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Notes on Some Less Known Early Contributions to Chemical Graph Theory*

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> »Research is to see what everybody has seen and think what nobody has thought«
> Albert Szent-Györgyi

A dozen less known, but important, contributions to the development and application of graph theory to chemistry are reviewed. The relevance of these works is pointed out. They include papers which appear to have been known to only a few involved in the recent revival of graph-theoretical methods in chemistry. Among such papers that have escaped wider attention are Flavitzky's enumeration of isomers (1874), Muirhead's work on the comparability of functions (1901) and the review article on graph theory in chemistry by Balandin (1940). A similar class includes works by Bloch, who first introduced the nearest neighbour approximation, well-known from the Hückel molecular orbital calculations; Wheland, who used the polynomial expansion for enumeration of valence structures prior to the well-known Polya's theorem and Sachs, who outlined a scheme for enumerating various cycles in a molecule years before more recent schemes have been developed. In addition, we review a work by Heilbronner who reveals an intriguing relationship between valence structures and molecular connectivity and a work by Marcus, concerned with bond-addi-

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tive properties of molecules, which anticipated much of the recent work on bond indices in benzenoid hydrocarbons and the role of circuits in such systems.

INTRODUCTION

The last two decades have witnessed an intensive development and application of graph theory in chemistry.[1-12] We like to call the development and application of graph theory in chemistry the *chemical graph theory*. Besides the purely structural aspects, such as characterization of molecular branching and cyclicity, or a search for structural elements to be associated with aromaticity, reactivity or properties of a system, there are some features of the subject that are of interest for a certain number of practical problems concerning the processing of chemical information by computer. Such work requires enumeration of possible structures and their construction as well as development of adequate coding, which can be meaningfully altered when a related, but different, structure is considered. All this indicates that graph theory, as well as some other branches of non-numerical mathematics,[13] are becoming important parts of our tools for solving chemical problems. Optimistically, we anticipate even greater expansion of these new methods in all branches of chemistry in times to come. It seems, therefore, that this is the proper time to draw attention to some earlier work in the chemical graph theory which has not been sufficiently well-recognized or almost completely escaped attention of current researchers.

In this review, we will mention a dozen papers which, in our own view, deserve more prominent attention. In some cases, a proper acknowledgement of such papers will revise the usually assumed priority of a particular concept, but we will not indulge in pursuing the historical issues nor do we wish to diminish the role and significance of subsequent works (which may have been quite independently developed). Our aim is to bring to the attention of interested readers some earlier publications which also provide a source for further elaboration or anticipate many of the more recent ideas.

STRUCTURAL MATRICES

Let us start this paper with a review article of Balandin[14] entitled: »*Structural Algebra in Chemistry*« (translated from Russian), published in 1940. This is probably the first review article on the application of graph theory in chemistry. Here, *structural matrices* are explicitly mentioned and discussed. However, the earliest reference to structural matrices is given by Brunel (1895).[15]

Balandin considered a special asymmetric form of structural matrices, in which only the elements below the main diagonal are taken into consideration. An example is given below.

$$\begin{bmatrix} a_{11} & 0 & 0 & 0 \\ a_{12} & a_{22} & 0 & 0 \\ 0 & a_{23} & a_{33} & 0 \\ 0 & a_{24} & 0 & a_{44} \end{bmatrix}$$

After a brief outline of mathematical operations with such structural matrices, a considerable part of the review is concerned with structural matrices in which the elements are substituted by suitable quantities. The topological elements a_{ij} (which we today call, more correctly, connectivity elements)[16] can be substituted by *objects*, and these objects can be substituted by their characteristic values. A sample of quantities the elements of which can be substituted in proper places of the structural matrix is given in Table I.

TABLE I

A sample of quantities the elements of which can be substituted in the structural matrix

Quantity	Diagonal elements a_{ii}	Off-diagonal elements a_{ij}
1. Atoms	nuclei, electrons	their interactions
2. Molecules	atoms	chemical bonds
3. Liquids and gases	molecules	their separation
4. Equilibria	components	reversed reactions
5. Consecutive reactions	components	reactions
6. Chain reactions	reactions, activations, branching	chains
7. Crystallization and related phase diagrams	points	lines
8. Spectra	equations	transitions

A sample list of substitution of objects by their characteristic values is given in Table II.

TABLE II

A sample list of substitution of objects from Table I by characteristic values. The ordinal number correspond to the order of quantities in Table I.

