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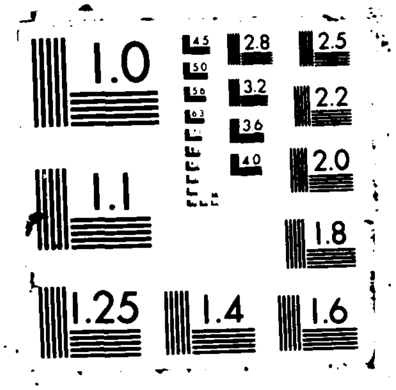
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Some Applications of Caterpillar (=Gutman = Benzenoid) Trees in Chemistry and Physics

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Relations of caterpillar trees (also called Gutman trees and benzenoid trees) to other mathematical objects such as polyhex graphs, Clar graphs, king polyominos, rook boards and Young diagrams are discussed. Potential uses of such trees in data reduction, computational graph theory, and in the ordering of graphs are considered. Combinatorial and physical properties of benzenoid hydrocarbons can be studied via related caterpillars. Thus it is possible to study the properties of large graphs such as benzenoid (= polyhex) graphs in terms of much smaller tree graphs. Generation of the cyclic structures of wreath and generalized wreath product groups through the use of caterpillar trees is illustrated.

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Some Applications of Caterpillar (=Gutman = Benzenoid) Trees in Chemistry and Physics

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Abstract

Relations of caterpillar trees (also called Gutman trees and benzenoid trees) to other mathematical objects such as polyhex graphs, Clar graphs, king polyominos, rook boards and Young diagrams are discussed. Potential uses of such trees in data reduction, computational graph theory, and in the ordering of graphs are considered. Combinatorial and physical properties of benzenoid hydrocarbons can be studied via related caterpillars. Thus it is possible to study the properties of large graphs such as benzenoid (= polyhex) graphs in terms of much smaller tree graphs. Generation of the cyclic structures of wreath and generalized wreath product groups through the use of caterpillar trees is illustrated.

Key words
Graph Theory
Caterpillar trees (Gutman trees)
Rook boards
Clar Graphs
Young Diagrams
Wreath-product groups

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1. Historical Introduction

The simplest way of defining a caterpillar tree, P_n (m_1, m_2, ..., m_n), is through the concept of the derivative of the graph.[1] Thus when all the end points of a graph G are deleted another graph G′ results called the derivative of G. A caterpillar tree is defined to be a tree graph the derivative of which is a path. The name caterpillars was suggested by A. Hobbs.[2] Thus a caterpillar tree P_n(m_1, m_2, ..., m_n) may be constructed by the addition of m_1 monovalent vertices to the the first vertex, v_1 of path, P_n, m_2 monovalent vertices to v_2 of P_n and so on. An example of a caterpillar tree and another of a noncaterpillar together with other graphs is shown in Fig. 1. It seems that Harary and Schwenk were among the first to study these trees in the mathematical literature.[1,3,4]

In chemistry the use of these trees resulted from studying the topological properties of benzenoid hydrocarbons, namely resonance relations among individual hexagons of a benzenoid system.[5] Two hexagons, in a benzenoid hydrocarbon are called resonant if an (aromatic) sextet (i.e. a set of three circularly conjugated double bonds) can be drawn in both of them such that the rest of the carbon atoms are spanned either by a double bond or by a sextet of electrons. Gutman[5] represented such resonance relations among hexagons of a benzenoid system by the edges of a caterpillar tree: two edges in a caterpillar tree are incident if and only if the corresponding hexagons in the benzenoid system are nonresonant. Thus the tree given by P_4 (3,0,4,2) corresponds to the benzenoid hydrocarbon B(P_4(3,0,4,2)) drawn in Fig. 1. There is a one-to-one correspondence between the labeling of the edges of the caterpillar and those of the hexagons of the benzenoid system. Explicitly these terms were considered in chemistry (synonomously under the name "Gutman trees") in three recent papers by this author.[6-8]

It is amazing that nearly all graphs that played an important role in what is now called "chemical graph theory" may be related to caterpillar trees. For this reason such objects are of great importance for understanding and simplifying combinatorial properties of much more complicated graphs. Three main areas involve uses of these trees, viz., *computational* methods, *ordering*[9] and *data reduction*.[10] It is convenient to give now important definitions for the development of this treatment.

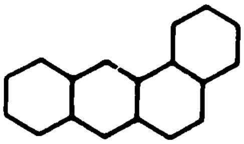
2. Definitions of Important Terms

2.a Graphs, Lattices and Diagrams

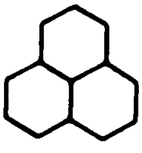
A caterpillar tree might be associated with the following objects:

2.a.1 Polyhex Graph[11] B

This term was first introduced by Hosoya et al.[11] to mean a graph composed only of hexagons which have an even number 2ℓ of points and thus can be spanned by disjoint lines. The polyhex B is one such type while B′ is not included in this definition



B



B′

Obviously the number of ways in which B can be spanned by the ℓ disjoint lines is well known in organic chemistry as the number of *Kekulé structures*[12] and is known in mathematics as the number of *perfect matchings*,[13] a synonym for a famous problem in *dimer statistics*.[14] Now a word on nomenclature:

A molecular network which is entirely composed of hexagons is called benzenoid.

If no three hexagons have a common atom, the system is called catacondensed. If every hexagon of a catacondensed system has at most two neighboring hexagons, it is said to be nonbranched. If there is at least one hexagon in a catacondensed hydrocarbon that is surrounded by three other hexagons it is said to be branched. If in a polyhex graph at least one vertex is common to three hexagons it is called pericondensed.

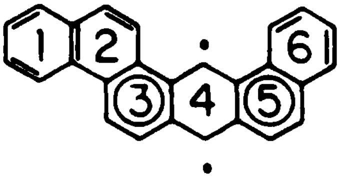
2.a.2 Clar graphs[15,16]

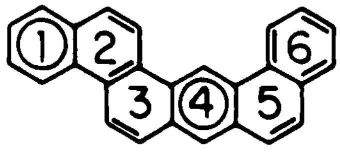
Gutman[15] seems to be the first who introduced this term in chemistry and the concept was later developed by Gutman and this author.[16] For nonbranched benzenoids a Clar graph is simply the line graph[17] of a caterpillar tree. In fact it can be seen that every caterpillar is associated with a Clar graph (c.f. Fig. 1).

For branched benzenoid hydrocarbons, however, no caterpillar tree is defined, nevertheless, a Clar graph can be defined[15] in the following way. Let h_1, h_2, ..., h_n be the hexagons of the branched system. Then the vertices of its Clar graph are v_1, v_2, ..., v_n such that v_i is connected to v_j only if h_i and h_j are nonresonant.

Relation between caterpillar trees, Clar and polyhex graphs

At this point it is important to digress on the relation between the three types of graphs defined above. We start by considering the polyhex graph again. First we observe that two hexagons in a polyhex may or may not be resonant. An illustration is considered below



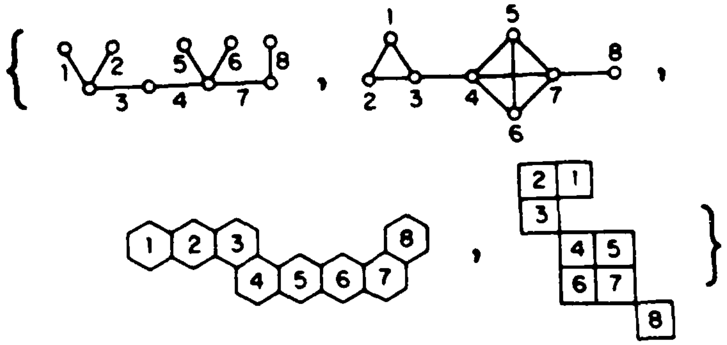


Thus hexagons 3 and 5 at left are *nonresonant* while 1 and 4 at right are.

