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Benzenoids with Branching Graphs that are Trees

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Benzenoid systems whose branching graphs are trees, and trees that are branching graphs of some benzenoid system, are properly characterized for the first time. An implication for the occurrence of Hamiltonian circuits is pointed out.

Key words: benzenoid system, polyhex, branching graph, tree, tree graph, benzenoid tree graph, Hamiltonian circuit.

INTRODUCTION

For any graph G containing vertices that branch (*i.e.* whose degree is greater than two) a subgraph known as the branching graph (BG) may be defined. In this subgraph appears every vertex of G that is of degree >2, together with every edge that connects a pair of such vertices, and nothing else. For a given graph, its branching graph is unique, but a given branching graph may be shared by more than one parent graph. A branching graph may or may not contain cycles, and it may or may not be connected (see Figure 1). In practice, most attention so far has been directed at branching graphs where no vertices are more than 3-valent, and this is because of the chemical importance of the many known benzenoids and other polycyclic systems that contain only trigonally hybridised (3-valent) carbon atoms and hydrogen.[1]

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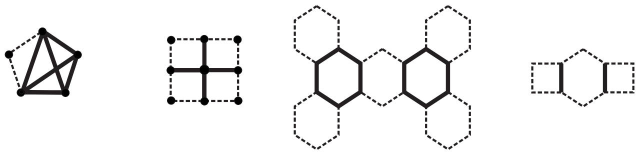


(a) (b) (c) (d)

Figure 1. Some examples of a graph G (dotted lines) and its superimposed branching graph BG (heavy lines), where BG is (a) cyclic and connected; (b) acyclic and connected; (c) cyclic and disconnected; and (d) acyclic and disconnected.

In earlier papers[2,3] we noted some 31 theorems and observations about the branching graphs of polyhexes, and this work has been extended by Hansen and Zheng,[4] and (more recently) by Chen.[5]

The concept of the branching graph was originally introduced[6–8] as a useful tool to assist both the transcription of structural information from a computer keyboard, and the understanding of certain aspects of the distribution of benzenoid structural types such as fully benzenoid (Clar type) systems. This arose from the fact that it can be of help in the location of Hamiltonian paths and cycles and other subgraphs that have no branches. Because of this it is also of some relevance to the problem of calculating π-electron ring currents in a conjugated system.[9–14]

A key property in these regards is that there is a one-to-one correspondence between the 2-factors of a polyhex and the 1-factors (*i.e.* the perfect matchings, or Kekulé structures) of its branching graph. (See reference 2 for a proof.) An implication of this to be noted in passing, is that the branching graph of a fullerene is a less useful object, because it is identical to its parent fullerene graph.

In this work we are concerned with the problem of characterizing benzenoid systems whose branching graphs are trees, and the related one of characterizing trees that are the branching graph of some (perhaps more than one) benzenoid system. This was briefly mentioned in our earlier paper,[3] but without obtaining any generally valid result. Hansen and Zheng tackled a distantly related problem, and characterized connected subgraphs of the infinite hexagonal lattice which are branching graphs of benzenoid systems.[4] In a recent work[5] Chen addressed the same more specific problem as ourselves and offered a »practical method for recognizing trees ... which can be branching graphs of benzenoids«. Chen's method, however, pertains not to trees as graphs, with undefined geometry, but to trees that are embedded in the hexagonal lattice. Such trees, obviously, conform to the geometry of this lattice and therefore they are not genuine graph-theoretic objects. In addition, Chen's characterization does seem prohibitively complicated, and yet provides hardly any information about the structure of trees which are BGs.

In this work we approach the problem from a different direction. We first characterize benzenoid systems whose BGs are trees. Then, in a relatively straightforward manner, we determine the actual structure of the associated trees.

Throughout this work a benzenoid system B, whose branching graph is a tree will be referred to as a »BT-benzenoid system« or »BT-benzenoid« and abbreviated to BTB. The respective branching graph will be called a »branching tree« and abbreviated to BT.

THE FIRST CHARACTERIZATION

We first characterize BT-benzenoids in a somewhat indirect manner.