1. Wave functions
2. Electron states, dipole moments, dissociation energies, potential curves
3. van der Waals forces, expressions for dispersion (interaction), the free-path lengths, collision frequencies
4. Equilibrium constants
5. Reaction rates, interaction constants, activation energies
6. Chain length
7. Analytical expressions for lines
8. Frequencies, intensities, polarisation

Balandin continues with a discussion of numerous examples, which include the constitution and structure of molecules, quantitative properties of chemical bonds, configuration and orientation of molecules, considers the trace and the determinant of the structural matrix. He also used structural matrices to follow certain chemical reactions. As examples, several substituted structural matrices for methyl alcohol are given below.

$$\begin{bmatrix} \mathrm{H} & & & & & \\ x & \mathrm{C} & & & & \\ & x & \mathrm{H} & & & \\ & x & & \mathrm{H} & & \\ & y & & & \mathrm{O} & \\ & & & & z & \mathrm{H} \end{bmatrix} \begin{bmatrix} \mathrm{H} & & & & & \\ 1.08 & \mathrm{C} & & & & \\ & 1.08 & \mathrm{H} & & & \\ & 1.08 & & \mathrm{H} & & \\ & 1.45 & & & \mathrm{O} & \\ & & & & 1.01 & \mathrm{H} \end{bmatrix}$$

$$\begin{bmatrix} \mathrm{H} & & & & & \\ 93 & \mathrm{C} & & & & \\ & 93 & \mathrm{H} & & & \\ & 93 & & \mathrm{H} & & \\ & 74 & & & \mathrm{O} & \\ & & & & 120 & \mathrm{H} \end{bmatrix} \begin{bmatrix} \mathrm{H} & & & & & \\ 2.17 & \mathrm{C} & & & & \\ & 2.17 & \mathrm{H} & & & \\ & 2.17 & & \mathrm{H} & & \\ & 2.17 & & & \mathrm{O} & \\ & & & & 2.17 & \mathrm{H} \end{bmatrix}$$

These matrices correspond, respectively, to interatomic distances (in Å), bond dissociation energies (in kcal) and vibrational force constants (in $\mathrm{cm}^{-1} \times 10^4$). We have used numerical values as given by Balandin – these should be revised, however, in accordance with advancement of experimental techniques.

Balandin clearly recognized the importance of *algebraic* schemes – in contrast to *arithmetic* manipulations with numerical quantities – and was particularly immersed in the study of isomorphic substitutions of the topological entries (*i.e.*, connectivities) by quantities that express certain properties of the considered objects (systems). Algebraic manipulations of structural matrices, such as the construction of their traces or determinants, appear to yield some physical content. We recognize the properties considered by Balandin as the so-called bond-additive properties, which received renewed attention by the advance of the chemical graph theory and its use in devising QSPR (quantitative structure-property relationships) and QSAR (quantitative structure-activity relationships) schemes with topological indices, *e.g.*[17-26]

We note that the concept of the *atom-connectivity matrix*, introduced by Spialter in 1964,[27] may be viewed as a special case of Balandin's substitution matrices as well as the concept of the *bond and electron matrix* (the so-called *be*-matrix) introduced by Ugi and Gillespie in 1971.[28] In this way, Balandin anticipated by many years a more recent work with modified structural matrices.