Gutman demonstrated[5] the following fact: Every nonbranched (catacondensed) polyhex graph, B, which contains n hexagons is associated with a caterpillar tree, T, containing n + 1 vertices such that: two (or more) *incident* edges in T correspond to two (or more) *nonresonant* hexagons in B and *vice-versa*, i.e. two (or more) *nonincident* edges in T correspond to two (or more) *resonant* hexagons in B. For example consider $B(P_4(3,0,4,2))$ of Fig. 1 and let h_i refer to the *ith* hexagon. One observes that linearly fused rings cannot be resonant. For example *none* of the hexagons in each of the following sets can be *resonant*: $\{h_1, h_2, h_3, h_4\}$; $\{h_4, h_5\}$; $\{h_5, h_6, h_7, h_8, h_9, h_{10}\}$; $\{h_{10}, h_{11}, h_{12}\}$. Similarly we say: *all* the edges in T in each of the following sets are *adjacent*: $\{e_1, e_2, e_3, e_4\}$; $\{e_4, e_5\}$; $\{e_5, e_6, e_7, e_8, e_9, e_{10}\}$; $\{e_{10}, e_{11}, e_{12}\}$. This one-to-one correspondence extends to the *vertices* of the Clar graph: All the vertices in each of the following sets are *adjacent* (refer to Λ $(P_4\ (3,0,4,2)))$: $\{v_1, v_2, v_3, v_4\}$; $\{v_4, v_5\}$; $\{v_5, v_6, v_7, v_8, v_9, v_{10}\}$; $\{v_{10}, v_{11}, v_{12}\}$. These fundamental relations have important implications in understanding the combinatorial structures of benzenoid hydrocarbons as we shall see later. Because of this relation to benzenoid systems, caterpillar trees will be also called *benzenoid trees.*

2.a.3 *King Polyomino Graphs*[18] p

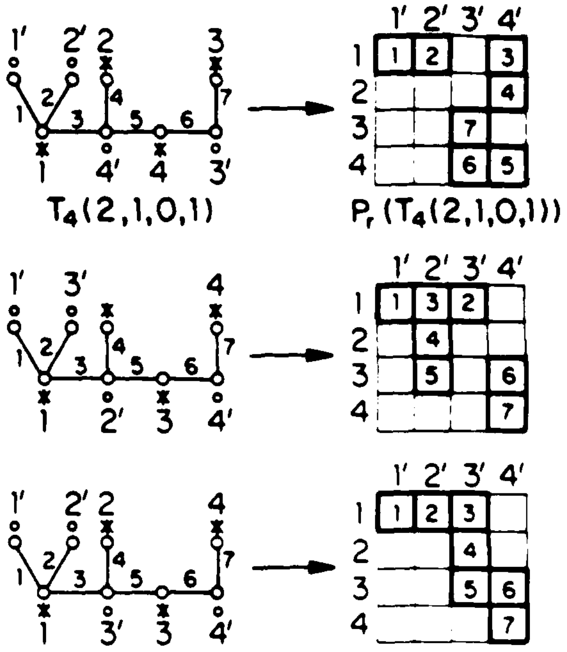
Consider a rectangular lattice composed of cells arranged in certain number of rows and columns. Such graphs are called polyominos or square animals. Two cells in a polyomino are defined[18] to be adjacent if they share at least one vertex. The maximum number of adjacent cells is therefore four. This corresponds to four *nonresonant* hexagons annellated in a linear fashion. Because of this fact king polyominos might be made to correspond to polyhex graph containing linear segments which are *no more* than four-hexagons long. As an illustration we consider the following set of graphs whose caterpillar tree is $P_4\ (2,0,2,1)$;



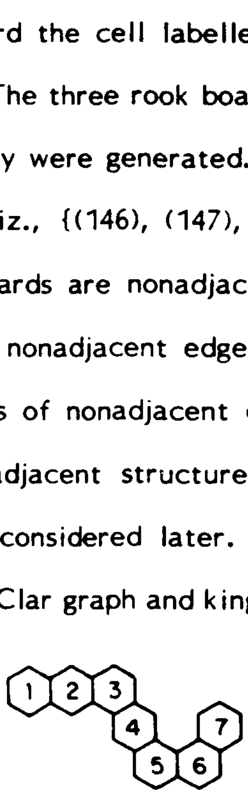
Therefore for every subset of adjacent cells there is a corresponding subset of nonresonant hexagons, incident edges and adjacent vertices.

2.a.4 Rook Boards[19] P_r

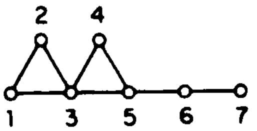
A rook board is a subset of cells of a j x j chessboard. Godsil and Gutman demonstrated[19] that every bipartite[20] graph G is associated with a rook board such that a cell c_{ij} (which is located in the ith row and jth column of the board) exists only if vertices i and j are connected in G. We illustrate how rook boards are constructed which correspond to bipartite caterpillar trees in the following chart



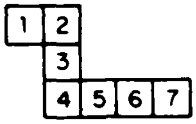
In the above Chart three different labellings of the bipartite caterpillar generated three different rook boards. These are shown by the heavily outlined squares. In a rook board two cells are adjacent if they share the same row and column. For example in the top board the cell labelled 3 is adjacent to 1,2,4,5 while cells in 4 and 7 are not adjacent. The three rook boards preserve the combinatorial counts in the caterpillar form which they were generated. Thus, e.g. there are six triplets of nonadjacent edges in that tree, viz., {(146), (147), (157), (257), (247), (246)}. The same subsets of cells in all three boards are nonadjacent. Similarly one can easily demonstrate that there are 13 sets of nonadjacent edges, each of cardinality 2 in the tree which correspond to 13 such sets of nonadjacent cells in any of the above boards. Such combinatorial counts of nonadjacent structures represent the coefficients of counting polynomials which will be considered later. Idential combinatorial counts exist in the associated polyhex graph, Clar graph and king polyomino graph, all shown below



$B(T_4\ (2,1,0,1))$



$\Lambda(T_4(2,1,0,1))$



$P\ (T_4(2,1,0,1))$

There are one-to-one correspondences between the labellings of the edges of T_4 (2,1,0,1), the hexagons of B, the vertices of Λ and the cells of P_r. Thus a knowledge of nonadjacent edges in T yields details of nonadjacent structures in other graphs, namely, polyhex graph, Clar graph, king and rook polyominos.

2.b Polynomials and Nonadjacent Structures

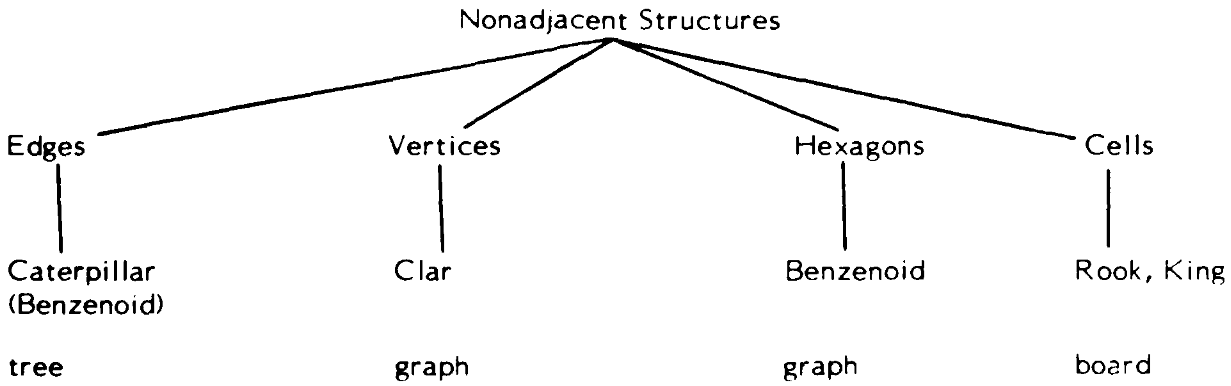
All polynomials of caterpillar trees and related graphs and lattices are combinatorial descriptors of the "nonadjacent structures" in a given object. It seems that Hosoya[21] was the first to introduce the concept of a nonadjacent structure in chemistry. For a graph, G, he defined a counting polynomial, H(G;x) by

$$H(G;x) = \sum_{k=0}^{m} p(G;k)\, x^k \qquad (1)$$

where p(G;k) is the number of ways of selecting k nonadjacent edges in G (i.e. k edges in which no two of them are adjacent). The term p(G;k) is called the number of k-matchings in G. Conveniently in H(G;x) (and in all other combinatorial polynomials) p(G;o) is taken to be unity and m is the maximal value of k. A more general expression of such polynomials[6,7] is given by Eq. (2), viz.,

$$\mathcal{F}(G;x) = \sum_{k}^{\text{max. }k} \rho\, \Theta(G;k)\, x^{f(k,n)} \qquad (2)$$

where ρ, $\Theta(G;k)$ and $f(k,n)$ are all functions of the particular polynomial. Table 1 lists several polynomials of some use in chemistry. As an illustration we consider the sextet polynomial[22] of a benzenoid system, $\sigma(B;x)$. This important polynomial plays quite a significant role in the chemistry of benzenoid hydrocarbons[23] and was first defined by Hosoya and Yamaguchi[22] as a combinatorial enumeration of the number of Kekulé structures of a benzenoid hydrocarbon. As can be inferred from Table 1 and Eq. (2), $\rho = 1$ and $f(k,n) = k$ for the sextet polynomial. Further, the generating function[24] is given by $r(B,k)\, x^k$ where r(B,k) is called the kth resonant number of the polyhex graph of the benzenoid system B. It measures the number of selections of k mutually resonant and disjoint hexagons in B. The "nonadjacent structures" of Table 1 may be depicted from the following diagram



