_- are related to $|t_+ - t_-|$:

$$D_+ = |N_+ - 2n| = |n + m - 2t_- - 2n| = |m - n - 2t_-| = |t - 1 - 2t_-| =$$
$$= |t_+ + t_- - 1 - 2t_-| = |t_+ - t_- - 1| \qquad (9)$$

The preceding result was derived by using the expressions (3) and (6). In an analogous way one gets: $D_- = |t_- - t_+ - 1|$. The expressions for D_+ and D_- show that one of them is always greater than zero. Therefore, at least one of the staggered benzenoids has zero(s) in the spectrum. Both of them may have exactly one zero only if $t_- = t_+$, which also implies equal and odd N_+ and N_-.

It is interesting to examine cases with $|t_+ - t_-| > 1$. Then D_+ and D_- are different and both greater than zero. Further, $(N_+ - 2n)$ and $(N_- - 2n)$ have opposite signs, which means that in one benzenoid, the number of overlapping vertices exceeds the number of avoiding vertices, while in the other there are less overlapping than avoiding vertices. This further implies that their zero eigenvectors do not overlap constructively: in one graph, the nonzero coefficients are associated with the overlapping vertices, while in the other, they are on the avoiding vertices (the example can be found in Fig. 9). In regard to their spin coupling possibilities, such systems would not be interesting. It is worth to notice that in systems with $t_- = t_+$, the number of overlapping vertices (n) exceeds the number of avoiding vertices exactly by one, as follows from (3) and (6):

$$N_{+/-} - n = n + m - t - n = m - t = n - 1 \tag{10}$$

Hence it is sure that the nonzero coefficients of the zero eigenvectors are on the overlapping, and not on the avoiding vertices.

By the results for D_+ and D_-, one can also show that two given staggered benzenoid graphs may overlap in a single way only – by the unique set of vertices in each graph, and no other overlapping combination is possible. When $N_- = N_+$, it follows from (10) that the number of overlapping vertices (n) must be greater by one than the number of avoiding vertices, which fixes the overlapping vertices in both graphs. When $N_- \neq N_+$ and both D_+ and D_- are greater than zero, the overlapping combination is again unique because in one graph the number of avoiding vertices must be greater, and in the other graph it must be smaller than the number of overlapping vertices. Only when either D_+ or D_- is equal to zero (both can not be), two overlapping combinations might be possible – with coloured or with uncoloured vertices in the graph where these two subsets are equal in size. However, since the overlapping set in the other graph is fixed (because $N_- \neq N_+$), the trigonal representation is also fixed, and the staggered pair must be the same for both overlapping combinations. This means that if two overlapping combinations are possible, they must be equal due to the automorphism of the benzenoid graph that switches coloured and uncoloured vertices. The staggered pair in Fig. 6b may serve as an example.

One should keep in mind that the colour excess determines only the lower limit of the number of zero-eigenvalues. The nullity of a benzenoid graph, Z, is fully determined by the maximum number of nonadjacent edges in the graph, also known as the size of the maximum matching, K [11] :

$$Z = N - 2K \tag{11}$$

By simple structural relations, it is clear that $2K \leq N-D$. When inequality holds, the benzenoid system has additional zeros, beyond those which are present due to $D > 0$. Their coefficients are not localized to the vertices of any particular color. Then, by the properties of degenerate eigenvectors, neither zero nor nonzero coefficients are localized on the vertices of a given colour. For this reason it could be difficult to predict and control spin coupling properties of the staggered benzenoid pairs with additional zeros in the HMO spectrum, although it remains to be seen to what extent is this character reproduced in more exact models of electronic structures. An example shown in Figure 10 has colour excess 1, yet there are 3 zeros in the graph spectrum since the maximum matching includes only 32 edges.

The concept of staggered benzenoids was initiated with radicals in mind, and the concept evolved by itself to include the benzenoid graphs with an even number of vertices which are not radicals necessarily. The result (9) for $D_{+/-}$ implies that in the staggered pairs with even numbers of vertices, at least one partner has colour excess greater than zero and, consequently, one or more zero HMO eigenvalues. It turns out that the staggering relation implies presence of zeros in the HMO spectra of benzenoids irrespectively of the size parity, which is a bit surprising.
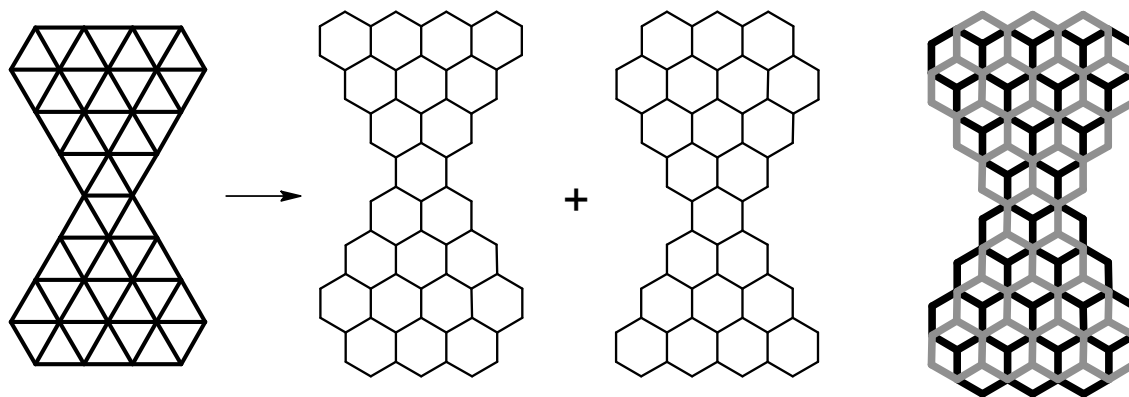
Figure 10. Example of staggered (equal) benzenoids with an odd number of vertices (N=67) and nullity (Z=3) greater than implied by the colour excess D=1. The maximum number K of nonadjacent edges is 32. The upper limit to K (32) can be deduced from the numbers of coloured vertices above and below the narrowest part of the graph.