ENUMERATION OF ISOMERS

Enumerations of isomers are generally considered as the first applications of what we now refer to as the chemical graph theory. Papers dealing with the topic started to appear in the 1870's. The first authors were Flavitzky from Kazan, Cayley from Cambridge, Schiff from Florence, Herrmann working in Germany and Lozanić who reported his work at meetings of the Croatian Academy of Sciences and Arts in Zagreb. We see in this early interest in enumeration of isomers quite a remarkable international competition, though it was common to all these early contributions that they were published in the same journal and same language, that is, in *Berichte der Deutschen Chemischen Gesellschaft*, then the leading chemical journal, and in German. It is somewhat surprising then to find repeated references to Cayley's count of alkane isomers[29] as the *first* contribution to the chemical graph theory – the work supposed to mark the beginning of the new field. Examining *Berichte* for 1875, we find for the first time in the same volume a paper by Cayley entitled: »*On Analytical Figures, Known in Mathematics as Trees, and Their Application to the Theory of Chemical Compounds*« (translated from German) on page 1056 (received on November 24, 1874)[29] and a paper by Schiff entitled: »*On Statistics of Chemical Compounds*« (translated from German) on page 1542 (received on November 24, 1874).[30] Hence, it appears that these two papers are quite independent, although Schiff is aware of Cayley being involved in this kind of problems, stating in the conclusion of his paper that an encouraging sign is that one of the leading mathematicians, like Cayley, is interested in these questions. However, Flavitzky[31] published a page long note in 1876 on the number of isomers for saturated aliphatic (primary, secondary and tertiary) alcohols with up to 12 carbon atoms, results that are also directly applicable to saturated aldehydes and ketones. The 1876 paper represents a summary of Flavitzy's work, published in 1871 in the *Journal of Russian Chemical Society*,[32] but also a comment on the above-mentioned paper by Schiff. Nevertheless, Flavitzky's work should have been known to all concerned since in the same year (1871) in the correspondence part of *Berichte*, there is a report of von Richter[33] describing the results presented at the Russian Chemical Society Meeting in St. Petersburg in May 1870, in which he devotes a dozen lines to the work reported by Flavitzky (like the other German authors he writes his name as Flawitzky), giving even the numbers for alkane isomers – from 6 to 10 carbon atoms. Thus, all the relevant information, either in the form of a summary or full length reports, appeared in *Berichte* in 1871 and 1876, and this should settle the question of chronology – until and unless we hear of yet another earlier result. Now, there may be sufficient arguments and evidence that earlier work of Cayley, published as early as 1857,[34] is to be considered as a contribution to chemical combinatorics and enumeration – which would justify retaining Cayley as the first contributor. This, however, would require adopting of those earlier dates as the »beginning« of the chemical graph theory. The matter deserves attention of a science historian and necessitates a more thorough search of the earlier literature. A very nice and scholarly article on the origins of the chemical graph theory was recently published by Rouvray.[35] The reader is directed to Rouvray's article for a fine presentation of the first use of chemical graphs. Rouvray[36] has also produced two excellent articles on the life and work of Cayley. These articles are recommended to those interested in the early history of the chemical graph theory.

Cayley's work is formulated in proper mathematical terminology (as it could have been expected) and illustrated accordingly. Schiff used a more chemical language and, for example, spoke of chains. He considered the problem of isomer enumeration to belong to chemical statistics, as a new chapter of stechiochemistry (more correct term, of course, would be not statistics but combinatorics, but it appears that, in those days, the term statistics implied also combinatorics, as Schiff explicitly used the words combinatorics and permutation).

It is interesting that even in those first days of the application of graph theory to chemistry there have been differing opinions on the subject. To Schiff, who for years had been »collecting« relevant material belonging to his chemical statistics, on his walks as well as during sleepless nights: »*I make these personal* *remarks intentionally, to confess bluntly that I have not considered these occupation as serious, but rather as a scientific game, and that is also the reason why, until now, I could not decide to publish something. When I have now overcome this objection, let me indicate how problems in chemical statistics can be adjusted and prudently resolved in a postulate, then I may mention as an excuse that a leading mathematician Cayley is not disdained to devote his attention to these questions...«* (translated from German). Part of this frank opinion appears to be objective to Flavitzky,[31] who replies with the following words: *»The full determination of the number of possible isomers can hardly be considered as 'scientific game'...«* (translated from German).

Let us conclude this section by mentioning the work of Lozanić[37] who was first to recognize the new field as a *new branch of chemistry*. Already Schiff mentioned that there we have a special aspect of chemistry – which he called statistics – but he did not anticipate the growth of the field and the diversity of problems associated only with enumeration. There have been no new works since the initial efforts of Flavitzky, Cayley, Schiff and Herrmann – but perhaps the time distance of 20 years and more made it clearer that these works represent a seed for a new branch of chemistry. Lozanić makes the following description of his vision of a new chemical branch: *»I also considered this question* (that is, enumeration of isomers) *years ago, but my work at school and in the laboratory prevented me from completing it. I considered it after I was separated from school and the laboratory; this issue has as I can see it, certain importance for both chemistry and mathematics. Thus, when we find all kinds of structural isomerisms of paraffins and their derivatives, and when the regularities in such sequencies are recognized, a division will be created, of* chemical permutations, combinations and variations, *which operations differ from similar mathematical operations, since in chemical permutations and variations chemical repetitions are omitted and separations of lateral members are taken into account in combinations. It would be too early to take also stereoisomerism into account; that theory is still associated with chemical structure and deals only with specific isolated questions....«* (translated from Croatian). The same contemplation on the new branch of chemistry, opened by the work on enumeration of isomers, is repeated by Lozanić[38] (who modified the spelling of his name to Lozanitsch to suit the German language) in his lengthy exposition in *Berichte* in a somewhat shorter form, emphasizing the difference between mathematical and chemical aspects of permutations and combinations.