The following identities can easily be written

$$H(T_4(2,1,0,1);x) = \omega(\Lambda(T_4(2,1,0,1);x)) =$$

$$\sigma(B(T_4(2,1,0,1);x)) = K(P_r(T_4(2,1,0,1);x)) =$$

$$K(P(T_4(2,1,0,1);x)) = 1 + 7x + 13x^2 + 6x^3 .$$

Naturally when we set $x = 1$ in the generating function we arrive at the number of Kekulé structures, $K(B) \equiv K$, a problem which is continuously being the focus of interest[25] despite its early history in chemical combinatorics.[26] Thus a knowledge of the counting polynomial of a given caterpillar leads to other polynomials such as sextet, independence, color, king and rook polynomials (if the latter two boards exist). The above treatment which applies to nonbranched benzenoid hydrocarbons can easily be extended to other systems as in the following.

2.c Branched Systems

By the application of the appropriate recursive relations of the sextet polynomial[23] one can associate a "pseudobenzenoid" tree (i.e. a benzenoid tree containing a variable x) with virtually any benzenoid hydrocarbon. The principle is simple: choose any row of hexagons and divide the set of Kekulé patterns[23] into the set of distinctive cases so that each vertical line in that row is chosen double. Caution should be taken for the possibility that the chosen double and the resultant fixed double bonds might produce a proper sextet[27] by assigning double bonds to the remaining skeleton. The sextet polynomial of the branched benzenoid hydrocarbon can be written in terms of polynomials of nonbranched systems. The nonbranched fragments can then be transformed into caterpillar trees whose counting polynomials are identical to the sextet polynomials of the nonbranched polyhex graphs. The algorithm is illustrated in Fig. 2 for a branched system, where the resulting pseudobenzenoid tree is shown in braces.

3. Benzenoid trees and Computation

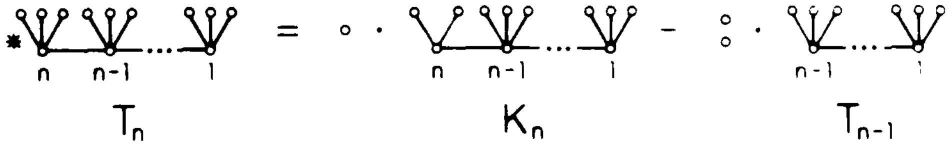
If the matching polynomial and/or the counting polynomial of a benzenoid tree is known all other polynomials of related graphs in Table 1 become immediately available. Now the matching and counting polynomials are related to each other as[28]

$$\alpha(T;x) = x^{N} H(T, -x^{-2}); \tag{3}$$

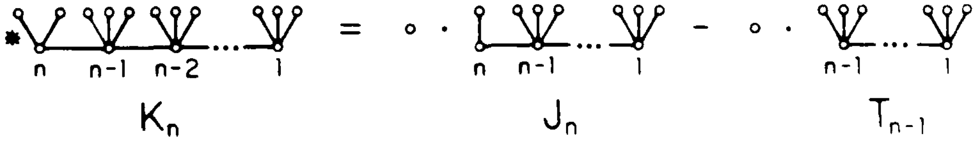
$$H(T;x) = i^{-N} x^{N/2} \alpha(T; ix^{-\frac{1}{2}}) \tag{4}$$

where N is the number of vertices in the given caterpillar tree. Using elegant operator algebra defined by Hosoya and Ohkami[23,28] it is possible to compute either functions (3) and/or (4) for families of caterpillar trees. As an illustration we calculate the matching polynomials of the family of caterpillars of $P_n(3,3, \ldots, 3)$ (where the 3's are repeated n times). We apply the recursion[29] to the starred edge as follows:

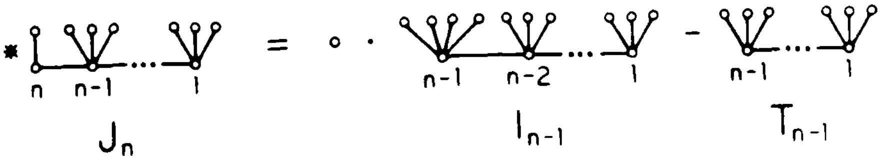
(1)



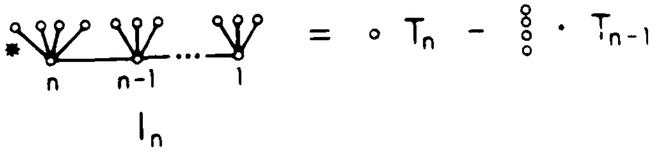
(2)



(3)



(4)



Defining the step-up operator $\hat{O}$ such as

$$\hat{O}\, T_n = T_{n+1} \tag{5}$$

Steps (1)-(4) can be re-written in the following form:

$$\begin{aligned} (\hat{O} + x^2)\; & T_{n-1} = xK_n - 0\, J_n - 0\, I_{n-1} = 0 \\ x\; & T_{n-1} + K_n - xJ_n - 0\, I_{n-1} = 0 \\ & T_{n-1} + 0\, K_n + J_n - x\, I_{n-1} = 0 \\ (x^3 - \hat{O}x)\; & T_{n-1} + 0\, K_n + 0\, J_n + \hat{O}\, I_{n-1} = 0 \end{aligned} \tag{6}$$

A nontrivial solution of (6) requires that

$$\begin{vmatrix} (\hat{O} + x^2) & -x & 0 & 0 \\ x & 1 & -x & 0 \\ 1 & 0 & 1 & -x \\ (x^3 - \hat{O}x) & 0 & 0 & \hat{O} \end{vmatrix} = 0 \tag{7}$$

i.e.

$$\hat{O}^2 + (3x^2 - x^4)\hat{O} + x^6 = 0 \tag{8}$$

Application of 8 on T_n leads to

$$T_{n+2} + (3x^2 - x^4)T_{n+1} + x^6 T_n = 0 \tag{9}$$

It is easy to show that for the general case, T_n (m,m, ..., m), the operatar eqn. 8, becomes:

$$\hat{O}^2 + (mx^{m-1} - x^{m+1})\,\hat{O} + x^{2m} = 0 \tag{10}$$

Using Eq. (10) and the following two identites:

$$\alpha(T_1(1);x) = x^2 - 1; \qquad \alpha(T_2(1,1);x) = x^4 - 3x^2 + 1$$

then repeated application of eqn. (10) (for m = 1) leads to

$$\alpha(T_8(1,1,1,1,1,1,1,1);x) \quad = \alpha(T_8(1^8);\, x) =$$

$$x^{16} - 15x^{14} + 74x^{12} - 290x^{10} + 258x^8 - 290x^6 + 74x^4 - 15x^2 + 1 \tag{11}$$

The graphs of this polynomial are shown in Fig. 3. Using relations (3) or (4) we can write the following identities (See Table 1):

$$\begin{aligned} &H(T_8(1^8);x) = \omega\,(\Lambda(T_8(1^8);x)) = \sigma(B(T_8(1^8);x)) \\ &= K(P(T_8(1^8);x)) = K(P_r(T_8(1^8);x)) \\ &= 1 + 15x + 74x^2 + 290x^3 + 258x^4 + 290x^5 + 74x^6 + 15x^7 + x^8 \end{aligned} \tag{12}$$

