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GRAPHICAL PROPERTIES OF POLYHEXES: PERFECT MATCHING VECTOR AND FORCING

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Abstract

From the viewpoint of graph theory and its applications, subgraphs of the tiling of the plane with unit squares have long been studied in statistical mechanics. In organic chemistry, a much more relevant case concerns subgraphs of the tiling with unit hexagons. Our purpose here is to take a mathematical view of such polyhex graphs G and study two novel concepts concerning perfect matchings M. First, the forcing number of M is the smallest number of edges of M which are not contained in any other perfect matching of G. Second, the perfect matching vector of M is written (n_3, n_2, n_1, n_0), where n_k is the number of hexagons with exactly k edges in M. We establish some initial results involving these two concepts and pose some questions.

1. Introduction

Consider the (honeycomb) paving P of the entire plane with regular hexagons, each of which has sides of unit length. For each Jordan curve J in P consisting entirely of the vertices and sides of the regular hexagons, we have a *polyhex*, which is the graph formed by all the nodes and edges which are either on J or in the interior of J. Thus, a polyhex is a 2-connected subgraph of P which is simply connected in the plane. This definition is analogous to that of a square cell graph, first called an *animal* in [1]. In general, we follow the graph-theoretic notation and terminology of [2].

The interest in polyhexes for theoretical chemistry is due to the hexagonal shape of a benzene ring, combinations of which form benzenoids. An entire book on benzenoids, by Cyvin and Gutman [3], includes several graph-theoretic results concerning polyhexes, particularly on the number $f_1(G)$ of so-called 1-factors of a polyhex G, to be defined shortly. There are several other recent books [4,5] on polyhexes. Further, there is a "classic" treatise on organic chemistry, by Clar [6], which lists the chapter titles as polyhexes. The smallest of these are shown in fig. 1, in which 4.3, for example, is the third polyhex with four hexagonal cells, in the order in which we happened to draw them.

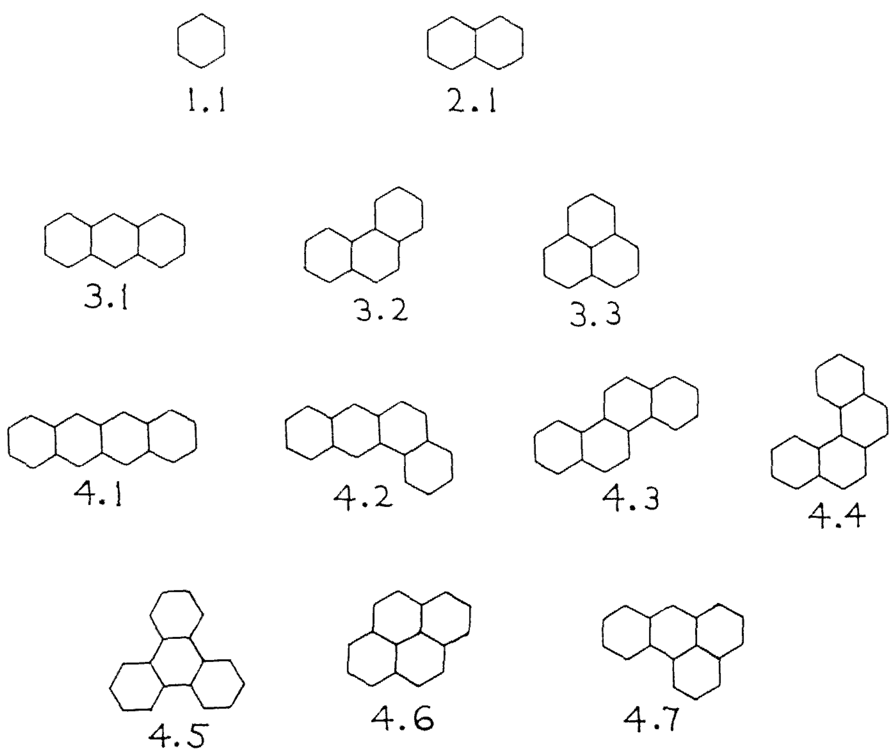

Fig. 1. All 12 polyhexes with at most four hexagons.