The above results provide general clues which are practically important for systematic generation of staggered benzenoids by using the trigonal representation. A simple algorithm and the corresponding *Fortran* program will be published elsewhere [12]. The smallest staggered benzenoids are shown in the Appendix for the perimeter lengths 6–12.

6. Possible applications

The staggered benzenoids are interesting by their potential for spin coupling and remarkable magnetic properties. Among the neutral systems, those odd-sized are obvious candidates for spin coupling, but only if their colour excess equals to 1. Otherwise nonzero components of their SOMOs do not match, as shown in the previous section for $|t_+ - t_-|>1$. If there is only one zero-eigenvalue, HMO can give a qualitative insight about the matching extent of the two SOMOs. With additional zero-eigenvalues due to $K<(N\text{-}D)/2$, more reliable electronic structure models are needed to assess the spin-coupling potential. Among the charged systems, only those with single positive or negative charge appear reasonably. The greater charges imply too strong electrostatic repulsion as the coupling radicals should be close to each other in order to couple their spins. Singly charged staggered benzenoids would be radicals for even sizes. Again, when $|t_+ - t_-|>1$, the nonzero components of their SOMOs do not match, and on the basis of the HMO model, they are not expected to form spin-coupled pairs. For $t_+ - t_- = 1$, one of the partners does not necessarily have a zero-eigenvector ($N_+ - 2n = 0$), and the nonzero components of the SOMO in the charged radical would not be limited to the overlapping vertices (even if there is the zero-eigenvector due to $K<N/2$). The other member has at least two zero-eigenvectors (due to colour excess equal to 2) with nonzero components on the overlapping vertices since $N_- - 2n = -2$. The SOMO of the charged radical would be the zero-eigenvector and HMO could serve for quick estimate of the spin-coupling quality, but in this case too, more reliable models should be considered.
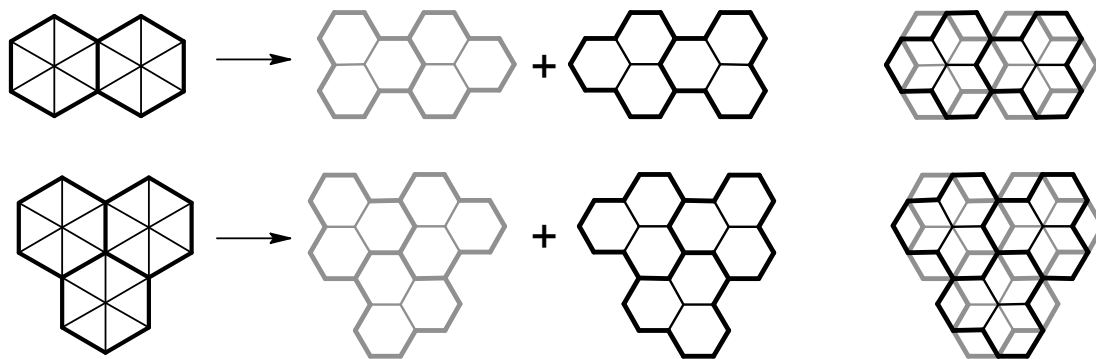
Figure 11. Examples of phenalenyl tilings. Staggered benzenoid pairs (in the middle) have two equal members. Their superposition is on the right. Note that perimeters of the trigonal representatives (on the left) change direction at every vertex (have only degrees 3 and 5).

Particularly promising seems to be a subclass of staggered benzenoids called *phenalenyl tilings*. The phenalenyl tilings are produced by fusing phenalenyl graphs so that adjacent phenalenyl fragments (called *tiles*) share exactly 2 edges and 3 vertices. It can be realized in only one way – by joining an