So we know immediately, e.g., that there are 290 ways of placing 3 or 5 nonattacking kings on the chessboard shown in Fig. 3. It is interesting to observe that there is only one way of selecting a subset of nonadjacent structures of maximum cardinality (= 8 in this case.) Polynomials of such types as counting, matching, etc. of graphs are symmetric in the sense of Eq. (13), viz.,

$$a_i = a_{N-i} \tag{13}$$

where N is the number of vertices in T (or N-1 = the number of hexagons in B = number of vertices in Λ etc.). Benzenoid hydrocarbons for which eqn. (13) holds (i.e. with a "symmetric" sextet polynomial) are known to have a single sextet formula (i.e. a single Clar representation[30]). For such types the number of aromatic sextets they contain is very close to the number of sextet-type resonance interactions per Kekulé structure.[31] This last statement is known as Aihara's conjecture.[6,31] The importance of Aihara's observation is because it specifies a condition of the benzenoid hydrocarbon in which case the simple Clar sextet formalism[30] roughly estimates its Dewar-type resonance energy[32] Gutman[33] commented on Aihara's conjecture by defining a function F(B) by

$$F(B) = M(B)\,K(B) - 2 \sum_{i}^{h} K(B - H_i) \tag{14}$$

where M(B) = max. k = the maximum cardinality of a set of mutually resonant but disjoint aromatic sextets in the benzenoid graph and K(B) is its Kekulé count. The summation of the second term is taken over all hexagons, H_i, of B where h is the total number of H_i. Gutman specified Aihara's condition that the hydrocarbon be represented by a single sextet formula by having

$$r(B; \max.k) = 1 \tag{15}$$

Fig. 4 shows an example of a hydrocarbon which satisfies Aihara's conjecture and another that does not. Furthermore, Gutman restated Aihara's postulate by defining F(B) = 0 whenever eqn. (15) holds. Benzenoid hydrocarbons for which F(B) vanishes define the "best conditions" where nearly all existing resonance-structure theories apply, viz., Clar's,[30] Dewar's[32] conjugated circuits theory of Randić (34) as well as the structure-resonance theory of Herndon.[35] In fact all such theories coincide for benzenoid systems for which Eq (15) applies.

For benzenoid trees which do not possess elements of symmetry or which do not belong to a given periodic network of trees the method of Balasubramanian and Randić[36] becomes particularly suitable for computation of $\alpha(T;x)$. For example for the caterpillar tree P_4 (2,0,2,1) shown above we have the following identities

The quotient tree, $Q = P_4$

$$\alpha_1 = \alpha_3 = \alpha(T_1(2)) = x^3 - 2x \text{ thus } \alpha_1' = \alpha_3' = x^2$$
$$\alpha_2 = (P_1(0)) = x; \ \alpha_2' = 1$$
$$\alpha_4 = x^2 - 1; \quad \alpha_4' = x \qquad (16)$$

From the adjacency matrix of Q, $\alpha(T;x) = \alpha(P_4(2,0,2,1);x)$ is given by the following determinant

$$\begin{vmatrix} -(x^3 - 2x) & x^2 & 0 & 0 \\ 1 & -x & 1 & 0 \\ 0 & x^2 & -(x^3 - 2x) & x^2 \\ 0 & 0 & x & -(x^2-1) \end{vmatrix} \qquad (17)$$

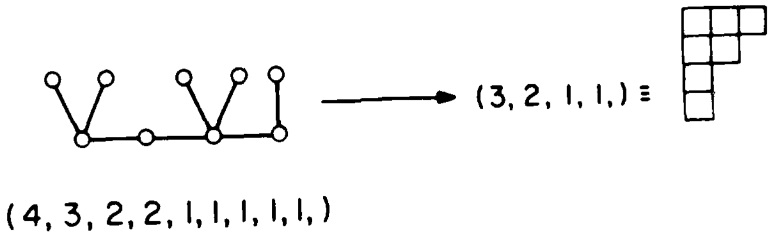
In the above notation the primed letter denotes the matching polynomial of a type, (such as $T_1(2)$) after its root vertex has been pruned. The notation is essentially that used in ref. 36.

4. Caterpillar Benzenoid trees and the Ordering of Graphs; A Relation with Young Diagrams

In their work on algebraic characterization of skeletal branching, Gutman and Randić[37] used theorems of Muirhead[38] to order and compare a set of trees (caterpillars and noncaterpillars). In their treatment two trees are characterized by a sequence of nonnegative integers $\{a_1, a_2, \ldots, a_k\}$ and $\{b_1, b_2, \ldots, b_j\}$ representing the degrees of their vertices when listed in descending orders. For example P_4 (3,0,4,2) would be associated with the sequence {6, 4, 3, 2, 1, 1, 1, 1, 1, 1, 1, 1, 1}. Muirhead's conditions state that T_a whose sequence is $\{a_1, a_2, \ldots, a_k\}$ is greater than T_b whose sequence is $\{b_1, b_2, \ldots, b_j\}$ if

$$\begin{gathered} a_1 \geq b_1 \\ a_1 + a_2 \geq b_1 + b_2 \\ \cdot \\ \cdot \\ \cdot \\ a_1 + a_2 + .. + a_k = b_1 + b_2 + .. + b_j \end{gathered} \tag{18}$$

Whenever $a_m + a_n + \ldots + a_o \geq b_m + b_n + \ldots + b_o$ but $a_r + a_s + \ldots + a_t \geq b_r + b_s + \ldots + b_t$, the two tree graphs are said to be noncomparable. The latter lead to bifurcation sites in the ordering hierarchy. Using the above criteria Gutman and Randić[37] ordered sets of trees for which N = 8,9 and 10. Furthermore they[37] discovered the very interesting observation that their ordering of trees can be made to overlap with Ruch and Schönhofer[39] ordering of a set of Young diagrams if: (a) information on the terminal vertices is suppressed and (b) the valency of each vertex is reduced by one. This significant result leads to a relation between a Young diagram and a caterpillar tree and whence between a Young diagram and nearly all other graphs and lattices used in chemistry and physics, namely, Clar graphs, king polyomino graphs, rook boards and polyhex graphs. As an illustration, the Young diagram which corresponds to the set of graphs of T = P_4 (2, 0, 2, 1) is shown below



which will be denoted as Y (3,2,1,1). There is a unique Young diagram for every caterpillar tree (or any of its associated graphs) but the reverse is not true, i.e. two (or more) caterpillars may be related to the same Young diagram. The following examples (from the set N = 8) illustrate this:

$\{ P_3(4,0,1), P_3(1,3,1) \} \varepsilon\ Y(4,1,1)$;

$\{ P_3\ (3, 0, 2); P_3\ (3, 1, 1), P_3\ (2, 2, 1)\} \varepsilon\ Y(3, 2, 1)$;

$\{ P_4(3, 0, 0, 1), P_4\ (1, 2, 0, 1)\} \varepsilon\ Y(3, 1, 1, 1)$;

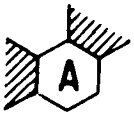
$\{ P_4(2, 0, 0\ 2), P_4(2, 0, 1, 1), P_4(2, 1, 0, 1), P_4(1, 1, 1, 1,)\} \varepsilon\ Y(2, 2, 1, 1)$;

$\{ P_5(2, 0, 0, 0, 1), P_5(1, 0, 1, 0, 1), P_5(1, 1, 0, 0, 1)\} \varepsilon\ Y(2, 1, 1, 1, 1)$

Fig. 5 shows the ordering of all Young diagrams containing six boxes. Fig. 6 is the corresponding order of the nonbranched benzenoid systems which correspond to the caterpillar trees. The numbers in parentheses are, respectively, γ_1, γ_2, γ_3 and γ_4, where γ_i is a permutation integral (of Herndon[35]) involving permutation of

(4i + 2) pi electrons in the benzenoid systems. Twice these numbers enumerate R_1, R_2, R_3 and R_4 (respectively) where R_i is a conjugated circuit[34] containing (4i + 2) pi electrons. It is obvious that the second number, γ_2 (or R_2) is almost constant for the same level of ordering of the Young diagram. In Fig. 6 the polyhex graphs are represented by their LA sequences[5]. Thus a hexagon may be annellated in two ways, viz.,

Linear



Angular

and by convention[5] the terminal hexagons are labelled by L. Thus, e.g. $B(P_4(3,0,4,2))$ is denoted by LLLAALLLLALL or $L^3A^2L^4AL^2$. In Fig.   the nonbranched benzenoid hydrocarbons containing seven hexagons are ordered. The numbers in parentheses are respectively γ_1, γ_2, γ_3 and γ_4 where γ_i is a Herndon permutation integral[35] involving permutation of (4i + 2) pi electrons. Naturally, twice these numbers lead to the corresponding conugated circuits,[34] R_1, R_2, R_3 and R_4.