2. Perimeter and interior nodes

Let polyhex graph G have p nodes, q edges, n cells, and *perimeter* π as the length of the exterior cycle. An *exterior node* is on that cycle; an *interior node* is not. Let $i(G)$ be the number of interior nodes. Table 1 lists these invariants for each of the polyhexes of fig. 1.

From table 1, one can make various observations, which sometimes may then be generally proved. Define *polyacenes* and a *polyphenacene* as suggested by fig. 2.

Table 1

The numbers p, q, π and i for the smallest polyhexes

Polyhex	1.1	2.1	3.1	3.2	3.3	4.1	4.2	4.3	4.4	4.5	4.5	4.7
p	6	10	14	14	13	18	18	18	18	18	16	17
q	6	11	16	16	15	21	21	21	21	21	19	20
π	6	10	14	14	12	18	18	18	18	18	14	16
i	0	0	0	0	1	0	0	0	0	0	2	1

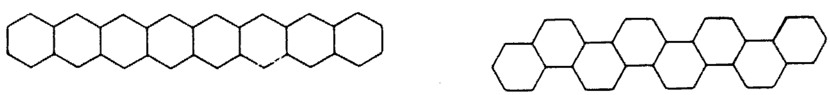

Fig. 2. The 8-acene and the 8-phenacene.

The number of nodes and of edges of both the n-acene and the n-phenacene may be readily seen to be given as

$$p = 4n + 2 \quad \text{and} \quad q = 5n + 1. \tag{1}$$

A generalization to arbitrary polyhexes is:

PROPOSITION 1

Every n-cell polyhex G satisfies:

$$p = 4n + 2 - i,$$

$$q = 5n + 1 - i,$$

$$\pi = 4n + 2 - 2i.$$

These results, which may be readily established by mathematical induction, are already known [5], although they may often be expressed in terms of different subclasses of nodes and/or edges. The subclass of degree-2 vertices is quite important, since its number $p_2 = 2n + 4 - i$ counts hydrogen atoms (which are "suppressed" in the current π-network graphs). Categorization, characterization and enumeration of polyhexes has been made [5] in terms of these indices.

3. Forcing perfect matchings

A *1-factor* of a graph G, also called a *perfect matching* (*pm*), or a *Kekulé structure*, is a spanning subgraph M which is regular of degree 1. That is, M consists of disjoint edges which cover all the nodes. The *number of perfect matchings* of G is written $f_1(G)$.

This number is of special interest for the chemical properties of a benzenoid (see [3–5]). It also is of importance mathematically [7].

When G is a bipartite graph, the number $f_1(G)$ is known to be given [8] by the permanent of a certain matrix associated with G. This fact was used in [9] to determine $f_1(Q_n)$, the number of perfect matchings in a hypercube, for $n \leq 5$. Also the scheme of John and Sachs [10] is notably elegant and practically implementable [11] to evaluate $f_1(G)$.

The classification of polyhexes, which have or do not have a pm, is a question of central interest. Clearly, a polyhex G must have p even to have a perfect matching M. A stronger criterion arises from the consideration of the partitioning of vertices into *starred* and *unstarred* sets such that any pair of neighboring vertices are in different sets. Then clearly for G to have a pm, there must be equal numbers of starred and unstarred sites. Although necessary, this condition is not sufficient, as witnessed by Clar [12], Gutman [13] and Balaban [14] in the examples of fig. 3. For

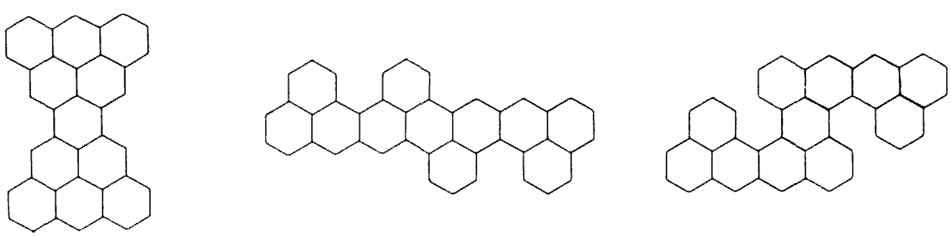

Fig. 3. Three polyhexes with equal numbers of starred and unstarred vertices, but no pm.

small polyhexes with $n \leq 10$ hexagons, Zhang et al. [15] have established this condition's sufficiency. Algorithmic schemes that are generally both necessary and sufficient for a pm to occur are known [16].

