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K. Balasubramanian and M. Randic

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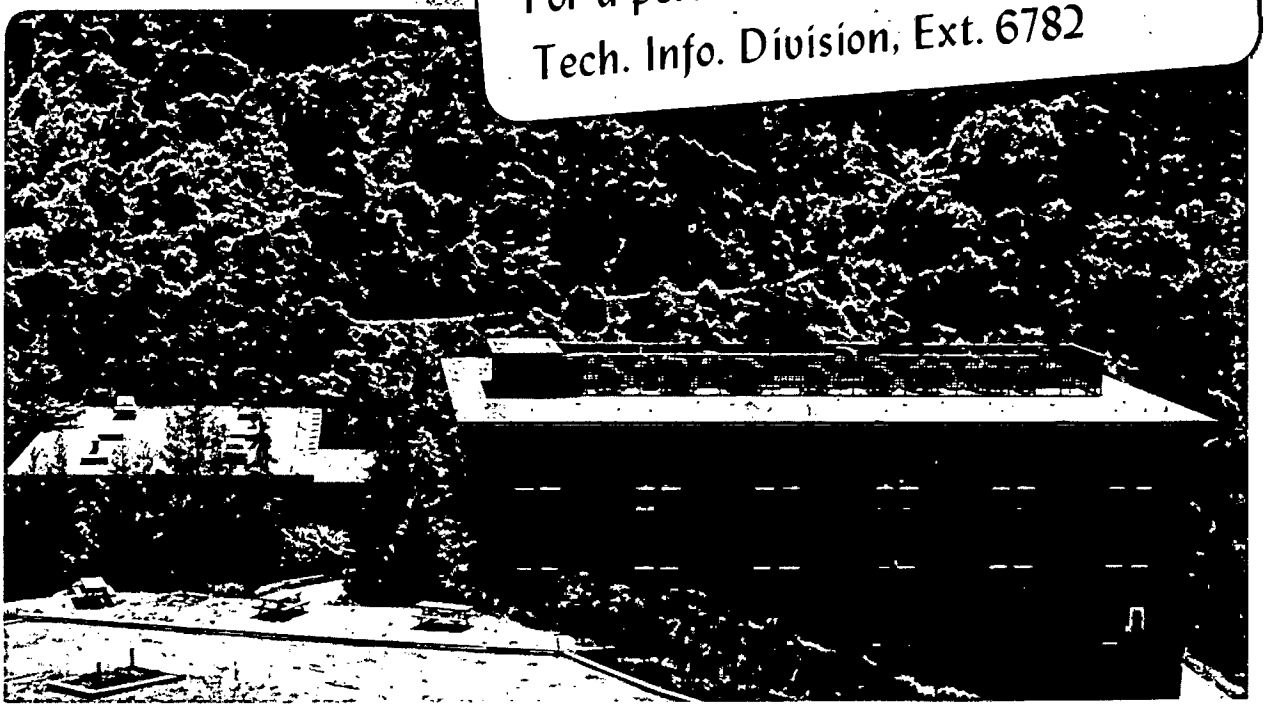

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THE CHARACTERISTIC POLYNOMIALS OF STRUCTURES WITH PENDING BONDS

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ABSTRACT

It is well known [1] that the characteristic polynomials of graphs of interest in Chemistry which are of any size is usually extremely tedious. This is primarily because of numerous combinations of contributions whether they were arrived at by non-imaginative expansion of the secular determinant or by the use of some of the available graph theoretical schemes based on the enumeration of partial coverings of a graph, etc. An efficient and quite general technique is outlined here for compounds that have pending bonds (i.e., bonds which have a terminal vertex). We have extended here the step-wise pruning of pending bonds developed for acyclic structures by one of the authors [2] for elegant evaluation of the characteristic polynomials of trees by accelerating this process, treating pending group as a unit. Further, it is demonstrated that this generalized pruning technique can be applied not only to trees but to cyclic and polycyclic graphs of any size. This technique factors the secular determinant to a considerable extent. The present technique cannot handle only polycyclic structures that have no pending bonds. However, it is known [3] that such structures can be reduced to a combination of polycyclic graphs with pending bonds so that the present scheme is applicable to these structures too, after such a reduction. Thus we have arrived at an efficient and quite a simple technique for the construction of the characteristic polynomials of graphs of any size.

1. Introduction

The characteristic polynomial of a graph (which may represent a molecule, molecular transformation or some other algebraic relation of interest in chemistry) has been a subject of considerable attention in mathematical and chemical literature. It is an important structural invariant, even though it is not unique [4]. In view of the early significance of the characteristic polynomial as secular determinant in the simple HMO method, this particular rather significant finding was in fact recognized relatively late [5]. Hence today's interest in characteristic polynomial is because graphs play an important role in chemistry, in general, and structural chemistry in particular. Characteristic polynomials, the graph spectrum, the spectral moments, and random walks are intimately related and study of one may answer important questions in the study of the other. In the past, both in mathematics and chemistry most of the attention was directed towards the spectral properties of graphs. In a way they are not quite the convenient quantities, which are, in general, irrational numbers whereas the coefficients of the characteristic polynomial, the spectral moments, and the count of random walks of different length [6] are all integers. However, their evaluation is not as simple as it may appear to uninitiated, whose past experience is with relatively small and highly symmetrical structures. Evaluation of the characteristic polynomials received due attention as early as 1940 by Coulson [7] who indicated that the coefficients of the polynomial are related to a count of pertinent subgraphs of the molecular

skeleton (in the case of pi-electron calculations of conjugated hydrocarbons, the relevant part of the skeleton is the structure formed by carbon atoms alone. Reviews on computing the characteristic polynomials are available [8] and useful references can also be found in reviews on the eigenvalue of graphs [9-11]. Several alternative graph theoretical procedures [12-23] for the construction of the characteristic polynomial are available. The situation can be inferred by a quote from a paper by Harary, King, Mowshowitz and Read[1]: "The calculation of characteristic polynomials of graphs of any size is usually extremely tedious, but there is a short cut which can be applied to any graphs having a node of degree 1, and in particular to trees." These authors [1] also derive a recursive relation (1.1)[24] for the characteristic polynomials of graphs

$$Ch(G) = Ch(G\text{-}E) - Ch(G\text{-}EE) \qquad (1.1)$$

where G is a graph, G-E is the graph obtained from G after deleting the edge E and G-EE is the graph with edge E and all its adjacent edges deleted. This formula, which was elevated to a status of a theorem [1], is known for long time and was used in chemistry to a considerable extent. This is the basis of the composition principle of Heilbronner [25] and takes particularly a simple form for special cases, like chains and rings.