It is emphasized here that through relating benzenoid trees to other graphs beside benzenoid hydrocarbons, such as Clar graphs, king polyominos and rook boards, they can all be ordered according to schemes of Ruch and Schönhofer adopted by Young diagrams.[39]

5. Benzenoid Trees and Data Reduction

An important part of an analysis of chemical data is the data-reduction step. In the past this involved mainly curve-fitting procedures. The role of graph theory was recognized in the work of Smolenskii[40] and later of Gordon and Kennedy.[41] The dualist graphs of Balaban and Harary[42] might also be regarded as a type of structure reduction representing polyhex graphs of benzenoid hydrocarbons. Recently this author[43] explored, for the first time, the possibility of using benzenoid trees to store and retrieve information on related benzenoid systems (i.e. a bezenoid system whose sextet polynomial is identical to the counting polynomial of the tree). Several physical and combinatorial properties including electronic absorption spectra, heats of atomizations, number of conjugated circuits, number of self-avoiding walks, number of Sachs graphs are studied and in all cases excellent correlations are found between the natural logarithms of a property of the benzenoid hydrocarbon and simple powers of the connectivity index of its tree graph.[44] As an illustration Fig. 7 shows a plot of the number of Kekulé structures in ln units of a homologous series of the zigzag polyacenes and the connectivity indices of their trees, $\chi(T)$'s, given by

$$\chi(T) = \Sigma(d_i\, d_j)^{-\frac{1}{2}} \tag{19}$$

where the summation is taken over all edge types in T, $(d_i\, d_j)$'s (d_i is the degree. i.e. valency of vertex i in T).

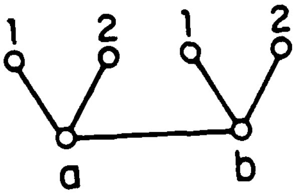
6. Other Avatars of Caterpillar trees. Generation of cycle indices of wreath product groups:[45]

The composition[45] of two groups A and B is denoted by A[B] (read: A around B) is known as the "wreath product" or the "Gruppenkranz". A permutation in A[B] is given by

$$(\alpha; \beta_1, \beta_2, \ldots, \beta_d)(x_i, y_j) = (\alpha x_i, \beta_i Y_j) \tag{20}$$

where $\alpha \epsilon A$, $\beta \epsilon$ B and the sequence $\beta_1 \ldots \beta_d$ may not involve necessarily distinct elements. The elements (x_i, y_j) arise from the cross product of $x = \{x_1, x_2, ..., x_d\}$ and $Y = \{y_1, y_2, ..., y_e\}$. Wreath product groups have a number of chemical and physical applications discovered recently by Balasubramanian[46] who revived interest in Polya's Theorem.[47] We show here that caterpillar trees might be used as a model to visualize the cyclic structure and the operations of Eq. (20). we take, as an illustration the group $S_2 [S_2]$. Then we have: $x = \{a,b\}$, $Y = \{1,2\}$ and

$x \times Y = \{a1, a2, b1, b2\}$. The system might be envisaged as



The operations in S_2's are: (1)(2), (12), (a)(b), (ab). Then the following $2.2^2 = 8$ elements exist in $S_2[S_2]$, viz.,

(1) ((a)(b); (1)(2), (1)(2))

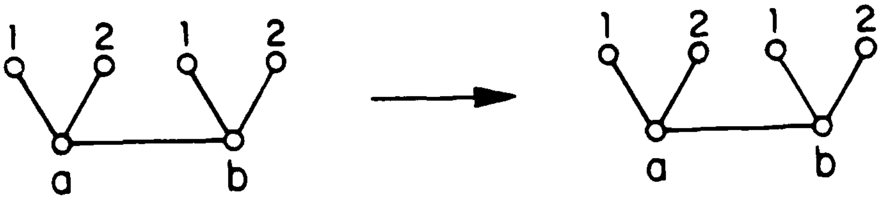
(2) ((a)(b); (12), (12))

(3) ((a)(b); (1)(2), (12))

(4) ((a)(b); (12), (1)(2))

and four other elements using the operation (ab) instead of (a)(b).

The element (1) is simply the identiy element which corresponds to the operation



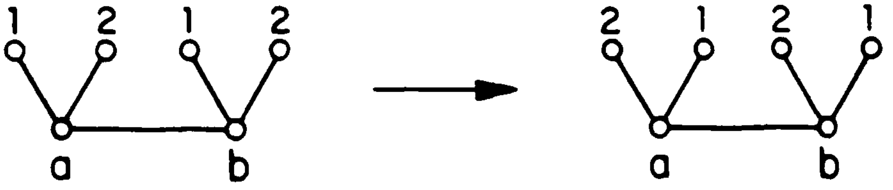
Such an element generates six one cycles, i.e, s^6. The element (2) operates as follows ((a)(b); (12), (12)) (a 1) = (a2)

((a)(b); (12), (12)) (a2) = (a1)

((a)(b); (12) (12)) (b1) = (b2)

((a)(b); (12), (12)) (b2) = (b1)

Whence this element is given by (a1 a2)(b1 b2) and corresponds to



The cyclic contribution from this element is s_2^2; i.e., two 2-cycles.

The third element involves the following operations

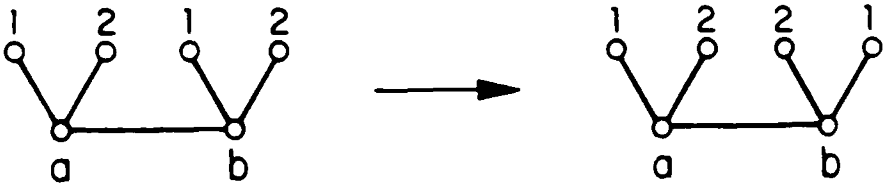
((a)(b); (1)(2), (12)) (a1) = (a1)

((a)(b); (1)(2), (12)) (a2) = (a2)

((a)(b); (1)(2), (12)) (b1) = (b2)

((a)(b); (1)(2), (12)) (b2) = (b1)

which may be represented as (a1)(a2)(b1 b2) i.e. contributes $s_1^2 s_2$, i.e., two one cycles and one 2-cycles to the cyclic structure of $S_2[S_2]$. The operation of this element can be modeled by a caterpillar tree as



The fourth element permutes the {X x Y} set in the following manner:

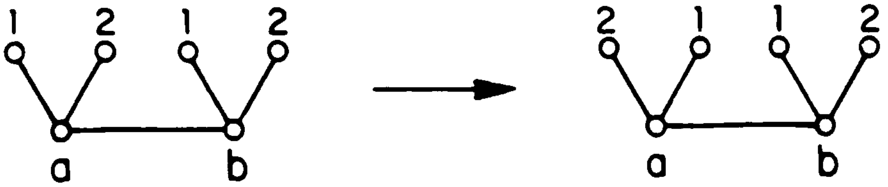
((a)(b); (12), (1)(2)) (a1) = (a2)

((a)(b); (12), (1)(2)) (a2) = (a1)

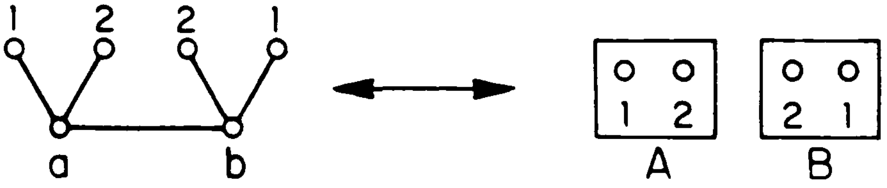
((a)(b); (12), (1)(2))(b1) = (b1)

((a)(b); (12), (1)(2))(b2) = (b2)

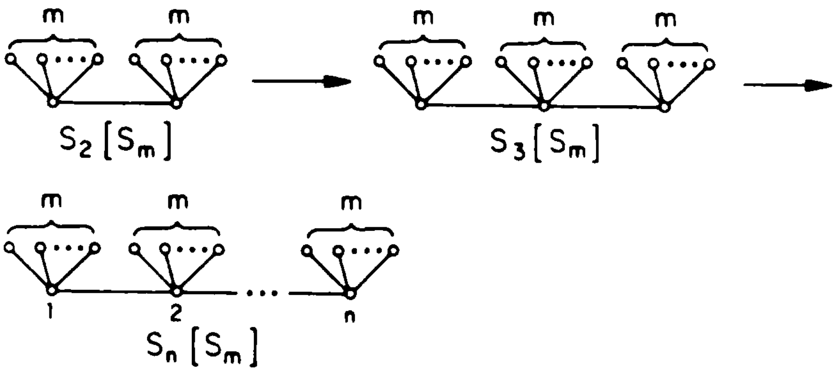
Hence this element is represented by (a1 a2)(b1)(b2) and also contributes $s_1^2\ s_2$. The caterpillar model is shown below



This "caterpillar-modeling" of the operations of the composition of two groups facilitates the understanding of the abstract algebra involved in the definition especially for beginners. A similar model is considered by Balasubramanian[52] where he uses a "particle-in-box" model, thus:



Actually either model generates the permutation group of the non-rigid N_2H_4 molecule[52] (i.e., the nitrogen atoms are represented by the root of vertices of $P_2(2,2)$ while its monovalent vertices represent the hydrogen atoms.). The above modeling can be extended as shown below



Extension to the recently defined[49] generalized wreath product is also possible. Thus the NMR group of butane might be modeled by $P_4(3,2,2,3)$ which represents S_2 $[S_3, S_2]$.

