The branching graphs of polyhexes: some elementary theorems, conjectures and open questions

Edward C. Kirby

Resource Use Institute, 14 Lower Oakfield, Pitlochry, Perthshire PH16 5DS, Scotland, UK

and

Ivan Gutman

Faculty of Science, University of Kragujevac, PO Box 60, YU-3400 Kragujevac, Yugoslavia

Received 30 April 1992

This paper presents a few novel results, and collects together what is known and conjectured about the branching graph of a polyhex.

1. Introduction

The branching graph (BG) of a graph (G) is the subgraph that contains the branching vertices (i.e. those of degree > 2) and the edges that connect pairs of such vertices. In this paper we offer a few novel results, and collect together what is known and conjectured about the properties of one particular class, namely the branching graph of polyhexes. Benzenoids (polyhexes that possess Kekulé structures) are well known and constitute an important and interesting class of hydrocarbon structure.

The concept of the branching graph was introduced [1] as a practical recognition tool to help in diagnosing whether a graph does or does not have a Hamiltonian path, i.e. a path that visits every vertex just once. This knowledge has chemical relevance in the fields of structural information transmission (for a structure that is path-Hamiltonian is often easier to encode from a keyboard than one that is not [2]), and of predicting the magnetic properties of molecules by use of the concept of spanning trees, for the methods available for calculating π-electron ring currents in a conjugated system depend on whether or not the system is traceable (i.e. has a Hamiltonian path) [3–12]. It has also been found [13] that branching graphs yield some insight into why there are so few Clar sextet 2-factorable polyhexes [#1] [15] among all those that theoretically are possible.

Although it is a simple device, the subject of branching graphs is quite complicated, in the sense that their application involves both graph-theoretical and geometric features [#2] and we have undertaken this study in order to try to understand and characterise such objects as fully as possible.

2. Definitions

By a *polyhex* we mean *any* structure comprising an assembly of hexagons in which any two hexagons are either disjoint or have a common edge, although in practice all results reported up to now concern polyhexes that can be embedded in a hexagon lattice. We use the term without qualification to refer to the molecular graph of a benzenoid hydrocarbon. An exact and universally accepted convention has not yet emerged, and other terms in use include "polyhex graph", "benzenoid graph" and "benzenoid system". Benzenoids are often treated as a sub class of "1-factorable polyhexes" (i.e. those that have Kekulé structures). See references such as [19–21] for a fuller discussion of the subject.

A *perfect matching* of a graph G is a set of independent (i.e. mutually non-incident) edges of G which cover all the vertices of G. Obviously G may possess a perfect matching only if it has an even number of vertices. A *k-defect matching* [#3] is a set of independent edges that cover all but k vertices of the respective graph. A perfect matching is therefore a zero-defect matching. By default, k will always be taken to have the minimum possible value.

Matchings, both perfect and defect, have been extensively studied in the mathematical literature [23,24] and have well known applications in chemistry [19,25].

POLYHEX BRANCHING GRAPHS THAT ARE OF GENERAL TYPE

(0) A complete characterisation of the branching graph of a general polyhex is not known and, bearing in mind our introductory remarks above, and our findings with regard to catacondensed polyhexes (points 5–9 below), any such characterisation will probably prove to be rather complicated.

(1) There is a one-to-one correspondence between the 2-factors of a polyhex

[#1] These are also referred to as "total resonant sextet benzenoids"; see, for example, ref. [14].

[#2] It should be noted that the branching graph, as defined, is indeed a *graph*, but that often, as when it is embedded in a hexagon lattice, it is observed in a particular geometric form (cf. "dualist", "skeleton" or "characteristic graph" [16–18]).

[#3] In an earlier paper [22] the term "*k*-branch factor" was used – in order to emphasise the analogy between these and principal resonance structures in chemistry.

and the 1-factors (= perfect matchings) of its branching graph. A proof of this result has been given [22].

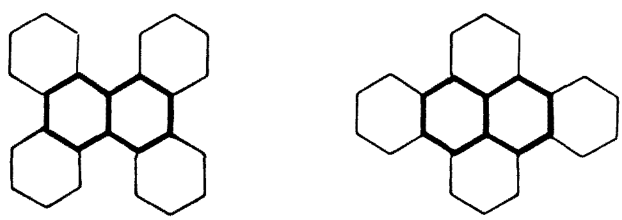
(2) A pericondensed polyhex has a branching graph with at least one vertex of degree three.

Proof

Any pericondensed polyhex contains at least one phenalene fragment. Phenalene has the (branched) 3-star graph as its BG. This latter graph is contained as a subgraph in any BG of a pericondensed polyhex.