apex of one phenalenyl tile to a fissure of the other. If the vertices of phenalenyl tiles are labeled in the alternant way, with the central vertex and the next nearest neighbours being coloured, the tiling will also be consistently labeled since the coloured vertices of one tile merge with the coloured vertices of another. It turns out that phenalenyl tilings always make staggered pairs: the partner of a given tiling is produced by inverting each tile through its central vertex – the inverted tiles tightly join as before inversion. Consequently, the phenalenyl motifs in the staggered tilings are superimposed in exactly the same way as in the phenalenyl dimer itself. The smallest phenalenyl tilings are shown in Figure 11 and some others are in Figure 12. Note that one member of the smallest isospectral benzenoids (Fig. 12a) is not expected to be planar due to the proximal hydrogen atoms in the perimeter cove, which emerged from two contiguous degrees 5 on the perimeter of the trigonal representation. The optimized geometry of this benzenoid system has been already shown in Fig. 3. The smallest pair of nonisomorphic phenalenyl tilings, expected to be planar, is shown in Fig. 12b.
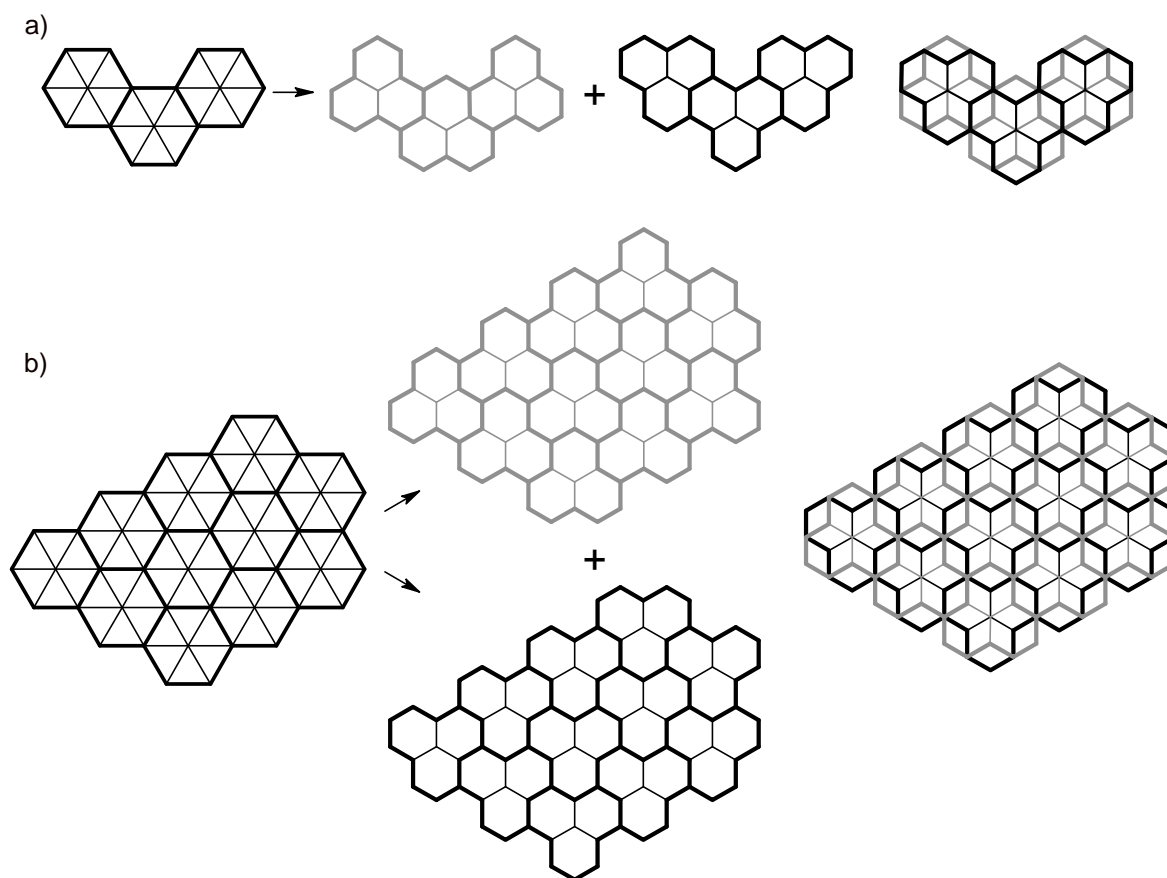
Figure 12. Isospectral phenalenyl tilings. a) The smallest pair, which is however not planar due to a cove on the perimeter of the right member. b) The smallest pair of isospectral, nonisomorphic and planar phenalenyl tilings (with formula $C_{91}H_{27}$).

The trigonal representation of the phenalenyl tiling may have only vertices of degrees 3 and 5 on the perimeter, with no vertices of degree 4. It means that the perimeter has no straight segments, changing direction at every vertex. To verify this, note that the trigonal representation of a phenalenyl tiling is a tiling composed of capped hexagons (Figs. 11 and 12, on the left). Therefore the trigonal representation can be viewed as the (capped) hexagonal graph. Clearly, its perimeter changes direction at every vertex. To see the reverse, that such a perimeter always corresponds to representation of a phenalenyl tiling, one should recognize that the trigonal lattice can be realized as a superposition of three hexagonal lattices shown in Figure 13. After initiating the perimeter at an edge of any of three hexagonal lattices in Fig. 13, by changing direction at every vertex, the perimeter always stays embedded in the initial hexagonal lattice. In other words, the perimeter does not turn from one hexagonal lattice to another because it would require either the straight segment (with the vertex of degree 4) or the sharp turn (with the vertex of degree 2 or 6, which are not allowed in trigonal representation of staggered benzenoids). After closing the perimeter, the resulting trigonal graph is a tiling of capped hexagons, and by construction, each capped hexagon turns into a phenalenyl tile in the staggered benzenoid graphs.
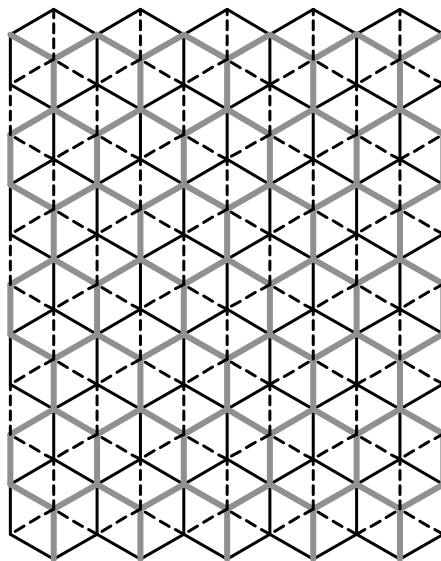
Figure 13.   Trigonal lattice depicted as superposition of three hexagonal lattices (the three lattices are drawn by full and dashed black lines, and by full grey line).