7. Conclusion

Although caterpillar (Benzenoid = Gutman) trees are not widely known in the chemical literature its uses span a wide range of applications including data reduction, computations, ordering and modeling notations of abstract groups (such as wreath and generalized wreath product groups) which are necessary for NMR spectrscopy and counting distereomers.[49]

Acknowledgments

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Table 1 Some polynomials, associated graphs and graph invariants in chemistry and physics

Polynomial	ρ	Graph-Invariants set	Associated Graph	$O(G;k)$	$f(k,n)$
1. Acyclic = Matching = $\alpha(G;x)$	$(-1)^k$	edges	Caterpillar Tree, T	$p(G;k)^a$	n-2k
1a. Counting (of Hosoya) = $H(G;x)$	1	edges	Caterpillar Tree, T	$p(G;k)^a$	k
2. Sextet $\equiv \sigma(B;x)$	1	hexagons	Polyhex Graph, B	$r(B;k)^b$	k
2a. Resonance, $A(B,x)$	$(-1)^k$	hexagons	Polyhex graph, B	$r(B;k)^b$	2M-2k
3. King $\equiv K(P;x)$	1	cells	Polyomino Graph, P	$\kappa(P;k)^c$	k
3a. Rook, $\equiv K(P_r;x)$	1 or $(-1)^k$	cells	Polyomino Graph, P	$\rho(P_r;k)^d$	k or n-2k
4. Independence $\omega(\Lambda;x)$	1	vertices	Clar Graph, Λ	$O(\Lambda;k)^e$	k
4a. Color, $C(G;x)$	1	vertices	Arbitrary graph, G	$\zeta(G;k)^f$	k

Table 1 (cont.)

a Number of selections of k independent edges ϵ T (i.e. no two edges are incident)

b Number of selections of k nonadjacent but mutally resonant hexagens B

c Number of ways of arranging k nontaking kings on a polyomino graph

d Number of ways of arranging k non-attacking kings

e Number of selections of k independent vertices $\epsilon \Lambda$ (No two are adjacent)

f Number of colorings in G in which there are k vertices of the same color so that no two of them are adjacent.

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Fig. Legends

Fig. 1

A caterpillar tree, $P_4(3,0,4,2)$, the corresponding Clar graph, $\Lambda(P_4(3, 0, 4, 2))$ and the corresponding benzenoid hydrocarbon, $B(P_4(3,0,4,2))$. A noncaterpillar tree is also shown.

Fig. 2

Recursive generation of "pseudocaterpillar" tree of a branched benzenoid hydrocarbon. The factor of X accounts of the proper sextet[23] in the graph to the right.

Fig. 3

Illustration of eqn. (13) for a caterpillar tree (i.e. benzenoid tree) and its associated graphs for Max k = 8. Simple application of eqn. (10) shows that there are 290 ways of placing either 3 or 5 non-attacking kings on the chessboard P or P_r. The subset of invariants leading to X^8 is heavily outlined.

Fig. 4

Examples of benzenoid hydrocarbons which possess one Clar representation (**1** and **2**) and a hydrocarbon with two Clar representations (**3a** and **3b**). Hydrocarbons **1** and **2** satisfies Aihara's conjecture (eqn. 15).

Fig. 5

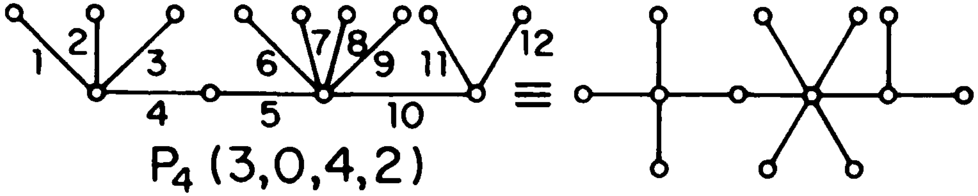
Ruch's ordering of all Young diagrams containing six boxes. Site of bifurcations indicate noncomparable diagrams.

Fig. 6

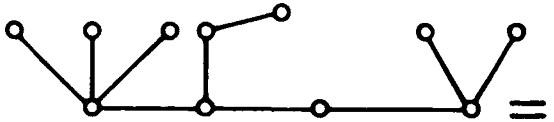
Ordering of nonbranched benzenoid hydrocarbons which are in one-to-one correspondence with the Young diagrams shown in Fig. 5. The polyhex graphs are denoted by their L-A sequences.[5] Numbers in parentheses are $(\gamma_1, \gamma_2, \gamma_3, \gamma_4)$ respectively, where $_i$ is a Herndon permutation intregral[35] involving permutation of (4i + 2) pi electrons. Twice these numbers lead to (R_1, R_2, R_3, R_4): the sequences of the corresponding conjugation circuits.[34]

Fig. 7

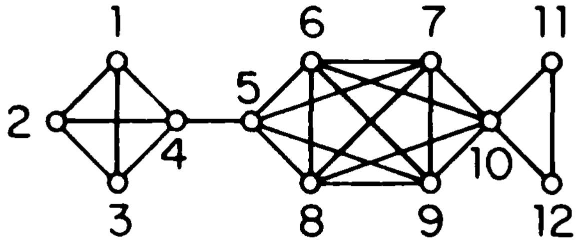
Correlation between ln K(B) i.e. the natural logarithms of the Kekulé counts of the zigzag polyacenes (1 = phenanthrene, 2 = chrysene, 3 = picene, 4 = fulminene, ...) and $\chi(T)$: the connectivity indices of the relevant caterpillar (i.e. benzenoid trees).



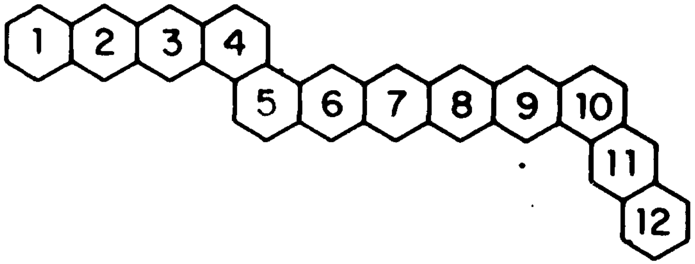
$P_4\,(3,0,4,2)$



= a noncaterpillar



$\Lambda\,(P_4\,(3,0,4,2))$



$B\,(P_4\,(3,0,4,2))$

Fig 1

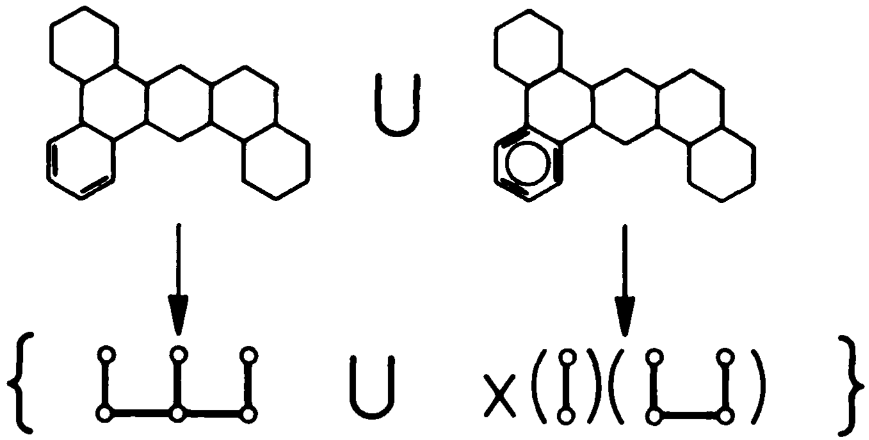
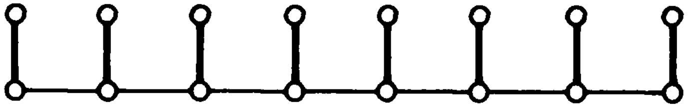
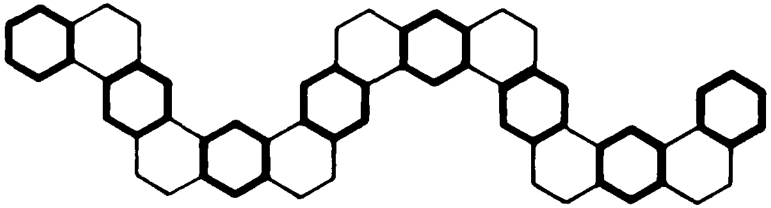