Several papers have recently appeared in this area such as alternative forms of the composition principles [26], contraction of graphs [27,28], and extending the above recursion formula to

include cycles [29] and even more general subgraphs [30]. In addition characteristic polynomials for special cases have been reported, which include linear polyenes with side groups [31] and certain long chain cata-condensed hydrocarbon series [32]. While these approaches, when properly used, will result in significant simplification in the evaluation of the coefficients of the characteristic polynomials, they do not appear to be quite general. The approach based on deletion of a bond and all the cycles which contain this bond is suitable, for instance, for catacondensed polycyclic structures when finding all such cycles is not difficult. Contractions of graphs based either on symmetry properties of special cases [27] or otherwise [28] appears to be promising. Such steps can probably be incorporated in other schemes, including the one outlined in the present paper.

The present situation is practically solved only for the acyclic graphs (trees) in that the proposed construction of the characteristic polynomial is quite efficient [2]. Recently a scheme was suggested [3] wherein the characteristic polynomial of a graph is obtained from the characteristic polynomials of qualified subgraphs. The derived subgraphs in general have pending bonds and may also represent smaller polycyclic structures. Such an approach also appears to be very efficient for large graphs. The contributions of pending bonds were reduced by repeated use of recursion. We will show here the use of repeated recursion to accelerate the previously proposed scheme for finding the characteristic polynomials of trees. Further

we extend this technique to polycyclic graphs with pending bonds. The cases of polycyclic graphs without pending bonds leads to graphs with pending bonds or polycyclic graphs with fewer rings. We conclude that combining these two approaches for the first time have lead to an efficient practical general scheme for the construction of the characteristic polynomials for graph of any size which is not "extremely tedious" or even tedious.

2. Characteristic Polynomials of Trees

A. Definitions and Preliminaries

The adjacency matrix of a graph is defined as follows:

$$A_{ij} = \begin{cases} 1 & \text{if the vertices } i \text{ and } j \text{ are connected.} \\ 0 & \text{otherwise.} \end{cases} \tag{2.1}$$

The secular determinant of the adjacency matrix of a graph is known as the characteristic polynomial of the graph. The eigenvalues of the adjacency matrix constitute the spectrum of a graph. Tree is a connected graph with no cycles. The vertices of a tree with degree (valence) more than 1 can be defined as the roots of the tree. Any tree can be expressed as a product of a quotient tree Q formed by a selected set of roots and the branches resulting from pruning the tree at these selected roots. For example, let us consider the tree in Fig. 1. When a tree is pruned at a set of roots branches of certain kind recur. A collection of such fragments is shown in Fig. 2 with the black dots identifying the roots. Let such a branch containing k vertices (including the root) be denoted by T_k and let the characteristic polynomial of the branch T_i be h_i. It

can be seen that $h_i = x^i - (i-1)\, x^{i-2}$. Let the fragments obtained by deleting the root in T_i be denoted by t_i. The characteristic polynomial of t_i, $h_i = x^{i-1}$. The tree in Fig. 1 can be pruned at the roots a, c and d, resulting in the tree Q shown in Fig. 2 and the fragments T_{11}, T_{21}, T_{31} and T_{41}. Let us group all the vertices of the same degree in the unpruned tree in Fig. 1 into the same sets. Then, the set thus obtained would be

$$Y_1 = \{a\},\ Y_2 = \{b\},\ Y_3 = \{c\} \text{ and } Y_4 = \{d\}.$$

The tree in Fig. 1 can be obtained by attaching each root in the set Y_i to the root of a copy of the type T_{i1}. Such a product was formulated by one of the authors [36] which was called root-to-root product and can be denoted as Q. $(T_{11}, T_{21}, \ldots)$

B. Elegant Evaluation of Characteristic Polynomials of Trees by Tree Pruning Techniques

It was shown in Ref. 2 that the tree pruning technique paves an elegant way for the evaluation of characteristic polynomials of trees by contracting the secular determinant of the unpruned tree in terms of the secular determinant of the pruned tree and the branches. Let Q be the quotient tree obtained in one-fold pruning and let T_{11}, $T_{21}, \ldots$ be the types. The vertices in Q are divided into sets Y_1, $Y_2 \ldots$ so that all the vertices in Y_i are attached to the root of a copy of the same type T_{i1}. Let H_i be the characteristic polynomial of T_{i1} (which is equal to h_k if T_{i1} contains k vertices) and H_i' be the characteristic polynomial of the type T_i with the root removed. Let q_{ij} be the adjacency matrix of the pruned tree (quotient tree). Define

a new contracted adjacency matrix of order mxm if m is the number of vertices in Q by the following recipe.

$$A_{ij} = \begin{cases} -H_k(x) & \text{if } i = j \text{ and } i \varepsilon Y_k \\ +q_{ij}H_k'(x) & \text{if } i \neq j \text{ and } i \varepsilon Y_k. \end{cases} \tag{2.2}$$

Then using a lemma of Schwenk [38] and a theorem of Godsil and McKay [39] the following result was established in Ref. 2.

<u>Theorem 1</u>: The characteristic polynomial of the root-to-root product Q. $(T_{11}, T_{21}, \ldots)$ is just the determinant of the matrix A defined above.

Consider now the tree in Fig. 1 and the pruned tree Q in Fig. 3. The adjacency matrix of the tree in Fig. 3 is shown below.

$$\begin{array}{c} \\ a \\ b \\ c \\ d \end{array} \begin{array}{c} \begin{array}{cccc} a & b & c & d \end{array} \\ \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \end{array} \tag{2.3}$$

By the above theorem 1 the characteristic polynomial of the tree in Fig. 2 is

$$\left| \begin{bmatrix} -H_1 & +H_1' & 0 & 0 \\ +H_2' & -H_2 & +H_2' & 0 \\ 0 & +H_3' & -H_3 & +H_3' \\ 0 & 0 & +H_4' & -H_4 \end{bmatrix} \right| = \begin{vmatrix} -h_4 & +h_4' & 0 & 0 \\ +1 & -x & +1 & 0 \\ 0 & h_2' & -h_2 & h_2' \\ 0 & 0 & h_3' & -h_3 \end{vmatrix} \tag{2.4}$$

Recall that h_i is the characteristic polynomial of a branch containing i vertices (including the root) and h_i' is the

characteristic polynomial obtained by deleting the root.