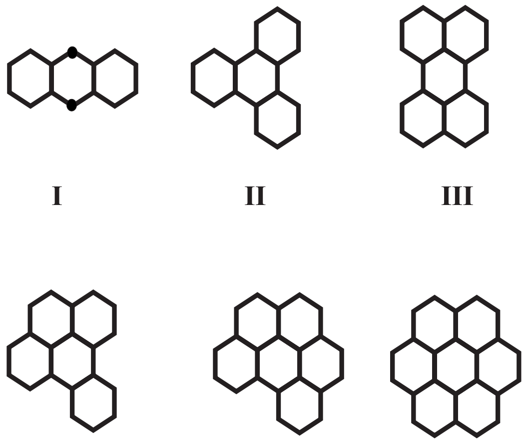
Lemma 1. *Let B be a benzenoid system and BG(B) its branching graph. Then BG(B) contains a cycle if and only if there exists a hexagon H in B having all six of its vertices in BG(B).*

Proof. We have only to prove the *only if* part, since the *if* part is trivial. If BG(B) contains a cycle, say C, then C is a simple closed curve in the plane which (by the Jordan Theorem) divides the plane into two parts: interior and exterior. Furthermore, each hexagon of B belongs to exactly one of two parts. Since B is simply connected, C is contractible (over the hexagons). Hence each hexagon in the interior of C has all of its vertices trivalent in B and thus belongs to BG(B).

We note in passing that the hexagons in the interior of C form a simply connected benzenoid which is a subgraph of BG(B).

Theorem 1. *Let B be a benzenoid system and BG(B) its branching graph. BG(B) is NOT a tree if and only if B possesses at least one of the structural details **I**, **II**, **III** (depicted in Figure 2, where the heavy dots in diagram **I** indicate vertices belonging to the perimeter of B). In other words, B is NOT a* BTB *if and only if it contains as a subgraph an anthracene fragment whose central hexagon possesses two bivalent vertices (**I**) and/or a triphenylene (**II**) and/or a perylene (**III**) fragment.*

Proof. It has been previously established (*cf.* property (11) in reference 3) that a branching graph is disconnected if and only if the underlying benzenoid system possesses a linearly annelated hexagon, see diagram **IV** in Figure 3. Clearly, the existence of a structural feature **IV** is tantamount to the existence of **I**.



I **II** **III**

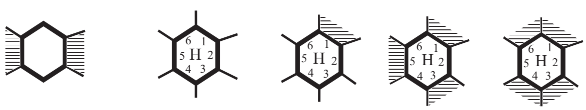
IIa **IIb** **IIc**

Figure 2. The forbidden subgraphs **I**, **II** and **III** occurring in Theorem 1. **IIa**, **IIb** and **IIc**, which can be generated from **II** or **III** by adding hexagons, are also forbidden. This contrasts with **I**, where addition of a hexagon to the central hexagon destroys this property.

For BG(B) to be cyclic, the hexagon H of B (*cf.* Lemma 1) must have all its vertices trivalent (diagram **V** in Figure 3), and this means that several hexagons are adjacent to H.

Suppose that one such adjacent hexagon is attached to H through the edge 1 (see diagram **VI**). Then the edges 2 and 6 may (but need not) belong only to the hexagon H, *i.e.* these edges need not belong to hexagons adjacent to H. If, however, they belong only to H, then two more hexagons must be adjacent to H, attached through edges 3 and 5, see diagram **VII**. In the case shown by diagram **VII**, three hexagons must be adjacent to H, attached to it through edges 1, 3 and 5; more adjacent hexagons may (but need not) be attached also through edges 2 and/or 4 and/or 6.

If a hexagon is attached to H also through the edge 6, then the edges 2 and 5 may (but need not) belong only to the hexagon H. If, however, they be-



IV **V** **VI** **VII** **VIII**

Figure 3. Diagrams used in the proof of Theorem 1.

long only to H, then two more hexagons must be adjacent to H, attached through edges 3 and 4, see diagram **VIII**. In the case shown by diagram **VIII**, four hexagons must be adjacent to H, attached to it through edges 1, 3, 4, and 6; additional hexagons may (but need not) be attached also through edges 2 and/or 5.