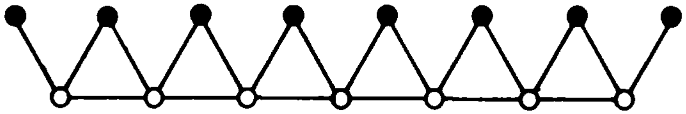
Fig 2



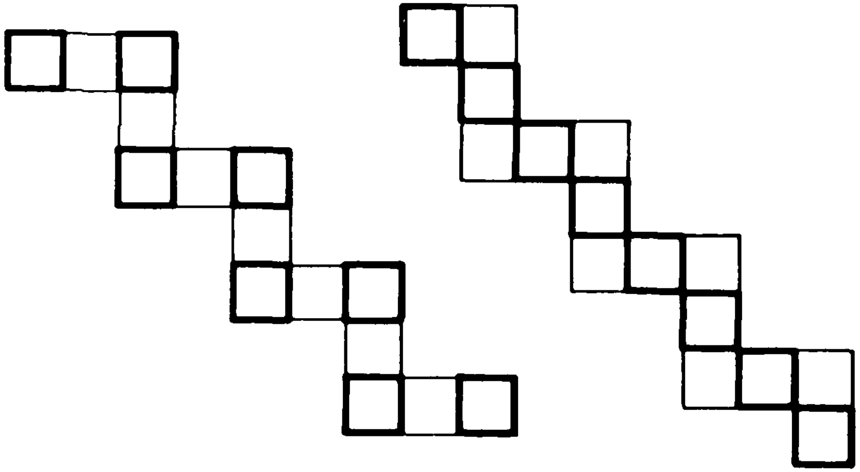
$T_8(1^8)$



$B(T_8(1^8))$

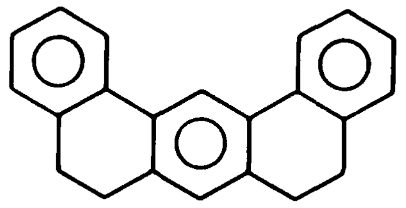


$\Lambda(T_8(1^8))$



$P(T_8(1^8))$ $P_r(T_8(1^8))$

Fig 3



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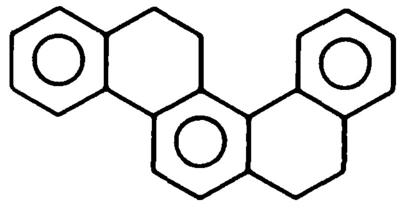

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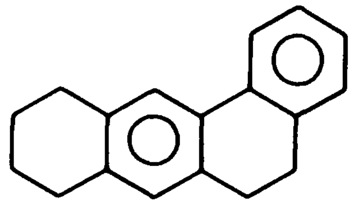
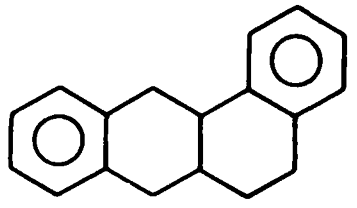