There are two aspects of the above scheme, even for trees, which have not been considered before. They are partial pruning and extensive pruning. The former is the procedure where only some of the terminal vertices are removed while in the latter procedure larger fragments involving terminal vertices are removed in one step. The latter procedure seems to be more efficient than the former. However, partial pruning will be of interest when comparisons of different trees are made (for example, to see if they are isospectral) because, this process can reduce a larger graph to a graph of desired form. The partial pruning is illustrated here only to emphasize that the procedure of contraction of secular determinants of graphs is quite general. Consider the same tree in Fig. 1 which will now be pruned selectively at the vertices a and d. This results in the tree shown in Fig. 4. The characteristic polynomial of the tree in Fig. 1 is shown below in terms of the tree in Fig. 4.

$$Ch(x) = \begin{array}{c} \\ a \\ b \\ c \\ d \\ e \end{array} \begin{array}{c} \begin{array}{ccccc} a & b & c & d & e \end{array} \\ \begin{vmatrix} -h_4 & h_4' & 0 & 0 & 0 \\ 1 & -x & 1 & 0 & 0 \\ 0 & 1 & -x & 1 & 1 \\ 0 & 0 & -h_3' & h_3 & 0 \\ 0 & 0 & 1 & 0 & -x \end{vmatrix} \end{array} \qquad (2.5)$$

The above determinant can be related to the determinant (2.4) as shown in the Appendix. This demonstrates the use of partial pruning.

C. The Use of Repeated Pruning

Consider the graph (2 methyl hexane) shown in Fig. 6. If one prunes the tree at the joints in either ends one obtains the contracted determinant of order 4 shown below.

$$\begin{vmatrix} -x(x^2-2) & x^2 & 0 & 0 \\ 1 & -x & 1 & 0 \\ 0 & 1 & -x & 1 \\ 0 & 0 & x & -(x^2-1) \end{vmatrix} \tag{2.6}$$

Expanding (2.6) with the elements of last row, one obtains (2.7)

$$-(x^2-1)\begin{vmatrix} -x(x^2-2) & x^2 & 0 \\ 1 & -x & 1 \\ 0 & 1 & -x \end{vmatrix} \quad -x\begin{vmatrix} -x(x^2-2) & x^2 & 0 \\ 1 & -x & 0 \\ 0 & 1 & 1 \end{vmatrix} \tag{2.7}$$

The determinants of similar molecules such as 2 methyl heptane, 2 methyl octane, etc. will look similar but for the presence of additional non-critical rows and columns. The determinants in (2.7) can be rearranged into a single determinant (2.8) shown below by using addition theorem for determinants and an interchange of the last column with the last row.

$$\begin{vmatrix} -x(x^2-2) & x^2 & 0 \\ 1 & -x & 1 \\ 0 & x^2-1 & -x(x^2-2) \end{vmatrix} \tag{2.8}$$

The determinant (2.8) is just the contracted determinant obtained if one prunes the tree on either side so as to create C-C-C branches with a terminal root in one case and a centered root in the other case. This process of selective pruning leads to a theorem.

Theorem 2: Let L_n be a chain of length n and let L'_{n-1} be the graph obtained after deleting the root in L_n. Let the characteristic polynomials of L_n and L'_{n-1} be ℓ_n and ℓ'_{n-1}, respectively. Then the characteristic polynomial of a graph which contains L_n is the determinant of the contracted matrix in which the rows corresponding to the roots of attachment are replaced by $-\ell_n$ (diagonal element) and $+\ell'_{n-1}$ (off diagonal elements), respectively.

The proof of theorem 2 (with $L_0 = -x$, $\ell'_0 = 1$) follows from theorem 1 if one identifies the point of attachment of the chain L_n in the unpruned graph as the root and considers the unpruned graph G as the root-to-root product of the pruned quotient graph with the rooted chain L_n. Note that theorem 2 holds independent of the nature of the quotient graph (acyclic or cyclic) as long as it gives the unpruned graph if the chain L_n is attached at the chosen root. This gives rise to an important corollary, stated below as corollary 1.

Corollary 1: The characteristic polynomial of a cyclic or a polycyclic structure with pending chain of length n can be constructed from the contracted determinant in which the row corresponding to the root is replaced by ℓ_n and ℓ'_{n-1}, respectively.

Structures with several pending chains require combined use of the simple pruning scheme outlined in Ref. 2 and the use of chains of varied length instead of "branches" T_{ij}'s which contain a single root.

3. Characteristic Polynomials of more General Pending Fragments

We consider here pending fragments which are acyclic. Consequently they necessarily involve terminal vertices. The process of pruning can now be applied by disconnecting a whole fragment, which may have several branches. We have already seen that the process of pruning is "additive". This additivity extends also to the presence of several fragments F_n, if one views each such branch separately. For example, in a graph of 3-methylalkanes (shown in Fig. 7) we may consider F_n as methyl and ethyl groups with characteristic polynomials: $x, (x^2-1)$, one at a time and contract the graph to shorter chain. However, if we view both of them as parts of a single fragment of four vertices the contracted determinant will be of the form:

$$(0 — 0 — 0 — 0),$$

$$\begin{vmatrix} -(x^4-3x^2+1) & x(x^2-1) & 0 & 0 & 0 & \cdots \\ 1 & -x & 1 & 0 & 0 & \cdots \\ \cdots & \cdots & \cdots & & & \end{vmatrix} \qquad (3.1)$$

Expanding the above determinant we obtain (3.2).

$$Ch(G) = -(x^4-3x^2+1)\ R_n - x(x^2-1)\ R_{n-1} \qquad (3.2)$$

where R_n and R_{n-1} are the residuals (the parts of the secular determinant involving the remaining rows and columns after the first (for R_n) and first two (for R_{n-1}) have been deleted. Here it is assumed that the atom next to the root has no neighbors except for linear chain (but this is not a severe restriction), since the expansion only requires first atom to

have a single neighbor. (However, additional neighbors can always be pruned). Now we can once again apply the recursion on R_n giving:

$$Ch(G) = -(x^4-3x^2+1)(-xR_{n-1}+R_{n-2}) - x(x^2-1)\ R_{n-1} \qquad (3.3)$$

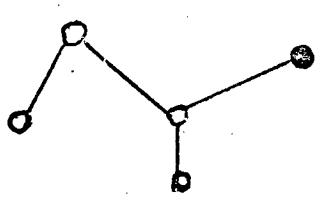
Expression (3.3) on simplification yields (3.4)

$$Ch(x) = -x(x^4-3x^2+1)R_{n-1} - x(x^2-1)\ R_{n-1} - (x^4-3x^2+1)\ R_{n-2} \qquad (3.4)$$

The combination of the first two terms in R_{n-1} in (3.4) gives (3.5)

$$Ch(x) = -(x^5-4x^3+2x)\ R_{n-1} - (x^4-3x^2+1)\ R_{n-2} \qquad (3.5)$$

This is equivalent to attaching at the root of the quotient tree shown below to the next atom in the chain.