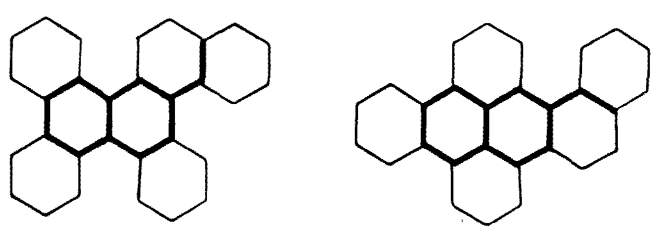
Whence, if a BG contains no vertex of degree three, then it corresponds to a catacondensed polyhex. If, however, it does contain vertices of degree three, then it may correspond to either a cata- or a pericondensed polyhex.

(3) In the general case, one cannot decide from the BG whether the parent polyhex is cata- or pericondensed.



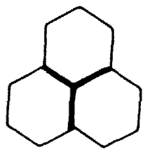
An example of a catacondensed and a pericondensed polyhex, both having the same BG. (Here and throughout this paper the branching graph is indicated by heavy lines.)

Sometimes this property (whether the polyhex is cata- or pericondensed) will depend on how it is embedded in the hexagonal lattice.

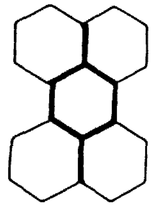


A catacondensed and a pericondensed polyhex, both having the same BG; the two BGs are, however, embedded differently in the hexagonal lattice.

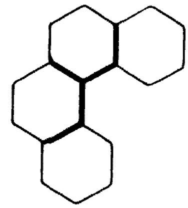
(4) The presence of the (branched) isopropyl subgraph in the branching graph is a necessary but not a sufficient condition for the polyhex to be pericondensed.



(a) This BG is the isopropyl graph.

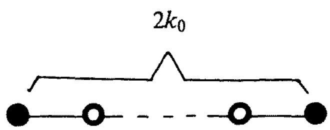


(b) This BG has an embedded isopropyl subgraph.

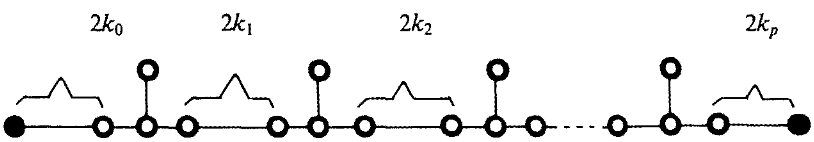


(c) This BG contains the isopropyl subgraph, yet the polyhex is catacondensed.

(5) If the graph G is the BG of a catacondensed polyhex, then G may have one or more components, and each component is constructed from the X-, Y- or Z-type blocks shown below. A component can be a single X-, Y- or Z-block, or it can be Y- and/or Z-blocks linked by, or just connected to, X-units. Only the vertices shown in solid black can be used for connections. In the case of an X_p-link or X_p-branch ($p \geqslant 1$), the condition $k_{i-1} + k_i > 0$ must hold for all $i = 1, 2, \ldots, p$.

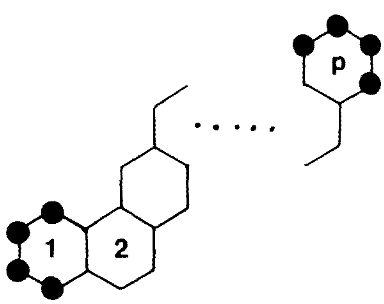


$x_0 = x_0(k_0); \quad k_0 \geqslant 0$



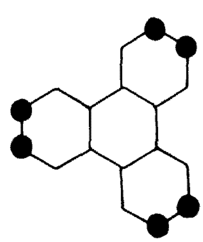
$x_p = x_p(k_0, k_1, \ldots, k_p); \quad p \geqslant 1, \quad k_0, k_1, \ldots k_p \geqslant 0$

"X-block" components of a catacondensed polyhex.



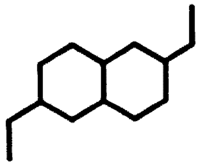
$Y = Y(p); \quad p \geqslant 1$

A "Y-block" component of the BG of a catacondensed polyhex.

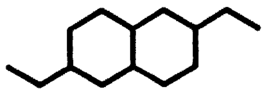


A "Z-block" component of the BG of a catacondensed polyhex.

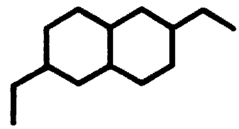
(6) Whether a graph with the structure described in point 5 is the BG of a catacondensed polyhex may depend on the mode of its embedding in the hexagonal lattice.



BG of a (unique) catacondensed polyhex.



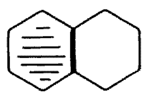
BG of a (unique) pericondensed polyhex.



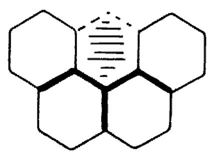
This mixed "axial/equatorial" arrangement is not the BG of any polyhex.

(7) A graph G having the structure described in point 5 is the BG of a catacondensed polyhex C if it can be embedded in a hexagon lattice so that each hexagon of the lattice has any one of six combinations of branching graph edges belonging also to C. This is illustrated below with hatched hexagons (broken edges denote hexagons external to C). Taken with the requirements of point 5, these constitute conditions for G to *be* the branching graph of C.