One fundamental aspect of a pm, M, it its *forcing number* $\varphi(M)$, which is the smallest number of edges in a subset $S \subset M$ such that S is in no other pm. When $\varphi(M) = 1$, there is an edge $e \in M$ not in any other pm; then, e is a *forcing edge* for M. In fig. 4, the first four polyhexes of fig. 1 are shown, with the forcing edges

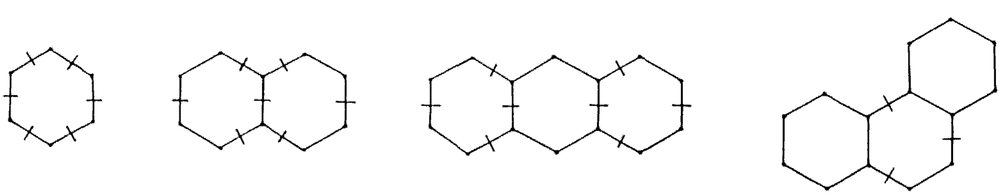

Fig. 4. The forcing edges of the first four polyhexes.

marked by a short perpendicular bisector. The polyhex 3.3 of fig. 1 is not shown since it has no pm, as is clear since $p = 13$ is odd. The 4-phenacene illustrates that in some cases no edges are forcing, and further such cases include the n-phenacenes with $n \geq 4$. A related question concerns those polyhexes with all edges forcing. This is solved completely by:

THEOREM A

The single-hexagon polyhex (i.e. benzene) is the only one in which every edge is forcing.

This is proved in appendix A.

Further questions are: Which edges are in no pms? Which are in every pm? The answer to the first of these questions directly answers the second: e is in every pm iff every edge of G adjacent to e is in no pm. Hence, the answer to the first question generally contains more information. This in turn may be answered via repeated use of an algorithm we have developed to decide whether any edge e is in no pm. This algorithm involves the exploration of various tentative pms through an application of what we might call a *matching edge deletion* for edge e, where e and the end nodes of e (as well as e's adjacent edges) are simultaneously deleted. Then, if any degree-0 node occurs in the resultant new graph G', it is identified as a *null* graph (with no pm possible). Our scheme analyzes a sequence of graphs obtained via such matching edge deletions.

ALGORITHM

Proceed through steps (a), (b), (c) below until either an empty non-null graph is obtained, whence edge e is in a pm, or else all graphs are null, whence e is in no pm.

(a) Make a matching edge deletion for e.

(b) If there is a degree-1 vertex (in the non-null graph considered), make a matching edge deletion for the edge incident there. Repeat for all degree-1 vertices.

(c) If there is a degree-2 vertex (in the non-null graph considered), form two new graphs obtained via matching edge deletions for the two edges incident there. For each non-null graph so generated, return to (b).

An application of this algorithm is illustrated in fig. 5. The algorithm is not in fact restricted to polyhexes , but in general, further steps (d), (e), etc. would be needed to check higher degree nodes. (We do not require these checks since a non-empty non-null graph deriving from a polyhex always has a vertex of degree 1 or 2.)

When e is in no pm, it is called (in the chemical literature) *essentially single*, while if e is in every pm, it is called *essentially double*. Another way to determine