Observe that the nature of R_{n-1} or R_{n-2} does not enter the consideration, so that the conclusions are valid for more general graphs with pending bonds on any cyclic or polycyclic frame, as long as we are confined to pending section of the skeleton. The illustration given motivates the statement of quite a general case of a graph with F_1 and F_2 being some fragments and R_n being residual, which can be cyclic, polycyclic, acyclic or even simple chain of length 1.

We then have a general theorem:

Theorem 3: The characteristic polynomial of a graph shown in Fig. 8, with F_1 and F_2 being acyclic fragments and R_1 being residual (having at least one bond length attachment to R_0, and arbitrary residual) is given by contracted determinant with $(f_1 + f_2)$ as the diagonal element and $f_1 \cdot f_2$ as off diagonal element if f_1 and f_2 are the characteristic polynomials of F_1 and F_2, respectively. The proof can be simply derived when R_1 is a single bond (R_0 being a single vertex) in which case the graph is reduced to cases already considered, but the validity of proof does not depend on choice of R_1 which involves fixed part of the determinant not used in expansion.

B. Illustrations with Cyclic Structures

Consider the simple graph of Fig. 9a. The cyclic part is considered as R_0 and the ethyl substitutent as F. One obtains the following contracted determinant.

$$\begin{vmatrix} -x(x^2-2) & (x^2-1) & (x^2-1) \\ 1 & -x & 1 \\ 1 & 1 & -x \end{vmatrix} \tag{3.6}$$

Expanding (3.6) one obtains (3.7)

$$Ch = x^5 + 5x^3 + 2x^2 - 4x - 2. \tag{3.7}$$

Expression (3.7) can be compared with available tables [33] (one should replace x by -x for the comparison due to an alternative definition of the characteristic polynomial) [34].

As another illustration consider graph b in Fig. 9. We have

here several but all pending fragments as single exocyclic bonds. The contracted determinant is given by (3.8)

$$\begin{vmatrix} -(x^2-1) & x & 0 & x \\ x^2 & -x(x^2-2) & x^2 & 0 \\ 0 & 1 & -x & 1 \\ 1 & 0 & 1 & -x \end{vmatrix} \tag{3.8}$$

Expanding (3.8) we obtain 3.9 which agrees with results that can be obtained by other methods

$$Ch = x^7 - 7x^5 + 8x^3 - 2. \tag{3.9}$$

4. Applications

Characteristic polynomials are given in a closed form for only few special class of graphs [9]: the complete graphs K_n, the n-cycle (or the ring C_n), the n-cube Q_n, the complete t-partite graph (which includes as special case the complete bipartite graphs $K_{m,n}$ and stars $K_{1,n}$), the wheels (i.e., K_1 + C_{n-1}), path (or linear chains) graphs P_n, and n-dimensional octaherda. We will now show that all the above mentioned classes can now be extended to include graphs in which all vertices have the same pending fragment. The simplest case is the class of radialenes [28] shown in Fig. 10. These are derived by attaching a single exocyclic bond to n-cycle. Consider for illustration the graph in Fig. 11. If one considers the 4 vertices of the 4-cycle in Fig. 11 as roots then one obtains the contracted determinant (4.1) for the characteristic polynomial of the graph in Fig. 11.

$$\begin{vmatrix} -(x^2-1) & x & x & x \\ x & -(x^2-1) & x & 0 \\ x & x & -(x^2-1) & x \\ x & 0 & x & -(x^2-1) \end{vmatrix} \tag{4.1}$$

Because of equal substitutions we can now factor out x^4 and introduce a substitution $(x^2-1)/x = y$, which transforms the determinant back into the form representing the characteristic polynomial of the quotient graph obtained after deleting the pending bonds. The characteristic polynomial of this quotient graph is shown in the expression (4.1)

$$Ch(Q;x) = x^4 - 5x^2 + 4x \tag{4.2}$$

The characteristic polynomial of the original graph is thus given by (4.3)

$$\begin{aligned} Ch(x) &= x^4\ (y^4 - 5y^2 + 4y) \\ &= (x^2-1)^4 - 5x^2(x^2-1)^2 + 4x^3(x^2-1) \\ &= (x^6 - 8x^4 + 4x^3 + 8x^2 - 1)\ (x^2-1) \end{aligned} \tag{4.3}$$

The result can be checked with available tabulation [21]. The presence of a factor in the characteristic determinant of the core will result in the factor for the exocyclic structure.

Using the above regularity, one can use available tables of characteristic polynomials to derive the characteristic polynomials of homogeneously substituted structures. In Table 1 we show the results for radialness and higher homologues.

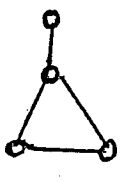
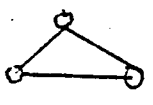
As another application consider graphs in Fig. 12. The contracted determinant for this graph with roots chosen as in Fig. 12a is shown in 4.4

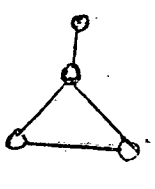
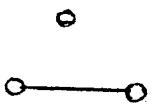
$$\begin{vmatrix} -x(x^2-2) & x^2-1 & x^2-1 & 0 & 0 \\ 1 & -x & 1 & 0 & 0 \\ 1 & 1 & -x & 1 & 1 \\ 0 & 0 & 1 & -x & 1 \\ 0 & 0 & 1 & 1 & -x \end{vmatrix} \tag{4.4}$$

The contracted determinant of the graph in Fig. 12b differs only in the first row which is shown below.