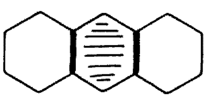
(a) No edges: present only as an external hexagon.



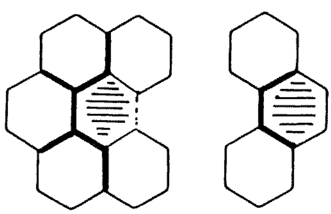
(b) One edge: the polyhex contains this hexagon.



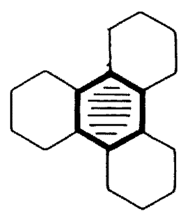
(c) Two incident edges: the hexagon must be external to the polyhex.



(d) Two opposite edges: contained within the polyhex.



(e) Three incident edges: this hexagon may be internal or external with respect to the polyhex.



(f) All six edges: this hexagon must be contained with the polyhex.

On the face of it there appear to be other possibilities; two staggered edges, and four and five incident edges. It can easily be verified however, that is not possible to construct a catacondensed polyhex that generates a hexagon with four incident BG edges. The others (two staggered and five incident edges) are precluded from appearing internally in a branching graph by definition, and, if external, the polyhex cannot be constructed.

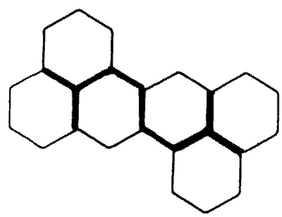
(8) It is conjectured that the conditions outlined in points 5 and 7 are not only necessary, but also sufficient for an (embedded) graph G to be the BG of a catacondensed polyhex.

(9) If a BG of a catacondensed polyhex has no cycles then the respective polyhex is unbranched.

Proof

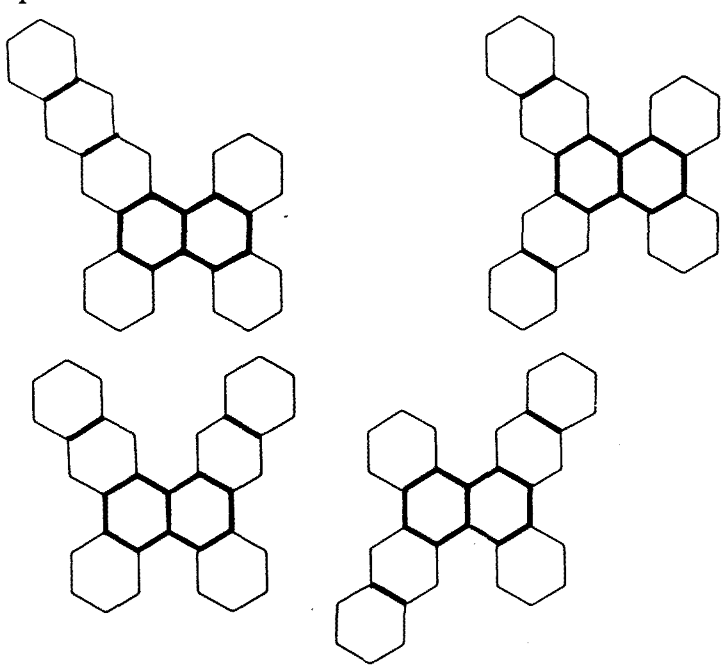
Any branched catacondensed polyhex contains as a subgraph at least one triphenylene fragment whose BG is the 6-cycle.

Note that acyclic BGs may correspond also to pericondensed polyhexes:

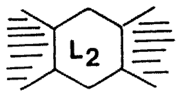


A pericondensed polyhex (zethrene) whose BG is acyclic.

(10) If the BG is not connected then it may correspond to several polyhexes. This example shows four catacondensed polyhexes having the same (disconnected) branching graph:

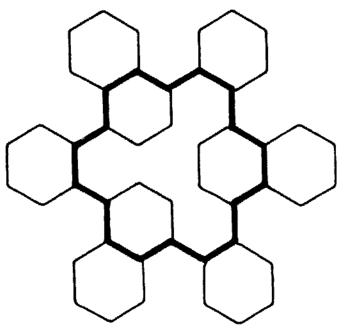


(11) The number of components of a BG is increased by one for each L_2 mode hexagon present in the parent polyhex.



An L_2 mode hexagon (one with two opposite degree-2 vertices).

(12) The 6-cycle is the only simple cycle (i.e. one whose vertices are all of degree 2) that is the branching graph of a polyhex. Other cycles can, however, be branching graphs of singly connected polyhex systems. The branching graph of a circulene for example is either branched or it is disconnected.



A cycle that is the BG of a singly connected polyhex system.

(13) In a k-defect matching of the BG of a polyhex, k is always even.

Proof

Each edge in a k-defect matching covers two vertices of the BG. Because the BG of a polyhex necessarily has an even number of vertices [22,26] it follows that the number of uncovered vertices ($= k$) must also be even.

(14) In a k-defect matching of the BG of a catacondensed polyhex, $k = 0$.