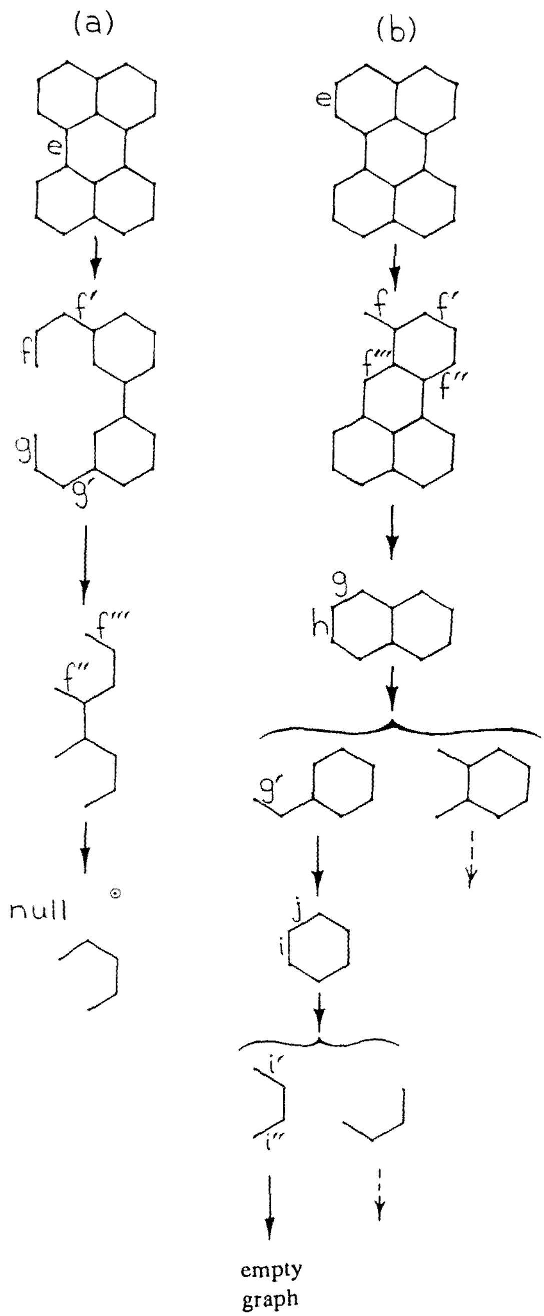

Fig. 5. Two examples of the application of the algorithm to determine whether the indicated edge is in a pm. In case (a), after deletion of e, one deletes f, f', g and g' using step (b) of the algorithm; the resulting graph still has degree-1 vertices, so one continues with the deletion of edges f'' and f''', whence a null graph (wherein the lone vertex is circled) results. Thus, in case (a), e is in no pm. In case (b) of the figure, "branching" occurs at two points along the way, but only one branch is followed by the algorithm to find that e is in at least one pm.

edges which are in no or all pms of a polyhex is to compute the inverse of the adjacency matrix, this inverse being known [17] to exist iff $f_1(G) \neq 0$, and its elements for adjoining pairs of sites yielding quantitatively [18] the proportion of perfect matchings containing the edge between the adjoining pair. Questions on the forcing number may be formulated, for G with $f_1(G) > 0$: What is the minimum forcing number for G, what is the maximum forcing number for G, and what is the average forcing number for G?

Some of the forcing number ideas and questions are found in previous articles [19] in the chemical literature. There, the forcing number has been termed the *degree of freedom* of a Kekulé structure (or pm), and the sum over all pms of these values was termed the "degree of freedom" $F(G)$ of the parent graph G. Then, the average forcing number is $F(G)/f_1(G)$, and this has been given [19] for a dozen or so of the smallest polyhexes as well as all the n-phenacenes. These ideas also relate to a type of (long range) ordering [20] for pms.

There are many other interesting forcing phenomena in graph theory. The pm forcing number can be generalized to define forcing for a maximum (but not necessarily perfect) matching. Similarly, a maximal set of independent nodes can be forced. The forcing number for the chromatic number of a graph is the topic of [21], where it is intended as a model for software applications. The forcing numbers for the edge chromatic numbers of the five platonic graphs have been derived [21]. Of course, forcing numbers can also be defined [21] for any other type of coloring of various structures, even when the coloring is described as a partition with no mention of colors.

4. The perfect matching vector

Let M be a perfect matching of a polyhex G with n cells. The *pm-vector* of M is defined as (n_3, n_2, n_1, n_0), where n_h is the number of cells of G which contain exactly h edges of M. The vectors of pms in polyhex 2.1 are (2, 0, 0, 0) and (1, 1, 0, 0). For polyhex 3.1, we have (1, 2, 0, 0) and (2, 1, 0, 0). The pm-vectors which occur in polyhex 3.2 are (3, 0, 0, 0), (2, 1, 0, 0), (2, 0, 1, 0) and (1, 2, 0, 0). The n-acene graphs each have 2 pms with pm-vector $(2, n-2, 0, 0)$ and the remaining $n-1$ pms have pm-vector $(1, n-1, 0, 0)$. Clearly, the pm-vector is only a partial characterization of a pm, but some key information is encoded. The value n_3 is termed in the chemical literature [22] the *conjugated 6-circuit count* for the pm. The average value of n_3 for a given G plays a central role in "conjugated circuit theory". These n_h seem also to have been mentioned by Sahini [23].