It is intriguing that these systems were already recognized as special benzenoid systems – namely, the staggered phenalenyl tiles are known to be isospectral within the HMO model [13]. These are the only isospectral benzenoid graphs known so far [14]. Thus whenever two staggered phenalenyl tilings are different - nonisomorphic, they must be isospectral. This can be an important factor that

favours their electronic interaction. Colour excess of phenalenyl tilings is exactly 1, as follows from the perimeter of the trigonal representation that switches direction at every vertex, resulting with t_- = t_+. Consequently, the lower limit to their nullity is 1, and it can be proven to be exactly 1 [15]. The HMO eigenvector with the unique zero eigenvalue has a very simple form. The coefficients are zero at the avoiding vertices, where normally expected, and also at the central vertices of the phenalenyl tiles. All other vertices participate with nonzero coefficients, which are by absolute value all equal and their signs strictly alternating along any path in the graph. It is easy to verify that the described eigenvector pattern satisfies the eigenvalue equation in the HMO model, as each avoiding vertex is adjacent to two overlapping vertices with nonzero coefficients whose sum is zero due to the opposite signs. Such SOMO implies evenly distributed charge and electronic interaction between overlapping monomers throughout the molecule. In other benzenoid radicals it is much more common to find SOMO with rather unevenly distributed charge which is concentrated in one part of the molecule. Even distribution of charge certainly favours spin coupling interaction between
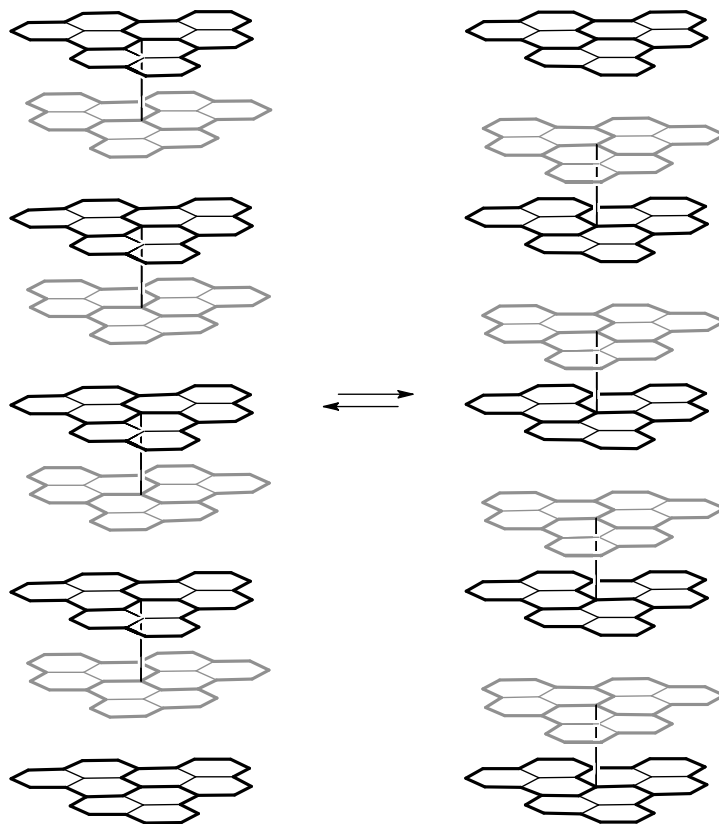
Figure 14. Two enantiomeric stacks of phenalenyl tilings from the bottom row of Fig. 11. The interconversion of the two columnar arrangements requires small shift of the molecules and possibly their rotation in the molecular plane.

monomers and for this reason phenalenyl tilings could be the best possible candidates. It could also make possible association between, say, the phenalenyl radical and a larger phenalenyl tiling that could accomodate the radical at different parts of the tiling. Perhaps a controlled movement of the phenalenyl radical over the larger tiling could also be realized.

Apart from an obvious potential of spin coupled benzenoid radicals to act as molecular magnets, another possible application may arise in the field of chiroptical switches. Note that the dimers produced by spin coupling of two isomorphic staggered benzenoids can be chiral even when the monomers are not; an example is given in Figure 14. Since benzenoid molecules tend to pack in columns [16], chiral dimers could be arranged in a vertical column as if the single dimer was translationally replicated along the column axis. Each monomer would be situated between two others – one at the smaller distance, and the other on the opposite side, at the larger distance. Presumably, the pairs with the smaller distances would be spin coupled, forming a specific enantiomer. A collective shift by which the smaller monomer distances were increased and the larger decreased, would result in complementary pairing of monomers: those that were initially coupled would be now uncoupled and vice versa. The new dimers would have the opposite chirality than at the beginning (Fig. 14). Such a system would have two states, equal in energy. Transition from one spacing (and pairing) to the complementary one should not be energy demanding, as it requires a relatively small translation of the molecules along the vertical axis (eventually with a rotation around the axis). Beside these two enantiomeric arrangements, another geometry is possible, with the radicals at uniform distances forming the Heisenberg spin chain. Besides magnetically different from the dimeric state, this structure would be achiral. Thus the system could have two phases: one paramagnetic and achiral and the other diamagnetic and chiral (though the precise magnetic manifestation also depends on the singlet-triplet gap). Similar systems with reversible dimeric and equidistant structures present at different temperatures are already known as e.g. spin-Peierls systems [17]. If realized, the system exemplified in Fig. 14 could have remarkable novel and interesting applications as a molecular optoelectronic device.