It is to be noted, that despite the early recognition of its specific character, at a time when stereochemistry – which is usually given the same »age« – was still undeveloped and concerned with »isolated problems«, while some generality of the combinatorial calculus was implicit, it happened that stereochemistry outgrew into a sizeable branch of chemistry, while the combinatorial graph theory (though enriched with numerous other contents) remained little known outside individual efforts until it was revived a few years ago, *e.g.*...[3,11] A possible reason for this is not lack of its importance, but the fact that chemistry, until very recently, has not been overwhelmingly concerned with the problems that have a *difficult combinatorial basis*. Just as one can deal with *simple* symmetry problems without the group theory and its apparatus, so in problems with a *limited* combinatorial content one can resolve most of the problems intuitively, not realizing that the schemes represent various aspects of combinatorial graph theory.

THE BLOCH APPROXIMATION

Amongst the few important historical contributions to the development of the current theoretical chemistry concerned with the nature of the chemical bond[39] is certainly the work by Hückel[40-44] in which he first applied quantum mechanical methods to the double bond and then to unsaturated organic molecules, such as benzene and benzenoid hydrocarbons. Thus, he has started the era of quantum chemistry of large molecules. It seems important to recognize that the significance of his work lies primarily in his bold determination to use a new theoretical tool to study molecular structure of systems that were of great chemical interest at his time. The scheme, as developed, was neither fully original nor computationally complex (of course, any computationally complex scheme in the early thirties would not have had a chance to be useful because of the lack of computing facilities) – but this does not undermine the significance of the work. Here, a comparison can be made with a more recent effort, in the early fifties, to upgrade the theoretical calculations from the semi-empirical to the *ab initio* level. Although a number of calculations on selected simpler systems were available at the time, it was Mulliken[45] who took the bold step to initiate a project involving rigorous evaluation of various molecular integrals.[46] It took courage to embark on such an ambitious task – the full outcome of which was hardly predictable.

The Hückel molecular orbital (MO) method for calculating wave-functions of conjugated systems led to a set of homogeneous equations, the matrix of which depended only on the *connectivity* of atoms in the system. This was not immediately and explicitly recognized as the representation of a simpler model, in which the input is the information on the vertex-adjacencies in the molecular graph,[12] *i.e.*, that the Hückel matrix (in the normalized form) is identical to the structural matrix (adjacency matrix) of the spectral graph theory.[47] The first reference to the close relationship between the Hückel method and graph theory was made almost a quarter of a century after the work of Hückel, when Ruedenberg[48] brought the connection to attention. Two years after the work of Ruedenberg, the relationship between the Hückel MO method and graph theory was discussed in detail by Günthard and Primas.[49] However, already in 1953,[50] Heilbronner used graph-theoretical arguments, albeit not identified as such, in proposing a method for computing characteristic (Hückel) polynomials of π-electron systems. Schmidtke[51] also studied the relationship between the simple MO theory and the theory of graphs and pointed out that the LCAO MO descriptions of molecules have topological and energetic aspects.

In their undertaking, Günthard and Primas were influenced by a report on the Collatz and Sinogowitz work on the spectra of graphs[52] which appeared in the »*Fiat Reviews of German Science* 1939–1946« (as Günthard told NT during the *International Symposium on the Electronic Structure and Properties of Molecules and Crystals* held in Cavtat, Croatia, from August 29 to September 3rd, 1988) which was later developed into a full paper by Collatz[53] because Dr Ulrich Sinogowitz was killed on September 12, 1944 during the bombing of Darmstadt. The Collatz and Sinogowitz paper contains a number of interesting results including the definition of the graph index based on the graph spectrum. The concept of the graph index was developed by Collatz in 1941 when he was in Karlsruhe. His paper was published in the »*Mathematische Zeitschrift*«[54] in the bitter years (1942/1943) of the second World War. It is interesting to note, with amazement, that, during the whole of the Second

World War, the scientific consultants (*Wissenschaftlicher Beirat*) whose names appeared on the front page of *»Mathematische Zeitschrift«* were, among others, perhaps the leading English mathematician in this century G. H. Hardy from Cambridge and H. Weyl from Princeton.