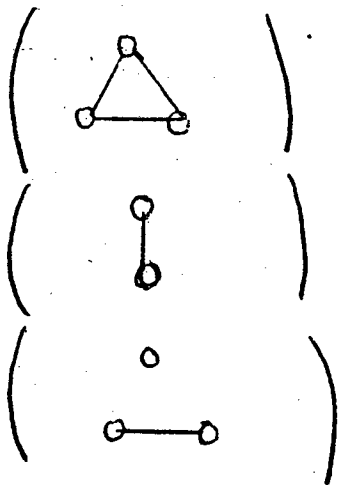
$$-x(x^2-2) \qquad x^2 \qquad x^2 \qquad 0 \qquad 0$$

The graphs represent a case of a <u>single</u> exocyclic group. In both cases we can factor out f (which is x^2-1 and x^2 respectively) restoring the first row of the determinant to represent adjacency conditions for the substituted vertex. The only difference is in the first diagonal element and the factor. Such a form allows easy comparison of the characteristic polynomials. In fact by expanding the secular determinants by elements of the first row one obtains: (for the a and the b graph, respectively):

$-x(x^2-2)$  $-(x^2-1)$ [ −] (4.5)

$-x(x^2-2)$  $-(x^2-1)$ [ −] (4.6)

Here we use notational device of Zykov [35], in which a graph also represents the polynomial [i.e., the characteristic polynomial in our discussions]. Substituting,



$= x^3 - 3x + 2$

$= x^2 - 1$

$= x(x^2 - 1)$

in (4.4) and (4.5) one obtains the difference between (4.4) and (4.5) to be 4.7.

$$2x^3 - 2x^2 - 4x + 4 \tag{4.7}$$

This can be compared with available characteristic polynomials for the two graphs [33]:

$$x^7 - 8x^5 + 4x^4 + 15x^3 - 10x^2 - 6x + 4 \tag{4.8}$$

$$x^7 - 8x^5 + 4x^4 + 13x^3 - 8x^2 - 2x \tag{4.9}$$

When molecules possess a number of common structural features many terms in the difference will cancel. This is therefore of interest when considering structurally related species. Then it may suffice only to obtain the characteristic polynomial for a single case, all others being derived from examination of the pertinent differences. It seems that in this way considerable simplification can result when studying or tabulating characteristic polynomials of a collection of structures -- an approach that deserves additional attention.

5. Concluding Remarks

We have shown in this paper that the construction of the characteristic polynomial for a large class of compounds in which a core (which may be acyclic, cyclic or polycyclic) is substituted by a number of pending fragments can be derived in an efficient way by the construction of a contracted secular determinant analogous to the approach previously described for trees and their pruned subgraphs [2]. Neither the core to which pending branches are attached ought to be tree, nor the pruning has to be made in single steps. This permits wider applications and accelerates the constructions of the characteristic polynomials. When this approach is combined with the scheme using Ulam subgraphs as a source for derivation of the characteristic polynomials [3] we arrive at quite general procedures suitable for any large structure. It seems that for the first time we have a tool for obtaining the characteristic polynomials of complex structures in a relatively simple and pragmatic way.

We therefore feel that the "problem of the characteristic polynomials" -- which has plagued theoretical chemistry and mathematical graph theory for quite a while -- has been finally successfully resolved in practical terms (and we do not wish to belittle the important theoretical developments that preceded and provided important insights, even if found "extremely tedious" due to their inherent n! character in proliferating combinatorial possibilities accompanying applications to large structures). Despite the present success we can anticipate some further developments, such as (1) the further study of related structures

(exploiting numerous coincidences in the coefficients that such structures may have; (2) possible incorporation of contraction of graphs of polycyclic structures (developed recently by the Chinese school of chemical graph theory); and (3) extending the present approach to more general pending fragments. In Table 2 we illustrate our method with the graph in Fig. 13 which has no pending bonds. When C_4 ring is considered as the core and ethylcyclopropane as fragment expansion of the contracted secular determinant gives correct answer for the characteristic polynomial even though the system has no acyclic pending fragments. This suggests a wider applicability of the approach now limited to acyclic fragments. However, if we view the same molecule as a C_3 core (cyclopropane ring) and take ethylcyclobutane part as the fragment one obtains correct answer by the development of the secular (contracted) determinant only if contributions arising from fragments without roots (f) are taken with opposite sign (but not those products involving x and f). This is suggesting that signs of the contributions may be governed by some rules depending on the number of components involved (as in Sachs' theorem for instance). Preliminary work suggests that indeed one may be in a position to extend the present scheme to cases having more general pending fragments. This is further strengthened by the fact that the graph shown in Fig. 13 can also be viewed as a derivative of C_3 chain with the three and four membered rings at the ends as substituted fragments. Again the expansion of the determinant gives the correct answer. This indicates such extensions need proper attention and adequate proofs. This is beyond the scope of the present work.

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Appendix

The relation between the characteristic polynomials of graphs in Figs 14. Using the elements of the fifth row for the expansion of the determinant one obtains

$$Ch(x) = (-x)\begin{vmatrix} -x^2(x^2-3) & x^3 & 0 & 0 \\ 1 & -x & 1 & 0 \\ 0 & 1 & -x & 1 \\ 0 & 0 & x^2 & -x(x^2-2) \end{vmatrix} +$$

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

The second determinant (corresponding rows being a, b, c, d and columns a, b, d, e) is now expanded using the Cost Column. The renet can be expressed as follows:

$$\begin{array}{c|cccc} & a & b & d & \\ \hline a & -x^2(x^2-3) & x^3 & 0 & 0 \\ b & 1 & -x & 0 & 0 \\ d & 0 & 0 & -x(x^2-2) & 0 \\ & a & b & d & 1 \end{array} \qquad (A.2)$$

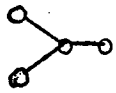
In (A.2) a row and column in the third position was added without affecting the value of the determinant, with a, b, d yet to be determined. By rearrangement of rows and columns one then obtains for the form of this determinant:

$$\begin{vmatrix} -x^2(x^2-3) & x^3 & 0 & 0 \\ 1 & -x & 0 & 0 \\ a & b & -1 & d \\ 0 & 0 & 0 & -x(x^2-2) \end{vmatrix} \tag{A.3}$$

(The minus sign was absorbed in the diagonal element). The parameters a, b, d are now chosen so that the columns of the first determinant in the expansion of Ch(x) and the last determinant agree, i.e., $a = 0$, $b = -x$, $d = -x$. The two determinants now differ only in single column and can therefore be added to give(A.4) (when factor $-x$ is associated with the third row)

$$\begin{vmatrix} -x^2(x^2-3) & x^3 & 0 & 0 \\ 1 & -x & 1 & 0 \\ 0 & -x & x^2-1 & -x \\ 0 & 0 & x^2 & -x(x^2-2) \end{vmatrix} \tag{A.4}$$

This differs trivially from the contracted determinant based on vertices a, b, c, d (the minus sign can be factored out). Hence the procedure of partial prunning yields the same result as that of complete pruning.