3a



3b

Fig 4

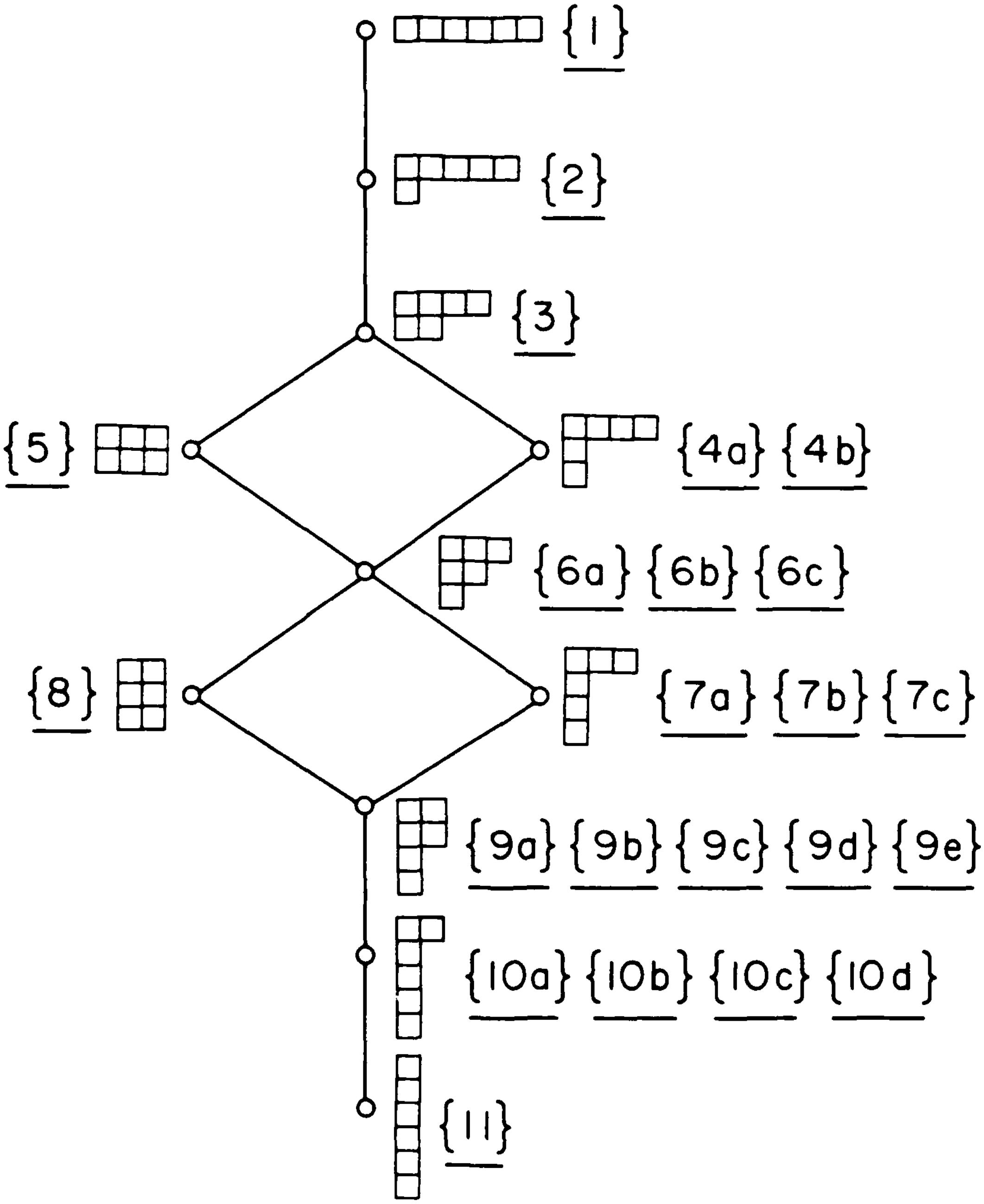


Fig 5

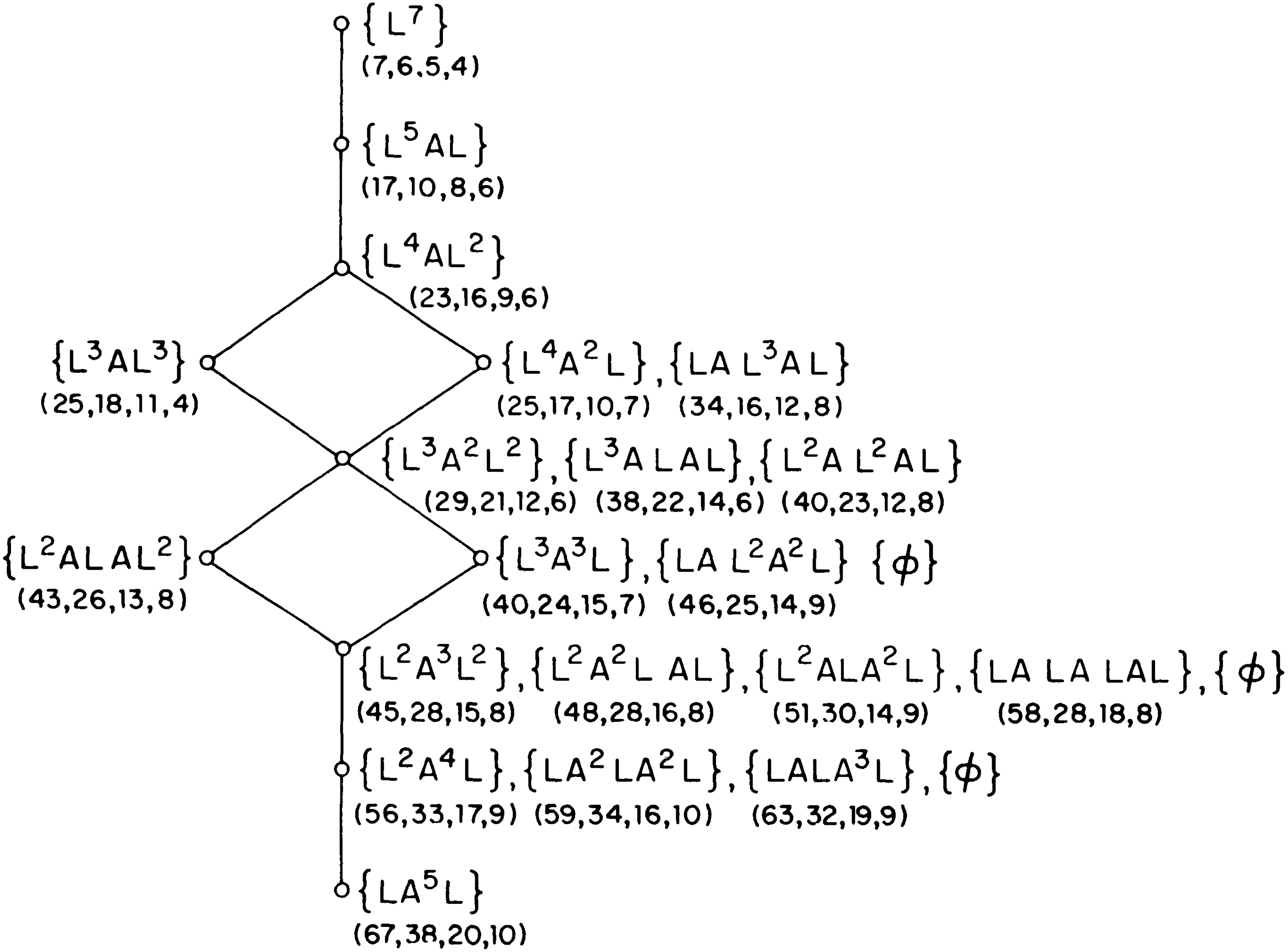

$\{L^7\}$
(7,6.5,4)
$\{L^5AL\}$
(17,10,8,6)
$\{L^4AL^2\}$
(23,16,9,6)
$\{L^3AL^3\}$
(25,18,11,4)
$\{L^4A^2L\}, \{LAL^3AL\}$
(25,17,10,7) (34,16,12,8)
$\{L^3A^2L^2\}, \{L^3ALAL\}, \{L^2AL^2AL\}$
(29,21,12,6) (38,22,14,6) (40,23,12,8)
$\{L^2ALAL^2\}$
(43,26,13,8)
$\{L^3A^3L\}, \{LAL^2A^2L\}$ $\{\phi\}$
(40,24,15,7) (46,25,14,9)
$\{L^2A^3L^2\}, \{L^2A^2LAL\}, \{L^2ALA^2L\}, \{LALALAL\}, \{\phi\}$
(45,28,15,8) (48,28,16,8) (51,30,14,9) (58,28,18,8)
$\{L^2A^4L\}, \{LA^2LA^2L\}, \{LALA^3L\}, \{\phi\}$
(56,33,17,9) (59,34,16,10) (63,32,19,9)
$\{LA^5L\}$
(67,38,20,10)

Fig 6

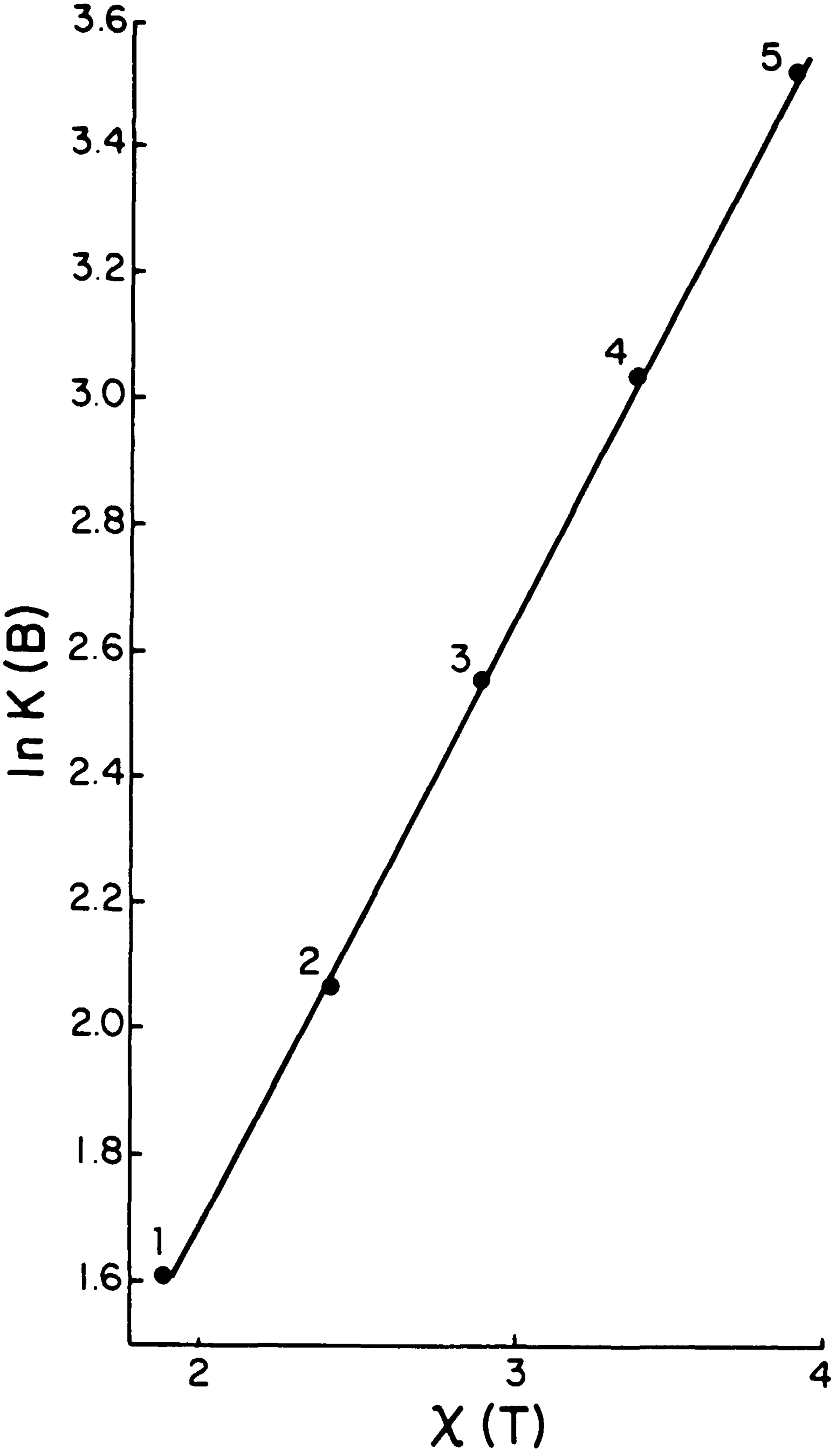


Fig 7

END
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