The situations shown by diagrams **VII** and **VIII** (tantamount to the existence of subgraphs **II** and **III**, respectively) are the only cases (disregarding rotations by 60 and 120 degrees) when all the six vertices of H in B are trivalent. Taken with the previously noted prohibition of fragment **I**, Theorem 1 follows.

Another way to formulate Theorem 1 is as:
Corollary 1.1. *B is a BT-benzenoid system if and only if neither fragment* ***I*** *nor* ***II*** *nor* ***III*** *is contained in B.*

From this we see that a BTB must not contain any of the three particular »forbidden subgraphs«. Results of this kind are often encountered in graph theory; two famous ones are Beineke's forbidden-subgraph characterization of line graphs (see reference 15, Chapter 8), and Kuratowski's theorem (see Ref. 16, p. 225) which states that a graph is planar if it contains no subgraph that is, or can be contracted to, either K_5 or $K_{3,3}$.

In the case we are considering, we notice that there is a subtle difference between forbidden subgraph **I** and forbidden subgraphs **II** and **III** – they are forbidden for different reasons; **I**, because it disconnects the branching graph, and the others because they generate cyclic branching graphs. Addition of a single hexagon to **I** destroys its forbidden property, whereas we can go on adding hexagons to **II** or **III** to generate other forbidden subgraphs (**IIa**, **IIb** and **IIc**) although, because these contain **II** or **III**, we need not include them explicitly in the prohibition.

At this point we should remind ourselves that a benzenoid system, by definition, is simply connected. Figure 4, for example, shows a structure de-

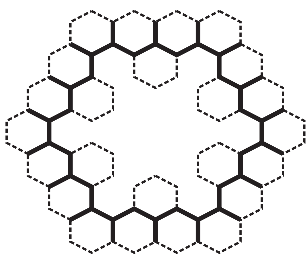


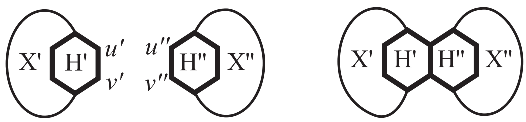
Figure 4. This structure has a branching graph that contains a cycle and yet it contains none of the forbidden subgraphs **I-III** shown in Figure 2. However, it is not simply connected, and is therefore not a benzenoid system. (It is in fact a coronoid.)

void of any of the forbidden subgraphs **I**, **II** or **III**, and whose branching graph is cyclic, but, it is not simply connected, and therefore not a benzenoid system.

Knowing what BTBs must not contain, it is not difficult to draw some inferences about their actual structure.

THE SECOND CHARACTERIZATION

Definition 1. *Let B′ be a benzenoid system and H′ one of its hexagons possessing two adjacent divalent vertices* u' *and* v'. *Let B″ be another benzenoid system and H″ one of its hexagons, possessing two adjacent divalent vertices* u'' *and* v''. *Let the benzenoid system B, be obtained by identifying* u' *with* u'' *and* v' *with* v''. *Then B is said to be the edge-join of B′ and B″, or to be edge-decomposable into B′ and B″. This edge-decomposition is said to involve the edges (*u',v'*) and (*u'',v''*).* This definition is illustrated in Figure 5.



B′ *B″* *B*

Figure 5. Illustrating Definition 1: the benzenoid system B is the edge-join of B' and B'', *i.e.*, B is edge-decomposable into B' and B''.

Definition 2. *A benzenoid system is said to be prime if it is not edge-decomposable into smaller benzenoid systems*.

As a direct consequence of Corollary 1.1 we now have:

Corollary 1.2. *The benzenoid systems shown in Figure 6 are the only prime BTBs.*

Definition 3. *Let B be a benzenoid system and (*u,v*) its edge connecting two divalent vertices* u *and* v. *Let B′ be a benzenoid system obtained from B by attaching a hexagon to its edge (*u,v*). The edge (*u,v*) of B is said to be BT-fit if both B and B′ are BT-benzenoid systems.*

In Figure 6 are indicated all the BT-fit edges of the prime BTBs, a fact which easily may be checked case-by-case.