Table 1. The Characteristic Polynomials for Radialenes with R being , ,  etc. The coefficients of the polynomial expressions are those of cyclic graphs C_n(n=3,4,5,6,7..) which are available (e.g., Ref. 25)

Radialene	R = i.e., (x^2-1)
n = 3	$(x^2-1)^3 - 3x^2(x^2-1) + 2x^3$
n = 4	$(x^2-1)^4 - 4x^2(x^2-1)^2$
n = 5	$(x^2-1)^5 - 5x^2(x^2-1)^3 + 5x^4(x^2-1) + 2x^5$
n = 6	$(x^2-1)^6 - 6x^2(x^2-1)^4 + 9x^4(x^2-1)^2 - 4x^6$
n = 7	$(x^2-1)^7 - 7x^2(x^2-1)^5 + 14x^4(x^2-1)^3 - 7x^6(x^2-1) + 2x$
	R = i.e., (x^3-2x)
n = 3	$(x^3-2x)^3 - 3x^2(x^3-2x) + 2x^3$
n = 4	$(x^3-2x)^4 - 4x^2(x^3-2x)^2$
n = 5	$(x^3-2x)^4 - 5x^2(x^3-2x)^3 + 5x^4(x^3-2x) + 2x^5$
n = 6	$(x^3-2x)^6 - 6x^2(x^3-2x)^4 + 9x^4(x^3-2x)^2 - 4x^6$
n = 7	$(x^3-2x)^7 - 7x^2(x^3-2x)^5 + 14x^4(x^3-2x)^2 - 7x^6(x^3-2x) + 2x^7$
	R = i.e., (x^4-3x^2)
n = 3	$(x^4-3x^2)^3 - 3x^2(x^4-3x^2) + 2x^3$
....	etc.
....	

Table 2. Alternative Ways of Prunning the Molecule in Fig. 13

A. Roots chosen as in Fig. 13a.

$$\begin{vmatrix} -(x^5-5x^3+2x^2+4x-2) & (x^4-4x^2+2x+1) & 0 & (x^4-4x^2+2x+1) \\ 1 & -x & 1 & 0 \\ 0 & 1 & -x & 1 \\ 1 & 0 & 1 & -x \end{vmatrix}$$

$$= -(x^3-5x^3+2x^2+4x-2)\ (-x^3+2x)\ -2(x^4-4x^2+2x+1)\ (x^2)$$

$$= x^8 - 9x^6 + 2x^5 + 22x^4 - 10x^3 - 10x^2 + 4x$$

B. Roots chosen as in Fig. 13b.

$$\begin{vmatrix} -(x^6-6x^4+6x^2) & (x^5-5x^3+2x) & (x^5-5x^3+2x) \\ 1 & -x & 1 \\ 1 & 1 & -x \end{vmatrix}$$

$$= -x^2(x^6-6x^4+6x^2)\ +2(-1)^*\ (x^5-5x^3+2x)$$

$$+\ (x^6-6x^4+6x^2)\ -2x(x^5-5x^3+2x)$$

C. Roots chosen as in Fig. 13c.

$$\begin{vmatrix} -(x^4-4x^2) & x^3-2x & 0 \\ 1 & -x & 1 \\ 0 & x^2-1 & -(x^3-3x+2) \end{vmatrix}$$

$$= -(x^4-4x^2)\ (x^3-3x^2+2)(x)\ +\ (x^4-4x^2)\ (x^2-1)\ +\ (x^3-2x)\ (x^3-3x+2)$$

$$= -[x^8-9x^6+2x^5+22x^4-10x^3-10x^2+4]$$

* In normal expansion this term would have positive, not negative contribution.

Figure Captions

1. A tree on 1o vertices with 6 pending bonds (i.e., bonds connected to a terminal vortex) which can be pruned to a quotient tree and branches. The characteristic polynomial of this tree can be obtained in terms of its quotient tree.
2. Several types of branches that result in prunning any tree. T_i stands for the branch containing i vertices including the root, which is denoted by a closed circle. h_i stands for the characteristic polynomial of the branch T_i.
3. The types of fragments resulting from deleting the root of the branches in Fig. 2. T_i' is the fragment obtained after deleting the root of T_i. The characteristic polynomial of T_i' is h_i'.
4. The quotient tree and the branches obtained when the tree in Fig. 1 is pruned at all the roots. Roots are differentiated by various symbols. To obtain the tree in Fig. 1 attach the root of a symbol with the root of the branch carrying that symbol.
5. An illustration of partial selective pruning. The same tree in Fig. 1 is selectively pruned.
6. The chemical graph of 2-methyl hexane: the use of repeated pruning.
7. A class of 3-methyl alkanes. For their characteristic polynomials see Sec 3.
8. A graph which has acyclic fragments F_1 and F_2 and R is a residual graph which may be cyclic.
9. Two graphs which contain cycles. For their characteristic polynomials see Sec. 3B.

10. A class of radialenes. Their characteristic polynomials can be obtained by an elegant technique outlined in Sec 4.
11. A graph which contains a 4-cycle. Its characteristic polynomial can be obtained by a substitution in the characteristic polynomial of the 4-cycle.
12. Two graphs which illustrate the concept of "difference". For a discussion of "difference" of characteristic polynomials see Sec 4.
13. A graph which has no pending bond. However, the technique developed here can be applied in 3 ways by "pruning" the graph in 3 ways. Table 2 discusses the characteristic polynomials for these 3 ways.

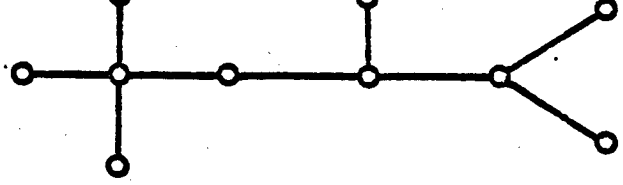


fig. 1

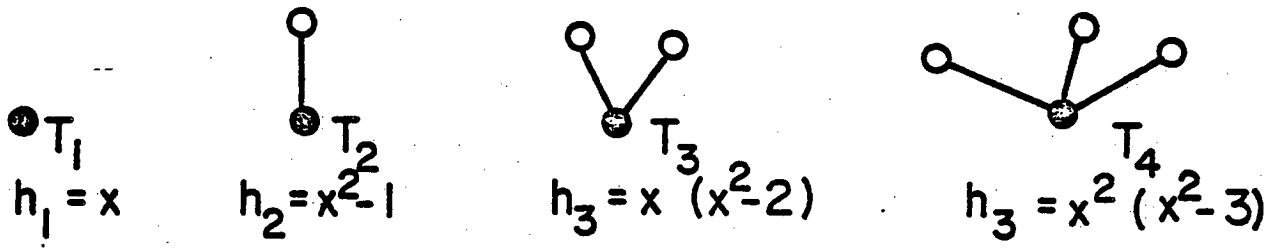
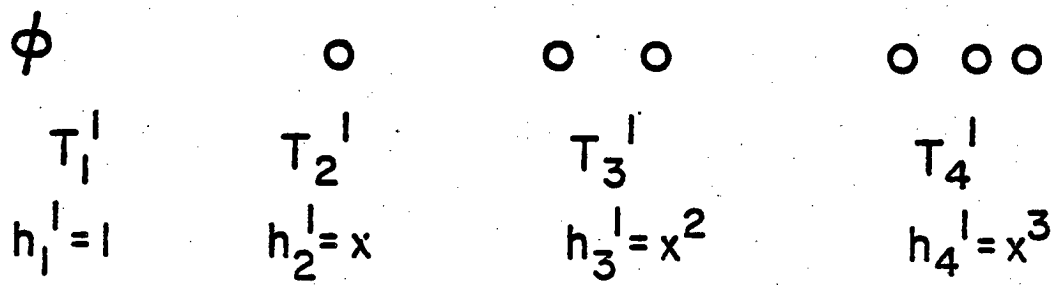