The initial success of the Hückel method was surprising because it was not clear why such relatively crude approximations, which include assumptions (i) on the linear combination of atomic orbitals; (ii) neglect of σ-electrons; (iii) neglect of electron repulsions; (iv) acknowledging only the nearest-neighbour interaction, should lead to any useful predictions. However, as we know today, the fact that the Hückel method takes into account the connectivity of π-centers, is the essential ingredient of success.

What appears to be less known today and is rarely acknowledged adequately is the fact that the approximation of the nearest-neighbour interaction is not due to Hückel. It was Bloch[55] who, a few years prior to Hückel, considered the electronic structure of crystals and introduced the approximation on molecular integrals that later Hückel found useful. Giving a lecture on the pioneers in quantum chemistry at the Sanibel Symposium 1977, dedicated to Walter Heitler, Friedrich Hund and Erich Hückel, Parr[56] mentioned explicitly that the known integrals of the Hückel MO model, α and β, have an antecedent in Bloch's works on crystals.

The Bloch approximation may be presented in the following way. Adopting Bloch's notation, we consider a point on the crystal grid:

$$\boldsymbol{r}_{g_1g_2g_3} = g_1\boldsymbol{a} + g_2\boldsymbol{b} + g_3\boldsymbol{c} \tag{1}$$

where $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$ are unit vectors along the grid axis. The potential is given by:

$$U_{g_1g_2g_3}(xyz) = U(x - g_1\boldsymbol{a}, y - g_2\boldsymbol{b}, z - g_3\boldsymbol{c}) \tag{2}$$

which originates from a charge at point $\boldsymbol{r}_{g_1g_2g_3}$. By summing up all the contributions arising from other grid points, the total potential V is obtained. In the expression for molecular integrals, however, appears the potential:

$$U'_{g_1g_2g_3}(xyz) = V(x, y, z) - U_{g_1g_2g_3}(xyz) \tag{3}$$

Then, the eigenfunctions $\phi_{g_1g_2g_3}$ (atomic orbitals) are different from zero only in the neighbourhood of the point (g_1, g_2, g_3), and when they are further assumed normalized (to 1), then the following holds:

$$\int \phi_{g_1g_2g_3}\, \phi_{h_1h_2h_3}\, d\tau = \begin{cases} 1 \text{ when } g_1{=}h_1,\ g_2{=}h_2,\ g_3{=}h_3, \\ 0 \text{ in all other cases} \end{cases} \tag{4}$$

The above is recognized as the assumption concerning overlap integrals, which are neglected in the Hückel method. Next, Bloch is concerned with approximating the interaction integrals:

$$J = \int U_{g_1g_2g_3}\, \phi_{g_1g_2g_3}\, \phi_{h_1h_2h_3}\, d\tau \tag{5}$$

One is reminded that $U_{g_1g_2g_3}$ quickly diminishes in the neighbourhood of point (g_1, g_2, g_3), *i.e.* equals the sum of contributions from other grid points potentials. Therefore, in the construction of J, the cases when the triplet (h_1, h_2, h_3) corresponds to one of nearby points of (g_1, g_2, g_3) on the grid, have also to be considered. The further removed points need not be considered, since there the magnitude of $\phi_{g_1g_2g_3}$ soon becomes small. In the following, we will take that we are dealing with the simplest cubic grid that functions $U(x, y, z)$ and $\phi(x, y, z)$ are of spherical symmetry. Then, we are allowed to state:

$$\int U_{g_1g_2g_3}\, \phi_{g_1g_2g_3}\, \phi_{h_1h_2h_3}\, d\tau = \begin{cases} \alpha \text{ when } (h_1, h_2, h_3) = (g_1, g_2, g_3) \\ \beta \text{ when } (h_1, h_2, h_3) \text{ is a neighbour of } (g_1, g_2, g_3) \\ 0 \text{ in all other cases} \end{cases} \tag{6}$$

We recognize the above as the approximation on the Coulomb integrals and resonance integrals of the Hückel method. Here, the assumptions of the spherical forms for atomic orbitals and cubic grid are not fundamental, the former only result in a non-zero contribution from all nearest neighbours, whilst if a charge had axial symmetry, only the contributions along the axis and perpendicular to the axis would have to be considered (as we do in the Hückel scheme).