7. Conclusions

On the basis of structural similarity with the phenalenyl dimers, we have defined a new class of paired benzenoid graphs, named *staggered benzenoids*. For the purpose of definition, staggered benzenoids are assumed to fit into the hexagonal lattice taken as geometrical object composed of the regular hexagons. Their vertices are considered as coloured or uncoloured, such that no two

adjacent vertices are with the same label. By definition, a pair of staggered benzenoid graphs fulfills two conditions. By the first, they must be superimposable so that the coloured vertices of one graph overlap with the uncoloured vertices of another, while all the remaining vertices are at the staggered positions avoid any overlapping. By the second condition, each pair of overlapping vertices with a common neighbour in one graph should have a common neighbour in the second graph, too. The first condition matches the maximin principle [4] which was recognized as the decisive factor for stabilizing intermolecular interaction between planar π-radicals. The second condition is necessary (but not sufficient) for planar geometries of the two benzenoids.

Convenient and faithful representation of staggered benzenoid pairs is realized by trigonal graphs – subgraphs of the trigonal lattice. A trigonal graph represents staggered benzenoid pair if and only if it is enclosed by the noncrossing perimeter involving only vertices of the degrees 3, 4 or 5, and no vertices of degrees 2 and 6. Sequence of the vertex degrees along the perimeter encodes all the information about the staggered benzenoids structures and some important details can be easily derived directly from the perimeter sequence. The parity of the perimeter length is opposite to the parity of the number of vertices in the benzenoids. Positions of the degrees 3 and 5 on the perimeter determine the colour excess, which represents the lower limit to the number of zero-eigenvalues (nullity of a graph). Even-sized staggered benzenoids have different numbers of vertices and at least one member has zero eigenvalues due to the nonzero colour excess. If the staggered benzenoids have different sizes, their zero-eigenvectors do not match either because one of them has no zero eigenvalue at all, or, if they both have it, the vertices with nonzero contributions in the zero-eigenvectors do not match. The most obvious candidates for spin coupling remain to be those with odd numbers of vertices which are equal in size. Their colour excess equals to 1, as needed.

Particularly important and interesting are *the phenalenyl tilings* - staggered benzenoids assembled from phenalenyl fragments joined pairwise by fusion of their perimeters at two incident edges (the apex of one matches the fissure on the other). All trigonal representations with no vertices of the degree 4 correspond to phenalenyl tilings. Staggered phenalenyl tilings are known to involve either isomorphic or isospectral benzenoids [13]. Within the HMO model, they have exactly one zero eigenvalue and the corresponding eigenvectors have particularly simple form with the nonzero coefficients being equal and evenly distributed throughout the molecule. For this reason, as well as for their isospectrality, they are particularly promising in regard to spin interaction ability.

Spin coupling staggered benzenoids could find an application as molecular magnets with two possible phases: with stacked dimers – presumably diamagnetic, and uniformly stacked monomers – presumably paramagnetic. Chiral pairs could additionally exhibit chiroptical properties as the dimers could eventually switch between two enantiomeric pairings in an easy and controlled manner. Possibly even the phase with achiral stacks of uniformly spaced radicals would also exist, finally resulting with a multifunctional system that may change both the magnetic and chiroptical properties.

References

[1]   K. Goto, T. Kubo, K. Yamamoto, K. Nakasuji, K. Sato, D. Shiomi, T. Takui, M. Kubota, T. Kobayashi, K. Yakusi, J. Ouyang, A stable neutral hydrocarbon radical: synthesis, crystal structure, and physical properties of 2,5,8-tri-tert-butyl-phenalenyl, *J. Am. Chem. Soc.* **121** (1999) 1619-1620.

[2]   S. Suzuki, Y. Morita, K. Fukui, K. Sato, D. Shiomi, T. Takui, K. Nakasuji, Aromaticity on the pancake-bonded dimer of neutral phenalenyl radical as studied by MS and NMR spectroscopies and NICS Analysis, *J. Am. Chem. Soc.* **128** (2006) 2530-2531.

[3]   for example: Y. Takano, T. Taniguchi, H. Isobe, T. Kubo, Y. Morita, K. Yamamoto, K. Nakasuji, T. Takui, K. Yamaguchi, Hybrid density functional theory studies on the magnetic interactions and the weak covalent bonding for the phenalenyl radical dimeric pair, *J. Am. Chem. Soc.* **124** (2002) 11122-11130; D. Small, V. Zaitsev, Y. Jung, S. V. Rosokha, M. Head-Gordon, J. K. Kochi, Intermolecular π-to-π Bonding between stacked aromatic dyads. Experimental and theoretical binding energies and near-IR optical transitions for phenalenyl radical/radical versus radical/cation dimerizations, *J. Am. Chem. Soc.* **126** (2004) 13850-13858.