fig. 2



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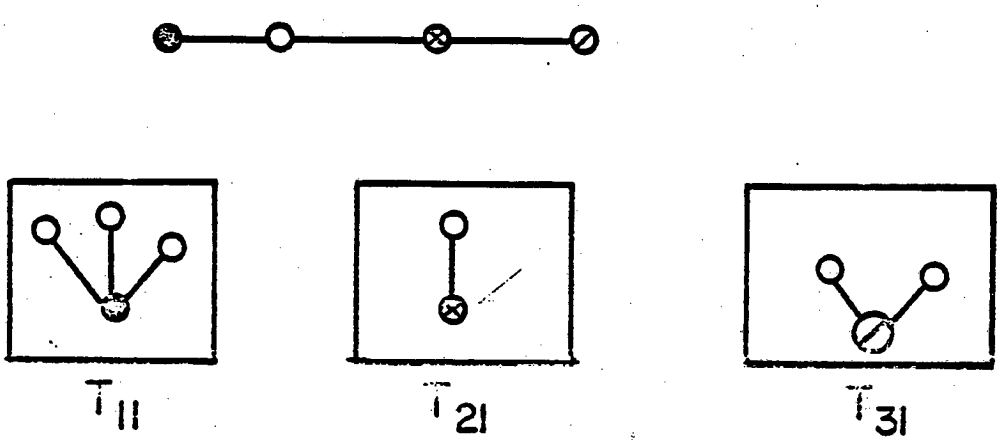


fig. 4

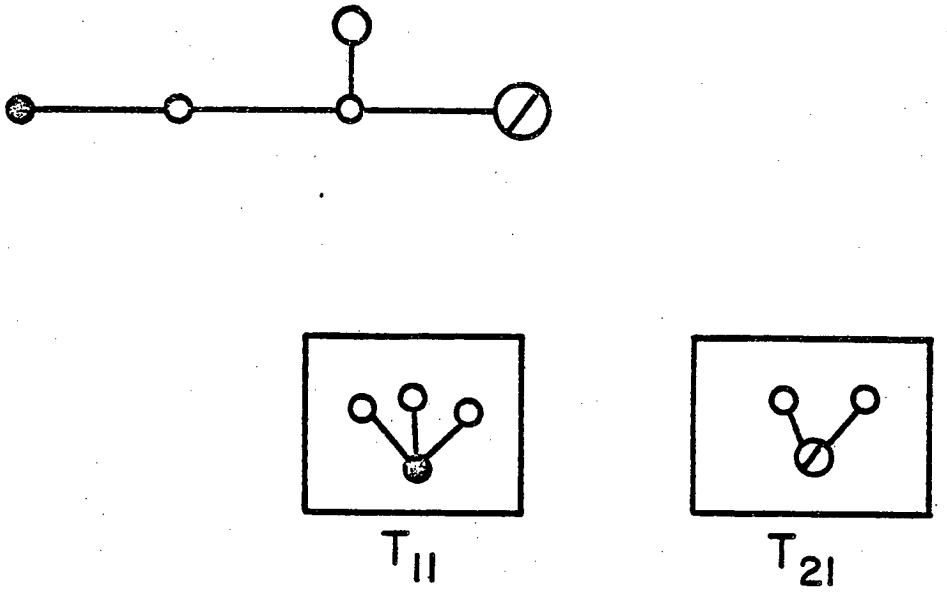


fig. 5

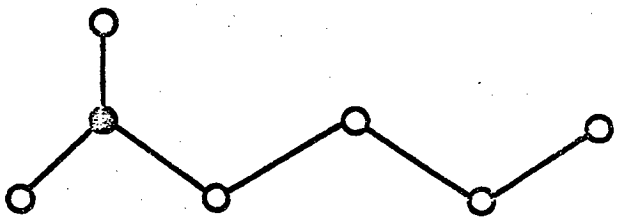
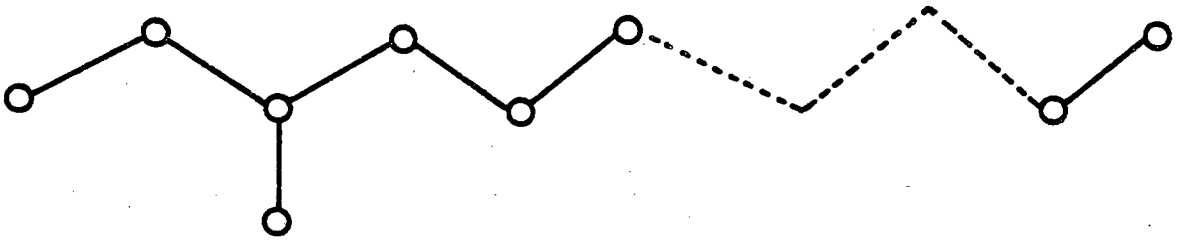


fig. 6



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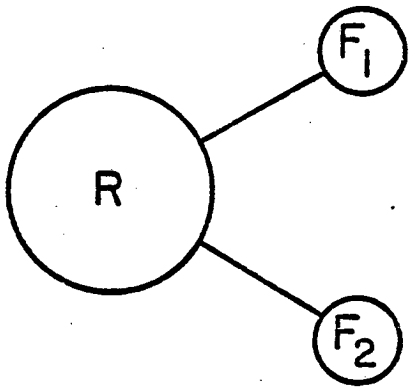