Natural invariants of G are: the maximum value of n_h, the minimum value of n_h, and the average value of n_h, $h = 0, 1, 2, 3$. One might also enquire as to which polyhexes G exhibit "extremal" pm-vectors. Necessary and sufficient structural conditions for one such type of extremum are given by:

THEOREM B

An n-cell polyhex has a pm M with pm-vector $(n, 0, 0, 0)$ iff the polyhex is catacondensed and does not contain the 3-acene subgraph. Moreover, a pm with this extremum vector is unique.

The definition [24] of "catacondensed" we use here utilizes the *inner dual* G^* of the polyhex G: vertices of G^* correspond to hexagons of G, and two such vertices are adjoined by an edge of G^* iff they correspond to adjacent hexagons (having one common edge). Then, a polyhex is *catacondensed* iff its inner dual is acyclic. The proof of theorem B is given in appendix B. Indeed, the proof is constructive for the extremum pm in the theorem – this extremum is simply that forced by all "internal" bonds. See fig. 6 for an example.

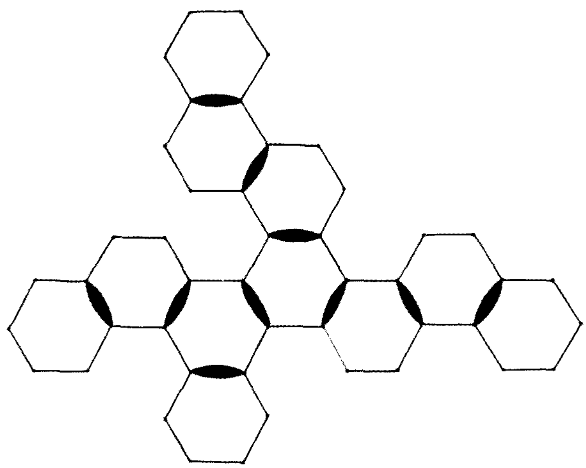

Fig. 6. An example of a 3-acene-free catahex whose extremum pm with pm-vector (11, 0, 0, 0) is forced by the internal edges indicated in boldface.

A point of some chemical interest is that the "extremal" pms of theorem B, and hence presumably also the structures of theorem B, are indicated by Fries [25] to be especially favorable for aromatic stability. That is, of all pms of a polyhex, Fries [25] argued that the most chemically significant are those with the maximum value of n_3. Clearly, of all possible n-cell polyhexes, the maximum value of this maximum occurs for 3-acene-free catacondensed polyhexes which then, according to Fries' ideas, would be presumed to be the most stable aromatic species. Of course, Fries' ideas differ somewhat from Clar's [12], although this also attends to the occurrence of triples of pm edges in single hexagons of the polyhex. In any event, we can say theorem B provides a complete (graph-theoretic) structural characterization of the polyhex systems most stable by Fries' criterion. Indeed, this criterion has previously been advocated by El-Basil [26], who termed polyhexes satisfying this criterion "all-benzenoid". The consequent structures in theorem B have been recently proposed by Randić (via verbal communication) to be termed "all-kink catahexes". Hence, theorem B could be rephrased to say: A polymer is all-benzenoid iff it is an all-kink catahex. Indeed, El-Basil [26] has anticipated such a result, at least for catahex chains.

5. Conclusions

A beginning of a mathematically oriented exploration of the graph-theoretic characteristics of the chemically relevant polyhex systems has been made. Here, pms on these polyhexes have been considered in terms of novel, little previously studied, concepts: forcing and pm-vectors. Some interesting results have been obtained, and some further questions have been indicated.

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Appendix A: Proof of theorem A

To begin the proof, note that if $f_1(G) = 0$, then no edge of the polyhex G would be forcing. If $f_1(G) = 1$, then none of the bonds absent from the single pm would be forcing.