Proof

The existence of a perfect matching ($k = 0$) in the BG of a catacondensed polyhex follows from either 1 or 5.

(15) The number of vertices in a branching graph represents an upper bound of the number of degree-3 vertices in any spanning tree of its associated polyhex.

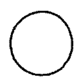
Proof

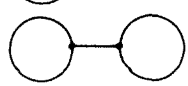
By definition every vertex of the branching graph appears in the spanning tree, and these are only vertices that can be, but need not be, of degree 3 there.

(16) If a branching graph has no k-defect matchings with $k < k'$ then its polyhex has no spanning trees with fewer than $(k'/2 - 1)$ branches. This represents a lower bound (cf. 15).

Proof

Consider the spanning subgraph G obtained from polyhex P by deletion of the edge set of a k'-defect matching of its branching graph. G has k' vertices of degree 3, and all other vertices are of degree 2. G can be regarded as the homeomorphic graph G', having k' vertices of degree 3 and v_{2p} edges, where v_{2p} represents the number of paths joining pairs of degree-3 vertices through a sequence of one or more degree-2 vertices. It can easily be seen that:

if $k' = 0$ then $v_{2p} = 1$ (i.e. G is a cycle) and $G' =$  ;

if $k' = 2$ then $v_{2p} = 3$ and $G' =$  or $G' =$ 

If this graph is converted successively into graphs that have more vertices of degree 3, then every subsequent addition of a pair of degree-3 vertices increases the number of edges by 3. (Each vertex divides an edge into two, and the pair also contributes the edge joining them) i.e. $v_{2p} = 3k'/2$ (for $k' > 0$, k' even).

Any tree with k' vertices has $k' - 1$ edges, therefore G' has $3k'/2 - (k' - 1) = k'/2 + 1$ more edges than a spanning tree with k' vertices. G can be converted to a spanning tree by deleting edges in such a manner as to eliminate cycles without causing disconnection. To select a minimally branched spanning tree, the edges chosen are adjacent to degree-3 vertices wherever possible. The equivalent procedure in graph G' is not deletion, but cutting, of edges adjacent to degree-3 vertices.

No more than $k'/2 + 1$ edges in G' may be cut without disconnection, and it follows that the minimum number of degree-3 vertices in a spanning tree of G', G and P is $k' - (k'/2 + 1) = k'/2 - 1$. ($k' > 0$, and k' even.)

Note: this result expresses in a more general form the procedure suggested [1] for diagnosing whether a polyhex is or is not traceable (path-Hamiltonian).

(17) Some graphs can be branching graphs, but cannot be branching graph components.

Examples are the 3-star, and the branching graph of perylene (cf. point 4).

They can be characterised as branching graphs of polyhexes that have no edge that is more than one edge distant from some vertex of their branching graph.

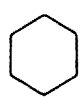
(18) A graph having vertices of degree one may be the BG of several polyhexes. Such a graph, embedded in the hexagonal lattice, is the BG of at most one polyhex.

POLYHEX BRANCHING GRAPHS THAT ARE POLYHEXES

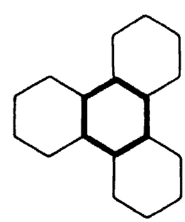
(19) If P is a sextet 2-factorable polyhex, then each component of its branching graph is either a polyhex or is composed of several disjoint polyhex units where each edge connecting these units corresponds to an essentially single bond. For a proof see Gutman and Kirby [22].

(20) A polyhex can be the branching graph of not more than two distinct parent polyhexes (cf. 18). For a proof see Gutman and Kirby [22].

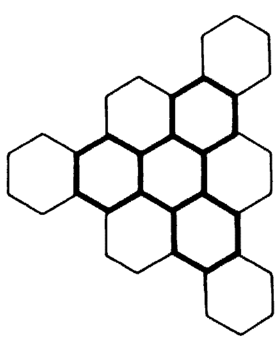
(21) For the case where the branching graph is a polyhex, there is one and only one infinite series of polyhexes $P_1, P_2, P_3, \ldots$ such that each polyhex is the branching graph of the next member of the series, i.e. $P_i = \mathrm{BG}(P_{i+1})$. This is the triangular sequence starting from the 6-cycle:



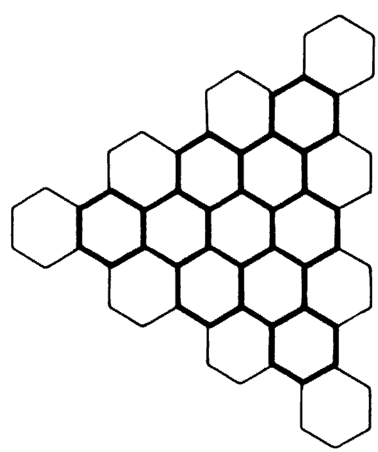
$P_1 = \mathrm{BG}(P_2)$



$P_2 = \mathrm{BG}(P_3)$

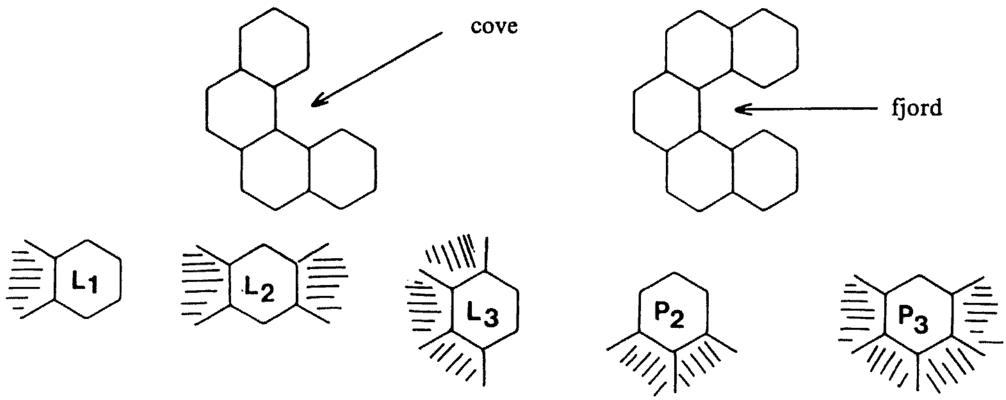


$P_3 = \mathrm{BG}(P_4)$



$P_4 = \mathrm{BG}(P_5)$

The proof of this is very lengthy and cumbersome. The idea, however, is simple: the triangular series $P_1, P_2, P_3, \ldots$ contains the only possible cove- and fjord-free polyhexes whose vertices of degree 2 belong only to L_1- and L_3-mode hexagons defined in accordance with the illustrations below (see also ref. [19]).

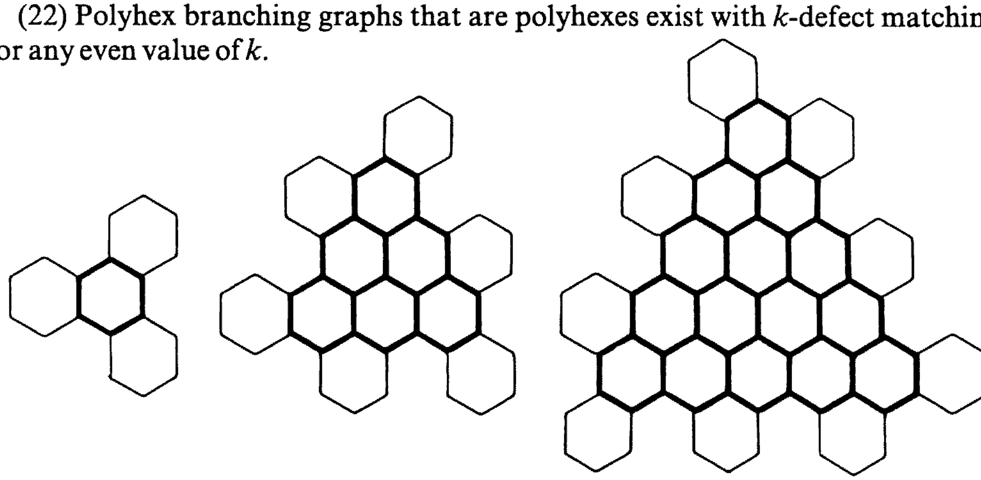


Fjords, coves and hexagon modes.

Now, the presence of a fjord makes it impossible to continue the construction. The presence of a cove will cause the occurrence of a fjord in one of the next generations. Similarly, the presence of hexagons of modes P_2 and P_3 will result in a fjord in one of the subsequent generations.

An example of a geometrically non-planar series with the property $P_i = \mathrm{BG}(P_{i+1})$ is a set of graphitic cylinders of constant diameter but increasing depth. Any cubic graph, such as an infinite hexagonal lattice, or a finite but closed one, e.g. a hexagon lattice covering a toroidal surface, has the property of being its own branching graph [27].

(22) Polyhex branching graphs that are polyhexes exist with k-defect matchings for any even value of k.



$k = 0$ $k = 2$ $k = 4$

A branching graph series where the best possible matchings have increasing defect (see ref. [28]).

POLYHEX BRANCHING GRAPHS THAT ARE TREES

(23) We would like to know how to recognise trees that can be polyhex branching graphs, and polyhexes that have tree branching graphs, but have only partially solved this problem. In general it seems more difficult to characterise branching graphs that are trees than branching graphs that are polyhexes, and this is because (in contrast to polyhexes with no substituents) they can be embedded in the hexagonal lattice in different ways, as is known in connection with the lattice tree problem [29,30].

(24) The characterisation of trees which are BGs of catacondensed polyhexes was achieved in point 5; those trees of the type X_0 and X_p. The respective catacondensed polyhexes are unbranched and contain no L_2-mode hexagon (cf. 9 and 11). There is a one-to-one correspondence between a BG of type X_0 or X_p and an unbranched catacondensed polyhex. In other words the way in which the BG has to be embedded in the hexagonal lattice is unique.