The following characterization of BTBs is based on Corollary 1.2 and the observation that by attaching hexagons to a prime BTB we obtain another BTB only if the hexagons are joined through BT-fit edges (indicated in Fig-

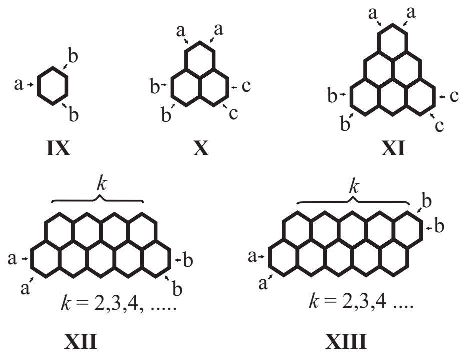


Figure 6. The compact BT-benzenoid systems and their BT-fit edges. (Structure **X** can be regarded as a special case of **XII**, where $k = 1$)

ure 6). Several hexagons may be attached, but only one to the edges marked by the same letter. Extending this constructive reasoning we arrive at:

Theorem 2. *Let B be a benzenoid system and G its branching graph. Then G is a tree if and only if B is either one of the prime BTBs (depicted in Figure 6) or is edge-decomposable into these prime BTBs, involving only BT-fit edges (indicated in Figure 6; no more than one among edges marked by the same letter).*

In Figure 7 are given some examples illustrating Theorem 2.

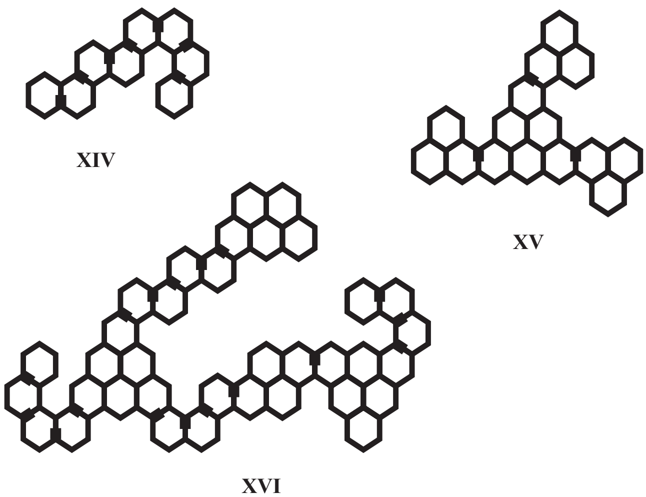


Figure 7. Examples of non-prime BT-benzenoid systems; the edges involved in their edge-decomposition into prime BT-benzenoids are marked by lines with added blocks; these are BT-fit edges of the respective prime components.

Corollary 2.1 (previously reported in reference 3 as property (9)). *A catacondensed BTB is unbranched (*i.e. *it is a chain of hexagons) and does not possess linearly annelated hexagons.*

THE STRUCTURAL CHARACTERIZATION OF BRANCHING TREES

Once the structure of BT-benzenoid systems is known (*via* Theorem 2), it is straightforward to determine the structure of branching trees. The considerations that follow can be understood as just a translation of Theorem 2 (expressed in terms of benzenoid systems) into terms pertaining to branching trees.

First of all notice that if a connected benzenoid system B is the edge-join of B' and B'' (*cf.* Figure 5), then the branching graph of B is obtained from the branching graphs of B' and B'', by connecting them *via* two additional vertices in one of the two modes shown in Figure 8.

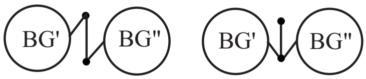


Figure 8. The structure of the branching graph of a benzenoid system B, being the edge-join of the systems B' and B'' (see Figure 3); BG' and BG'' are the branching graphs of B' and B'', respectively.