[4]   T. Devic, M. Yuan, J. Adams, D. C. Fredrickson, S. Lee, D. Venkataraman, The maximin principle of π-radical packings, *J. Am. Chem. Soc.* **127** (2005) 14616-14627.

[5]   Y. Morita, S. Suzuki, K. Sato, T. Takui, Synthetic organic spin chemistry for structurally well-defined open-shell graphene fragments, *Nature Chem.* **3** (2011) 197-204.

[6]   N. Trinajstic, *Chemical graph theory*, 2nd rev. ed., CRC Press, Boca Raton, 1992.

[7]   A. Graovac, I. Gutman and N. Trinajstić, *Topological approach to the chemistry of conjugated molecules*, Springer-Verlag, Berlin 1977; I. Gutman and O. E. Polansky, *Mathematical concepts in organic chemistry*, Springer-Verlag, Berlin 1986.

[8]   I. Gutman, S. J. Cyvin, *Introduction to the theory of benzenoid hydrocarbons*, Springer-Verlag, Berlin, 1989.

[9] P. W. Fowler, J. I. Steer, The leapfrog principle – a rule for electron counts of carbon clusters, *J. Chem. Soc. Chem. Comm.* (1987) 1403–1405.

[10] D. Cvetković, I. Gutman, N. Trinajstić, Graph theory and molecular orbitals. VII. The role of resonance structures, *J. Chem. Phys.* **61** (1974) 2700-2706.

[11] B. Borovićanin and I. Gutman, Nullity of graphs, *Zbornik radova*, Mathematical Institute SANU, Belgrade, http://elib.mi.sanu.ac.rs/files/journals/zr/21/n021p107.pdf (checked on Oct 13, 2011); S. Fajtlowicz, P. E. John, H. Sachs, On maximum matchings and eigenvalues of benzenoid graphs, *Croat. Chem. Acta* **78** (2005) 195-201; I. Gutman, Characteristic and matching polynomials of benzenoid hydrocarbons, *J. Chem. Soc. Faraday Trans. II* **79** (1983) 337-345.

[12] D. Babic, to be published. The program can be obtained by the request to dbabic@irb.hr.

[13] D. Babic, I. Gutman, On isospectral benzenoid graphs, *J. Math. Chem.* **9** (1992) 261-278; D. Babic, Isospectral benzenoid graphs with an odd number of vertices, *J. Math. Chem.* **12** (1993) 137-146.

[14] X. Liang, J. Meng, Computer search for isospectral benzenoid graphs, *MATCH Commun. Math. Comput. Chem.* **65** (2011) 427-430.

[15] D. J. Klein, Y. Yang, unpublished result

[16] J. Wu, W. Pisula, K. Müllen, Graphenes as potential material for electronics, *Chem. Rev.* **107** (2007) 718-747.

[17] J. W. Bray, H. R. Jr. Hart, L. V. Interrante, I. S. Jacobs, J. S. Kasper, G. D. Watkins, S. H. Wee, J. C. Bonner, Observation of a spin-Peierls transition in a Heisenberg antiferromagnetic linear-chain system, *Phys. Rev. Lett.* **35** (1975) 744-747; A. Kosaki, M. Sorai, H. Suga, S. Seki, Heat capacity of potassium p-chloranil anion radical salt between 13 and 330 K, *Bull. Chem. Soc. Jpn.* **50** (1977) 810-816.

Appendix

The list of staggered benzenoids and their trigonal representations for perimeter lengths 6-12