(25) The n-vertex branching graph that is a single chain is associated with the zig-zag polyhex with $n/2+1$ hexagons. (This is the same polyhex as $Y(p), p = n/2 + 1$ in point 5. The value of n is, of course, even.)

(26) The n-vertex branching graph that consists of $n/2$ disjoint edges is associated with the linear polyacene with $n/2 + 1$ hexagons.

(27) A complete characterisation of the trees which are BGs of pericondensed polyhexes is not known. That such trees exist is shown in point 9.

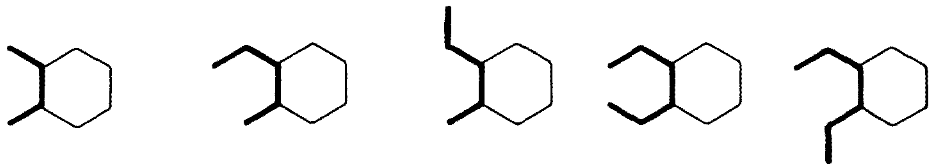
(28) It would be interesting to determine the number of distinct polyhexes that have the same tree BG. In other words: how many embeddings of 3-trees (and which) are polyhex BGs? For branching graphs with up to ten vertices, the maximum number is three [30].

(29) For the purpose of reconstructing a polyhex from a tree branching graph embedded in a hexagon lattice, two limiting conditions may be stated:

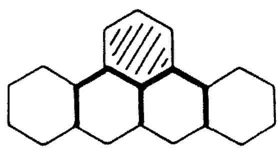
(29a) There are just three possible ways of adding a hexagon to a pair of degree-2 vertices.

(29b) There are just twenty-three possible ways of adding a pair of hexagons to a terminal edge.

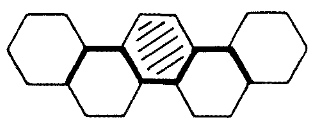
When one hexagon is added to a pair of vertices of degree 1/degree 1 or degree 1/degree 2, then all four addition modes are possible, giving eight in total for one side of a degree-1 vertex. The addition of a pair of hexagons to a terminal edge should thus be possible in thirty-six different ways (the number of pairs – which can be two of the same – that can be chosen from eight items) but, in practice only twenty-three of these are available.



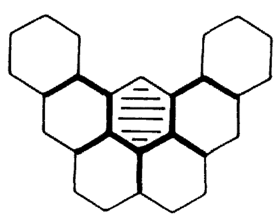
The failure of 1-contact addition (it is not possible to complete a polyhex from these drawings). Note that this mode *is* possible if the BG is *not* a tree.