Based on this observation we define a class of so-called W-trees.

Definition 4. *Let Γ be the graph consisting of two vertices,* u *and* v*, connected by an edge. For* n = *1,2,3,...,* *take* n *copies of Γ, denoted by Γ_1, Γ_2,..., Γ_n; the vertices of Γ_i are labelled by* u_i *and* v_i. *Γ_1 itself is a W-tree (the 2-vertex W-tree). For* n > *1 and* i = *1,2,...,*n–*1 connect (by one edge) either* u_i *or* v_i *with either* $u_{\{i+1\}}$ *or* $v_{\{i+1\}}$. *Each graph obtained in this manner is a W-tree* (possessing $2n$ vertices).

The vertices u_1,v_1 and u_n,v_n are the left and right terminal vertices of the respective W-tree. Examples of W-trees are given in Figure 9. BT(**XIV**) in Figure 11 is another example.

Theorem 3a. *If the branching graph of a catacondensed benzenoid system is a tree, then it is a W-tree.*

The opposite is not strictly true, but does apply if helicenic species are allowed. Hence:

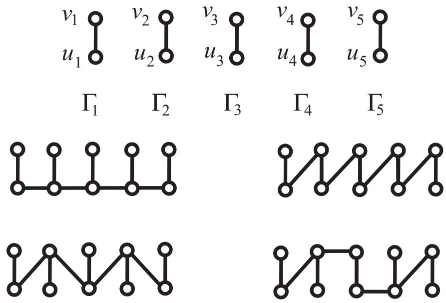


Figure 9. Labelling of the vertices of W-trees (for the case where $n = 5$) and four examples of 10-vertex W-trees.

Theorem 3b. *Every W-tree is the branching graph of a catacondensed benzenoid system or helicenic benzenoid system.*

Using the W-tree-concept we are now able to give a complete characterization of branching trees.

Theorem 4. *Let the tree T be the branching graph of some benzenoid system. Then T is either*

*(a) a W-tree (*cf. *Figure 9), or*

(b) the branching tree of one of the prime BTBs (depicted in Figure 10), or

(c) is obtained by joining trees of type (b) by means of W-trees, or

(d) is obtained by attaching W-trees to trees of type (b) and (c).

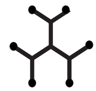
In Figure 11 are given a few examples of branching trees. Trees of type (c) and (d) are obtained by inserting edges between vertices marked in Figure 10 and left and/or right terminal vertices of W-trees.

Such edges connect one (either left or right) terminal vertex of a W-tree and a vertex of BT(**X**), BT(**XI**), BT(**XII**) or BT(**XIII**) marked in Figure 10 by heavy dots. To each such marked vertex at most one new edge can be attached. Exceptionally, in the case of acenaphthenyl (**X**) two new edges may be attached to one marked vertex (*cf.* diagram BT(**XVIII**) in Figure 12), but not more than three edges to all the three marked vertices. For an illustration see Figure 12.

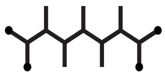
From Theorems 3 and 4 we see that branching trees are graphs with a quite complicated structure, but they enable us to now make an observation pertaining to the difficult problem of characterizing benzenoid systems that are Hamiltonian.

Theorem 5. *If the branching graph of a benzenoid system is a tree, then that benzenoid system will have a Hamiltonian circuit if and only if it is catacondensed.*

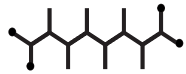
BT (**X**)



BT (**XI**)

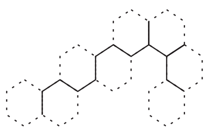


BT (**XII**)

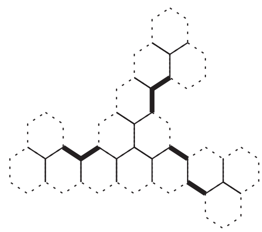


BT (**XIII**)

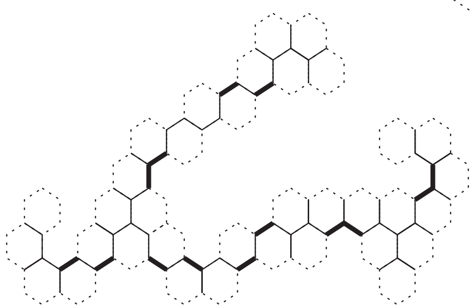
Figure 10. The branching trees of the compact BT-Benzenoids **X-XIII** shown in Figure 6; the vertices through which these trees can be joined with W-trees are marked by heavy dots. (The branching graph of the single hexagon (**IX**) is not shown, because this is the null graph.)