p=6

$C_{13}H_9$

p=8

$C_{19}H_{11}$

p=9

$C_{22}H_{12}$ $C_{24}H_{12}$

p=10

$C_{23}H_{13}$

$C_{25}H_{13}$

$C_{27}H_{13}$
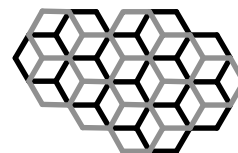

$C_{25}H_{13}$

p=11

$C_{30}H_{14}$ + $C_{28}H_{14}$

$C_{30}H_{14}$ + $C_{32}H_{14}$

p=12

$C_{31}H_{15}$

$C_{29}H_{15}$

$C_{31}H_{15}$

$C_{27}H_{15}$
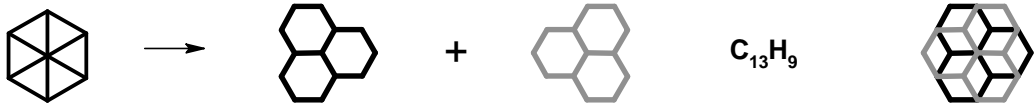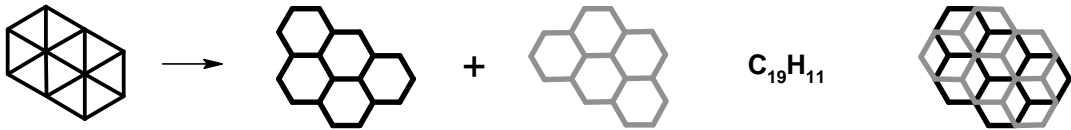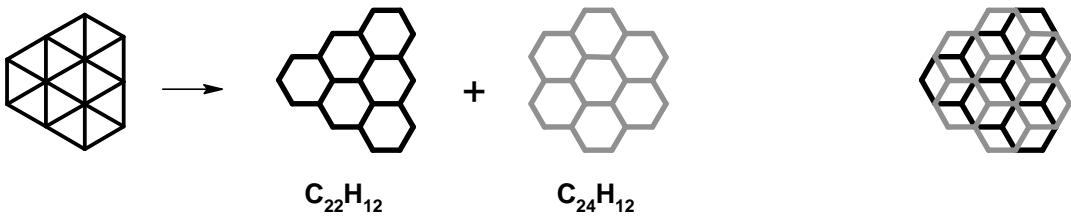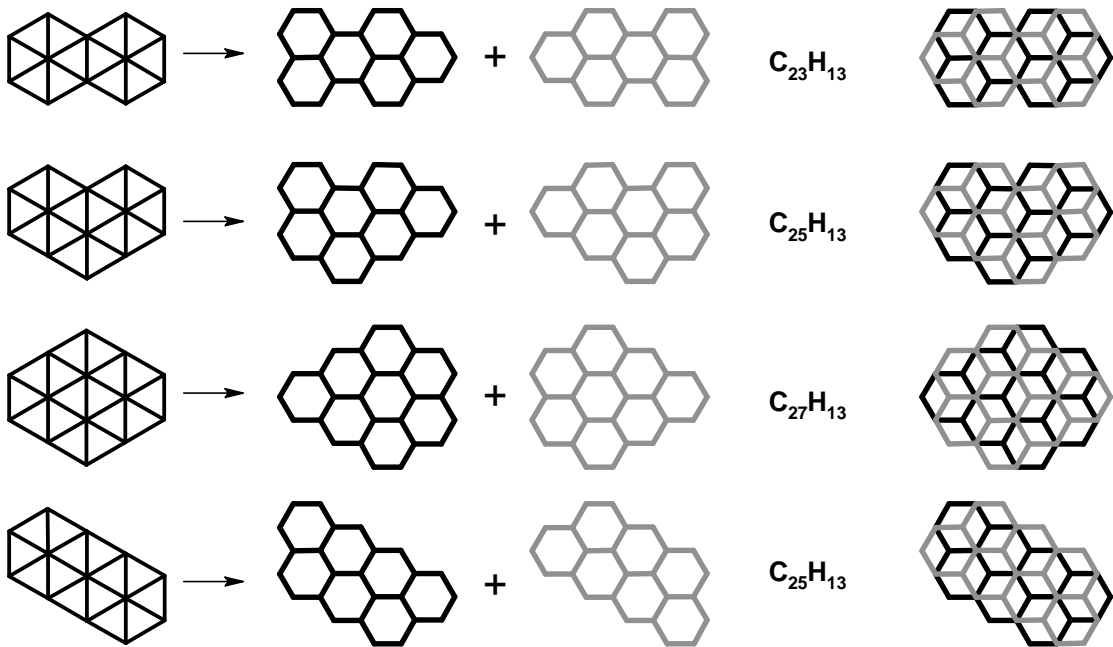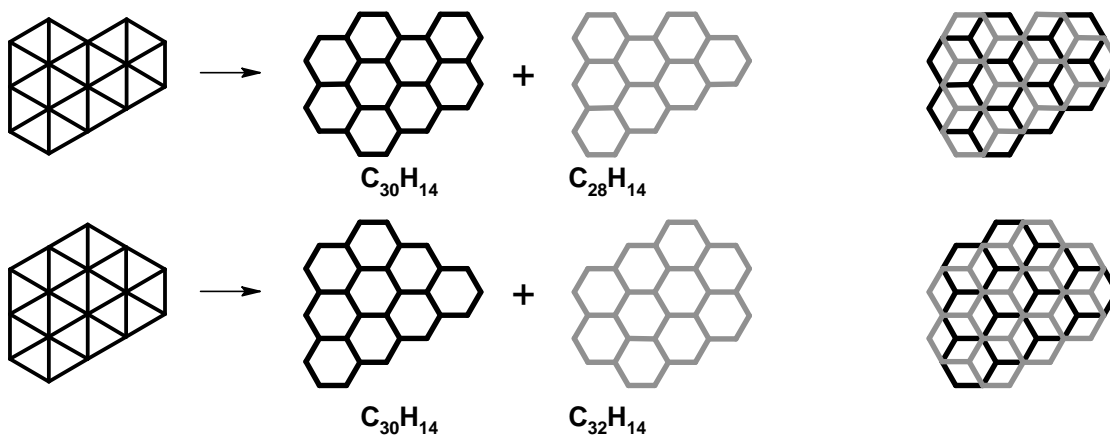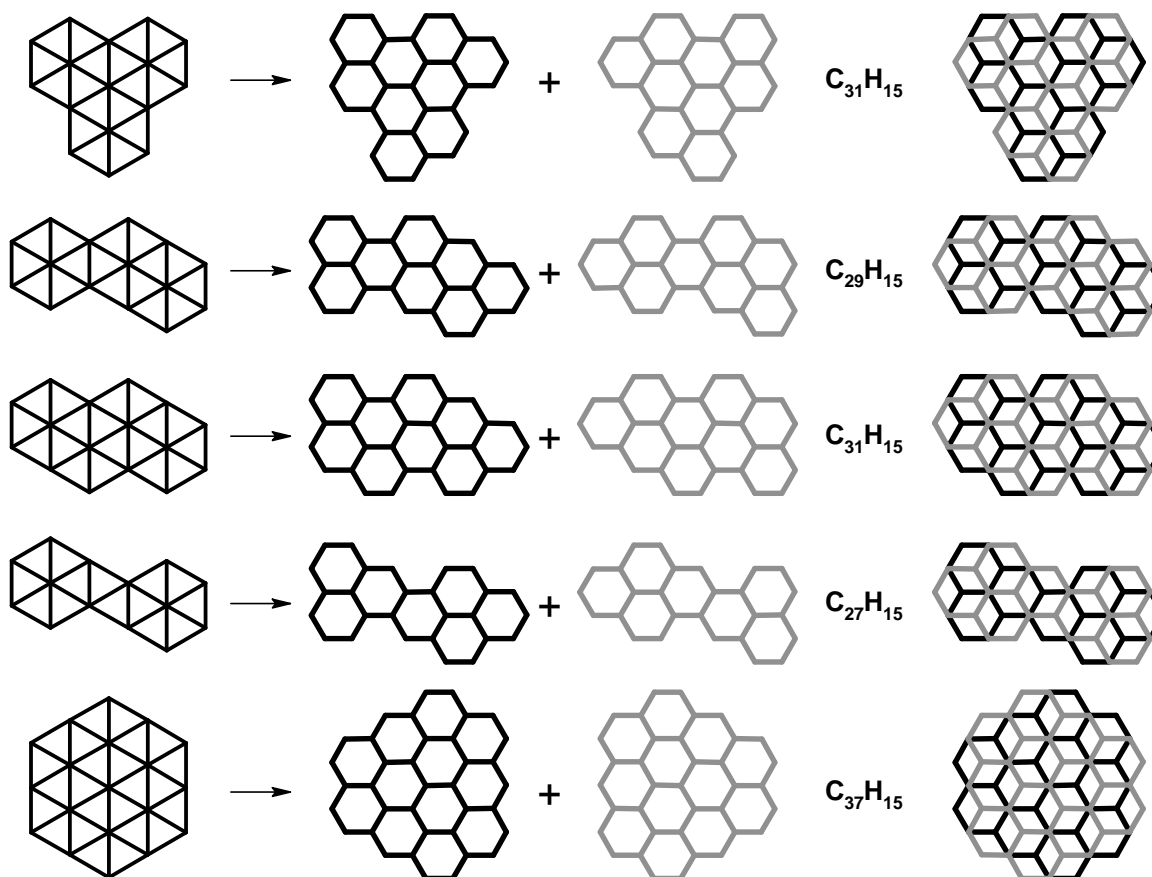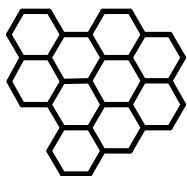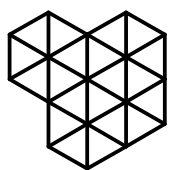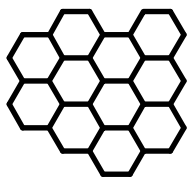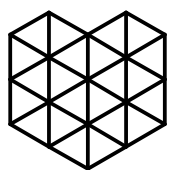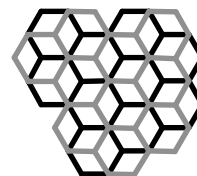