2-contact addition

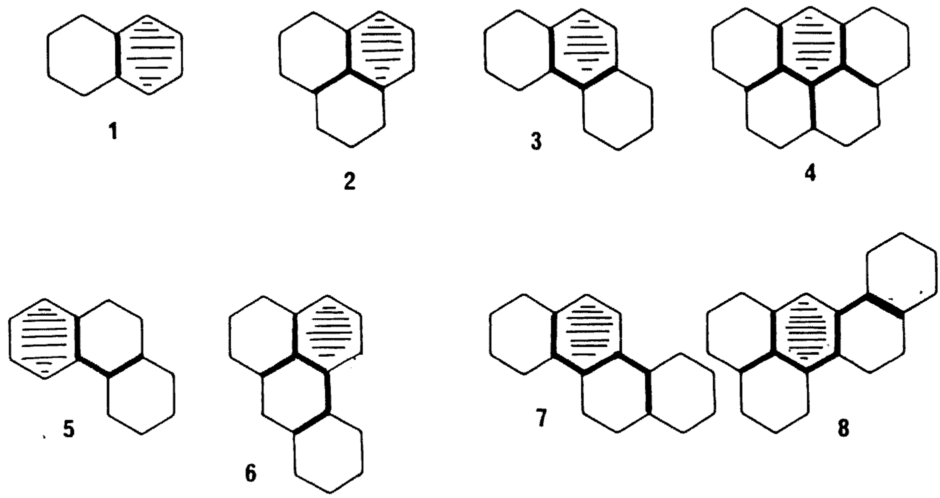


3-contact addition

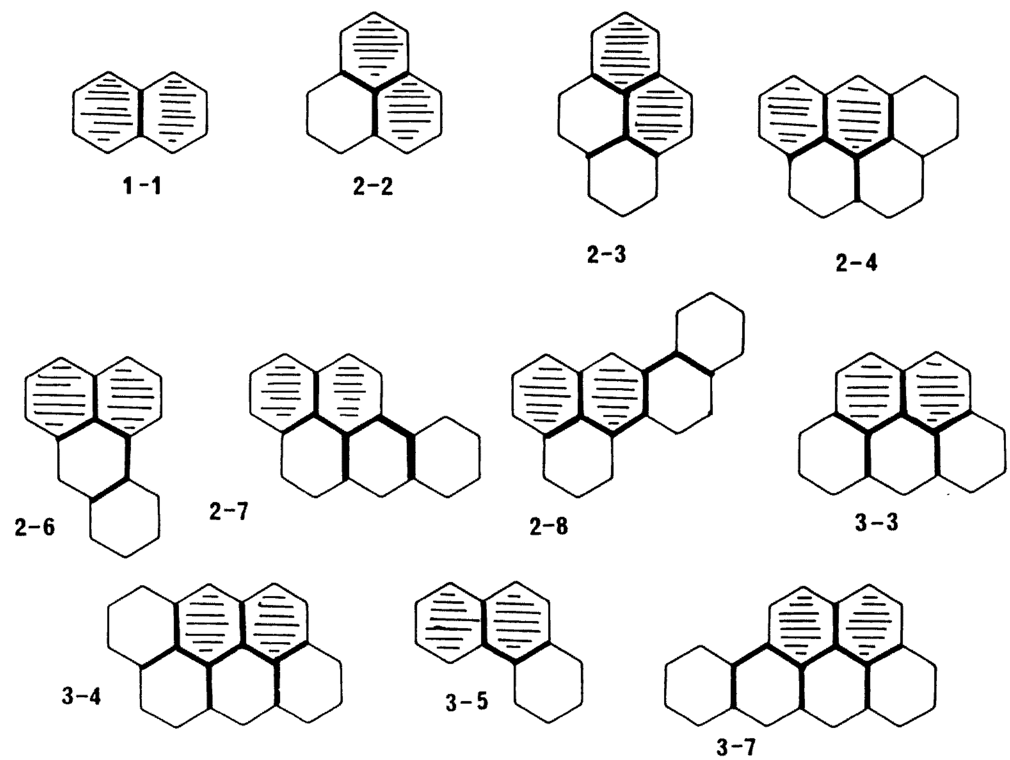


4-contact addition

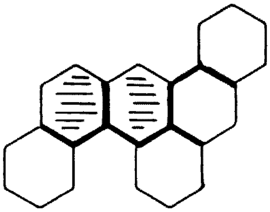
Reconstruction of a polyhex from a branching graph that is a tree: addition of a hexagon to a pair of degree-2 vertices. In principle there are four possible modes of adding hexagons, namely 1-, 2-, 3- or 4-contact addition. 1-contact addition to a pair of degree-2 vertices fails, but examples of the other three addition modes can be drawn, and are shown here by hatched hexagons.



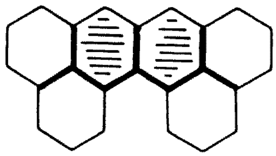
Reconstruction of a polyhex from a branching graph that is a tree: the addition of a hexagon to a pair of vertices of degree 1 / degree 1 or degree 1 / degree 2.



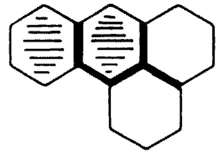
Reconstruction of a polyhex from a branching graph that is a tree: the addition of a pair of hexagons to a terminal edge. (The numbers refer to the addition mode of each hexagon (see previous diagram.) (Continued on next page.)



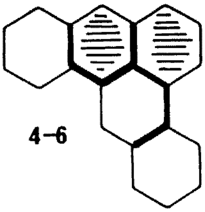
3-8



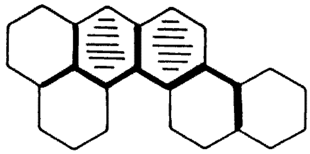
4-4



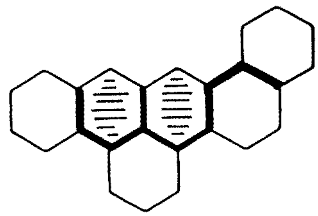
4-5



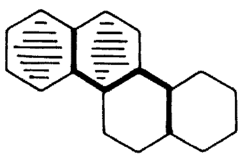
4-6



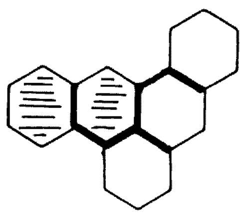
4-7



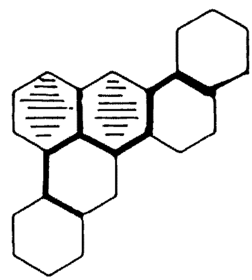
4-8



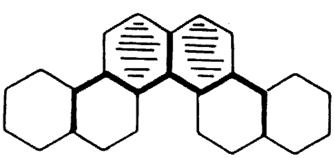
5-7



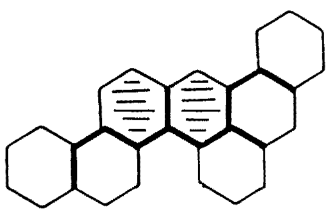
5-8



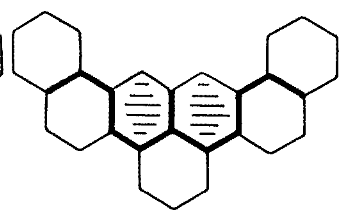
6-8



7-7



7-8



8-8

(continued)

THE RELATIONSHIP OF POLYHEX BGS TO THE DIAS "EXCISED INTERNAL STRUCTURE"

(30) The set of edges in the branching graph contains the same set of "internal edges" which Dias has used to generate an invariant (d_s) by counting the number of "tree disconnections". This was used in his periodic classification of benzenoids

[31]. The set of edges in the branching graph, however, includes any that connect two vertices of degree 3, and is not restricted to those that are internal.