fig. 8

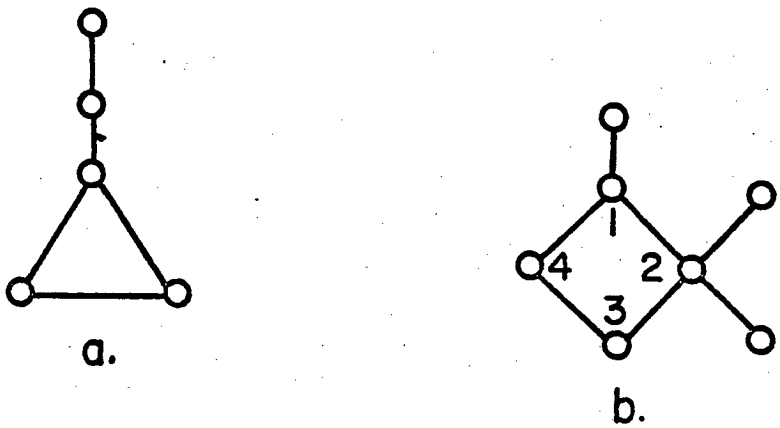


fig. 9

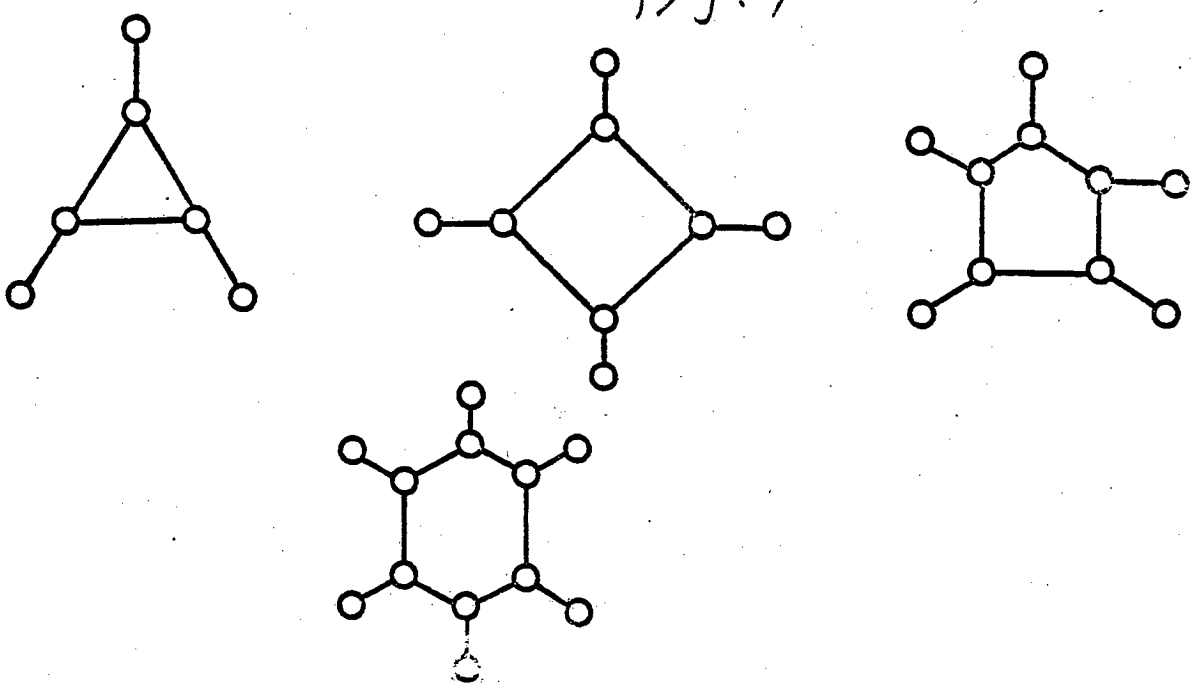


fig. 10

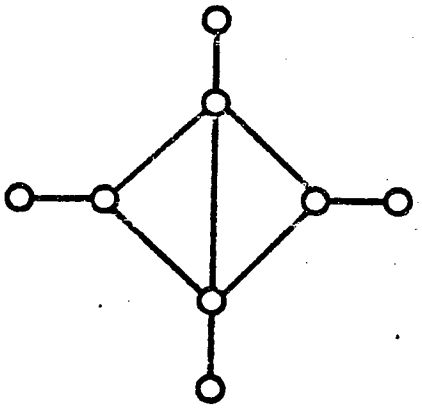
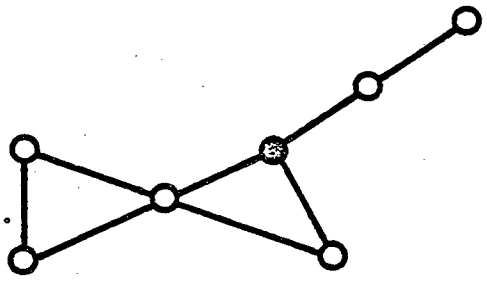


fig. 11



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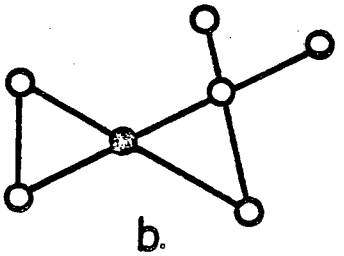
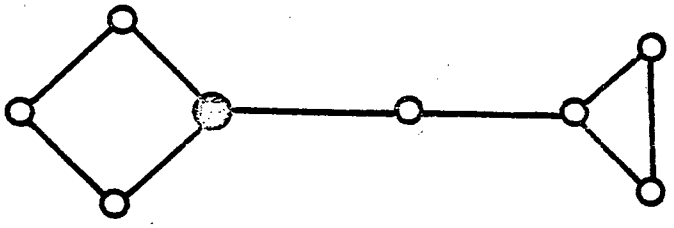


b.

fig. 12



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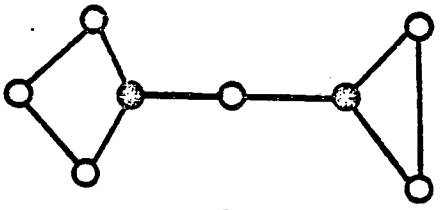

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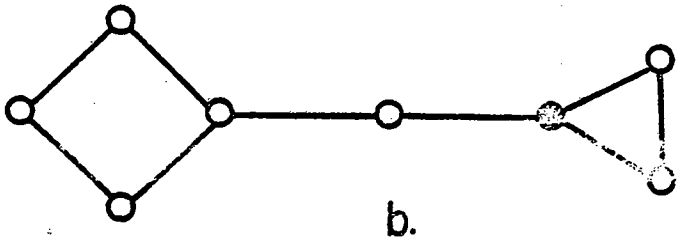

b.

fig. 13

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