$C_{37}H_{15}$
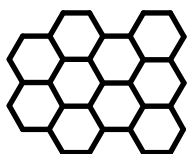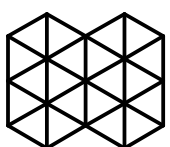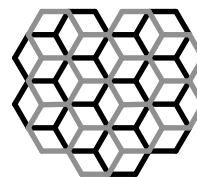
$C_{33}H_{15}$
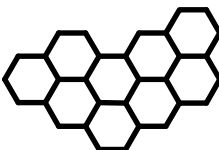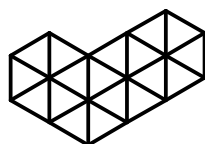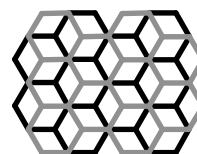
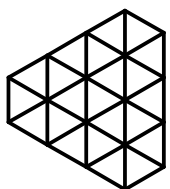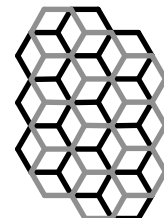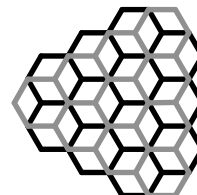$C_{35}H_{15}$

$C_{33}H_{15}$

$C_{31}H_{15}$
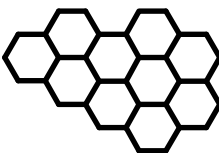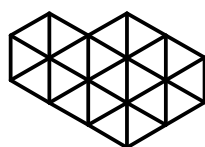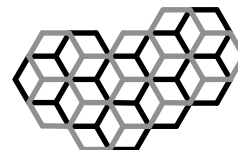
$C_{33}H_{15}$
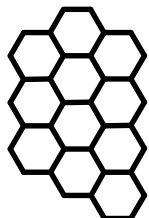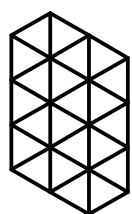
$C_{35}H_{15}$

$C_{37}H_{15}$

p=12, completed

$$\longrightarrow \quad + \quad C_{31}H_{15}$$