(31) If a branching graph has no degree-2 vertices then, when stripped of its terminal edges, it becomes the Dias "excised internal structure" of its polyhex, e.g. refs. [26,32,33].

Note that the absence of degree-2 vertices in the branching graph appears to be a sufficient but not a necessary condition for its polyhex to be what Dias calls "strictly pericondensed", and that the presence of degree-2 vertices is associated with the presence of bay regions in such structures [34].

References

[1] E.C. Kirby, J. Math. Chem. 4 (1990) 31; 8 (1991) 77.
[2] E.C. Kirby, J. Math. Chem. 1 (1987) 175.
[3] R.B. Mallion, Proc. Roy. Soc. A 341 (1975) 429; Chem. Phys. Lett. 36 (1975) 170.
[4] J. Gayoso and A. Boucekkine, Compt. Rend. Acad. Sci. (Paris) C 272 (1971) 184.
[5] R. McWeeny, Mol. Phys. 1 (1958) 311.
[6] R.B. Mallion, Mol. Phys. 25 (1973) 1415.
[7] C.W. Haigh and R.B. Mallion, Prog. NMR Spectry. 13 (1979) 303.
[8] J. Aihara, J. Am. Chem. Soc. 101 (1979) 5913; Bull. Chem. Soc. Japan 54 (1981) 1245; 58 (1985) 1045; 59 (1986) 3781;
J. Aihara and T. Horikawa, Bull. Chem. Soc. Japan 56 (1983) 1853.
[9] A. Baba Ahmed and J. Gayoso, Int. J. Quant. Chem. 23 (1983) 71.
[10] B. O'Leary and R.B. Mallion, J. Math. Chem. 3 (1989) 323.
[11] N. Mizoguchi, Bull. Chem. Soc. Japan 60 (1987) 2005.
[12] C.W. Haigh and R.B. Mallion, Croat. Chem. Acta 62 (1989) 1.
[13] E.C. Kirby, J. Chem. Soc. Faraday Trans. 86 (1990) 447.
[14] J.R. Dias, Thermochim. Acta 122 (1987) 313; J. Chem. Inf. Comput. Sci. 31 (1991) 89.
[15] J.V. Knop, W.R. Müller, K. Szymanski and N. Trinajstić, J. Comput. Chem. 7 (1986) 547.
[16] R.J. Wilson, *Introduction to Graph Theory*, 3rd Ed. (Longman, New York, 1988).
[17] A.T. Balaban and F. Harary, Tetrahedron 24 (1968) 2505.
[18] A.T. Balaban, Pure Appl. Chem. 54 (1985) 335.
[19] I. Gutman and S.J. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons* (Springer, Berlin, 1989).
[20] N. Trinajstić, J. Math. Chem. 5 (1990) 171.
[21] N. Trinajstić, *Chemical Graph Theory*, 2nd Ed. (CRC Press, Boca Raton, 1992).
[22] I. Gutman and E.C. Kirby, MATCH 26 (1991) 111.
[23] C. Berge, *Graphs and Hypergraphs* (North-Holland, Amsterdam, 1973).
[24] L. Lovász and M.D. Plummer, *Matching Theory* (North-Holland, Amsterdam, 1986).
[25] S.J. Cyvin and I. Gutman, *Kekulé Structures in Benzenoid Hydrocarbons* (Springer, Berlin, 1988).
[26] I. Gutman, Topics Current Chem. 162 (1992) 1.
[27] E.C. Kirby, R.B. Mallion and P. Pollak, J. Chem. Soc. Faraday Trans., in press;
E.C. Kirby, Croat. Chem. Acta, in press.
[28] I. Gutman, Croat. Chem. Acta 46 (1974) 209.
[29] C.E. Soteros and S.G. Whittington, J. Math. Chem. 5 (1990) 307.

[30] E.C. Kirby, J. Math. Chem. 11 (1992) 187.
[31] J.R. Dias, J. Chem. Inf. Comput. Sci. 22 (1982) 15.
[32] J.R. Dias, J. Mol. Struct. (THEOCHEM) 137 (1986) 9.
[33] I. Gutman and J.R. Dias, in: R. Bodendiek (ed.), *Contemporary Methods in Graph Theory* (BI-Wissenschaftsverlag, Mannheim, 1990) pp. 249–259.
[34] J.R. Dias, MATCH 26 (1991) 87.