BT (**XIV**)



BT (**XV**)



BT (**XVI**)

Figure 11. The branching trees of the BT-benzenoids **XIV-XVI** from Figure 7; the branching-trees (solid lines) are shown embedded in their associated benzenoid systems (dotted lines), and the edges by means of which the branching trees of the compact BTBs and of W-trees are joined together are marked by heavy lines.

Proof: Catacondensed benzenoid systems have no internal vertices and thus are well known to be Hamiltonian (see reference 17, p. 163). A Benzenoid system has a 2-factor if and only if its branching graph has a perfect matching.[2,18]

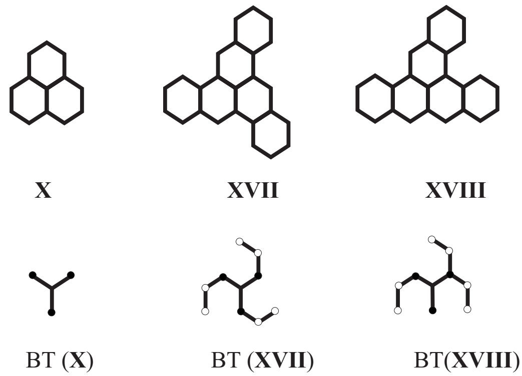


Figure 12. At most three new edges can be attached to the marked vertices of the branching tree BT(**X**) of acenaphthenyl, either in a (1,1,1)-mode, as in BT(**XVII**), or in a (2,1,0)-mode, as in BT(**XVIII**).

A forest of 2-vertex trees, n in number, has a perfect matching, and conversion to any possible $2n$-vertex W-tree (Definition 4) does not affect this, *i.e.* any W-tree also has a perfect matching.

It may be seen by inspection that no branching graph of any possible BTB (Figure 6) has a perfect matching; at best (for BTB(**X**) for example) it has a single defect matching. Furthermore, because a W-tree does have a perfect matching, it can only propagate a defect when joined to the branching graph of a BTB; it cannot terminate it. The only way to do this would be to connect the sequence head-to-tail in the final step, but then it would no longer be a tree. It follows that the only branching trees encompassed by Theorem 4 that have perfect matchings are the W-trees, the BTs of catacondensed benzenoids (Theorem 3).

CONCLUSIONS

We have obtained a full characterization of those benzenoid systems whose branching graphs are trees, and of these trees themselves. Arising from this work we offer a small addition to knowledge of the conditions for a benzenoid system to have a Hamiltonian circuit. This problem is known to be difficult, and no one has yet succeeded in defining sufficient and necessary conditions for an arbitrary graph to be Hamiltonian, yet it remains one of great practical importance and interest; in efficient utilization of transport and communication systems of all kinds, for example, as well as sometimes in chemical information transmission as discussed.

The aim of this study was to characterize benzenoid systems whose branching graphs are trees. However, with minor modifications we could characterize also the helicenic systems with the same property. Indeed, Theorems 1, 2, 3a, 4, and 5 remain valid if »helicenic system« is substituted for »benzenoid system«. The authors thank one of the anonymous referees for pointing out this detail.

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SAŽETAK

Benzenoidi čiji su razapinjući grafovi stabla

Ivan Gutman i Edward C. Kirby

Po prvi put su karakterizirani benzenoidi čiji su razapinjući grafovi stabla, te stabla koja su razapinjući grafovi nekog benzenoida. Ukazano je na važnost postojanja hamiltonskog prstena u rješavanju gornjeg problema.