Therefore, we are left with the case $f_1(G) \geq 2$ which the remainder of the proof concerns. Given two different pms, consider the spanning subgraph S of G with edge set the union of the two pms. Pauling [27], in 1933, called such an S a *superposition diagram*. As noted by Pauling, the components of S consist of one or more even cycles and possibly some isolated edges. If there are any isolated edges in S, then any one of them would not be forcing, since there are two possibilities for the assignment of pm edges around a cycle of S. Similarly, if there are two (or more) cycles in S, none of the edges in either cycle is forcing, since assignment of one would not force a choice in the other cycle.

Thus, we consider the remaining circumstance that there is but a single cycle in C in S. Since S is spanning, all the vertices of G are in S. If all the edges of G are in C, then one has a single hexagon, for which all the edges are forcing. Otherwise, there is at least one edge not in C. Without loss of generality, the nodes of C may be numbered consecutively around C (as $1, 2, \ldots, p$) and an additional edge may be taken as $\{1, n\}$ (for some $n \in \{3, 4, \ldots, p-2\}$). Evidently, n must be even since the sequence $1, 2, \ldots, n$ identifies a cycle of the bipartite graph G. Then, the edge $\{p, p-1\}$ is not forcing because it occurs both in the pm with edge set

$$\{\{2i-1, 2i\};\ i = 1 \text{ to } p/2\}$$

and in the pm with edge set

$$\{\{2i-1, 2i-2\};\ i = 1 \text{ to } n/2\} \cup \{\{2j, 2j-1\};\ j = n/2+1 \text{ to } p/2\}.$$

Thus, the only polyhex for which all the edges are forcing is benzene, consisting of just one hexagon.

Appendix B: Proof of theorem B

To begin the proof, assume that graph 3.3 of fig. 1 is a subgraph of a polyhex G. Any pm of G must contain exactly one of the three edges radiating from the central node of 3.3. Clearly, this node is in three hexagons although the associated pm edge is in only two, so that not all three rings can contribute to n_3 for any pm – that is, at least one ring must contribute to n_0, n_1 or n_2. Since the substructure of 3.3 must occur in any pericondensed (i.e. non-catacondensed) polyhex (without "holes"), the extremum pm-vector with $n_0 = n_1 = n_2 = 0$ is unrealizable for this case.

Second, for the catacondensed case consider the possibility that the 3-acene graph 3.1 of fig. 1 is a subgraph of G. For the central hexagon to contribute to n_3 for a particular pm, the bonds therein must be disposed in one of the two ways indicated in fig. 7. However, then the adjacent hexagons marked by an asterisk

Fig. 7. Constructions for the 3-acene graph, as used in the proof of theorem B.

cannot contribute to n_3, and must contribute to n_0, n_1 or n_2. Hence, these polyhexes too cannot have an extremum pm-vector with $n_0 = n_1 = n_2 = 0$.

Finally, consider the possibility of a catacondensed polyhex G with no subgraph of the 3-acene type. Begin the construction of a certain spanning subgraph M by choosing every edge shared between two rings to be included in the edge set of M. If there is just one hexagon in G, then the extremum pm-vector is clearly achieved. Otherwise, consider a typical hexagon joined to (at least) one other, say on the left-hand side as in fig. 8, so that the boldface edge on the left is to be included in M. We also include the two other boldface edges, either (or both) possibly being shared with another hexagon. None of the non-boldface edges can be shared with another hexagon, since this would then yield one of the currently excluded subgraphs 3.1 or 3.3. Evidently, M is an extremum pm with $n_0 = n_1 = n_2 = 0$.

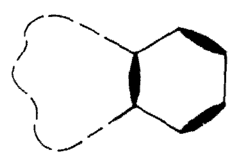

Fig. 8. The typical hexagon sharing of at least the leftmost edge with other rings of the polyhex.

The uniqueness of M of the preceding paragraph is seen upon first noting that in order for matching M to be an "extremum", the shared edges would need to be included in order that both hexagons, sharing such an edge, contribute to n_3. These shared edges are then seen to force the remaining edges, so that M is unique. Hence, the proof of the theorem is completed.

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