The recent increasing interest in graph theory and its applications to chemistry, in particular to the chemistry of organic conjugated systems,[1,4,6,7,11,12,57-59] provides an opportunity to draw attention of the chemists back to the work of Bloch. It appears that an early single call for attention by Hartmann,[60] in a readily available journal, was not sufficient. It should also be mentioned that Hückel himself gave Bloch the credit for the approximations involved. In a book on chemical graph theory by one of us (Vol. 1, p. 64),[6] the term *Bloch-Hückel approximations* is used.

THE RUMER SCHEME FOR DERIVATION OF VB STRUCTURES

We continue with some lesser known results from the valence bond (VB) theory, which played an important role in the early development of the quantum chemistry and have been prematurely abandoned. In a way, it is a shame that the interest in the VB method suddenly declined as the well-known difficulties appeared associated with the problem of handling an enormous number of structural components – instead of taking up the challenge![61] In part, its neglect was due to the sudden popularity of the MO method, which proved to be free from such mathematical and computational complexities, and could be used with limited mathematical experience (usually not beyond high-school education) – frequently solving problems »on the back of an envelope«. All this is a compliment to the MO method, but should the interest in the VB method have continued, today the field of chemical graph theory could probably be expanded by several orders of magnitude! It is not infrequent in science that interest of a large fraction of researchers is shifted for such and similar reasons – until a breakthrough in another field indicates that the difficulties have not been unsurmountable and a revival of the field is in sight. An example can be quoted from the *ab intio*-type calculations concerned with the use of Slater-type orbitals (STOs) as a basis. The problems of solving multicentre integrals are well known and much effort has been devoted to resolving the difficulties. However, before the »end« of these efforts was in sight availability of Gaussian-type functions almost completely cut the interest in STOs.[46] Again, difficulties have been exchanged for the comfort and convenience of an alternative which *is not* equivalent, but can be used for the »production« of results currently advertised as »acceptable«. The problem of efficiency of schemes using different bases has been mainly laid aside awaiting its resurrection. The situation would be different if we had resolved all the difficulties in evaluating molecular integrals over STOs and if we had fully understood their limitations. But this is not the case, and this kind of mathematical problems may take some time to convince those interested that all the reasonable avenues have been thoroughly exploited. As an illustration, let us mention the problem of solving the three-centre nuclear attraction molecular integrals – some of the first integrals to be considered difficult (in comparison with two-centre Coulomb and hybrid integrals). It took 30 years from the initial work of Coulson[62] to approach these integrals in a more systematic fashion, until a pleasingly simple *and* analytical scheme has been developed,[63] in which only the familiar auxiliary functions appear. Another promising line, that of expressing one kind of (complex) molecular integrals *via* others (simpler), initiated a few years back by Harris,[64] has hardly been properly examined, yet it may offer interesting (at least so far unexplored) possibilities.

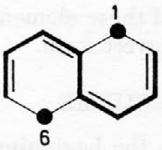
Among less known earlier results of the VB method is limitation of the well-known scheme of Rumer[65] for derivation of all valence structures of interest. In his scheme, all orbitals (atoms) are first arranged formally in a circle, and then coupled in a way that no crossing of lines, representing the pairing, occurs. The obtained set of valence structures is linearly independent. However, instead of these, one could use structures with a crossing of the coupling lines (these could be simply derived from the first set by appropriate linear combinations) – there is no a priori reason why the former set should be preferred. The arbitrary nature of sets derived from the Rumer diagrams has been emphasized by Wheland,[66] but it is generally not sufficiently well-appreciated (except by those involved in actual VB calculations). The Rumer scheme has a more serious limitation since it does not apply to a general conjugated system. It was Klement[67] who first realized its restrictive nature when he considered the valence structure of acenaphthylene. It appears that the scheme is not applicable to those systems where there are three fused conjugated rings – so, in fact, the scheme only works for systems in which all atoms are on the molecular periphery. Since the distribution of single bonds within the atoms of the periphery does not enter the considerations (thus, the total of all structures among isomers such as anthracene and phenanthrene is the same, the difference emerges when structures of different degree of excitation are considered, since the underlying sigma bonds may, for the same Rumer diagram, point to a different kind of valence structure) – one sees that the scheme applies to situations when atoms already make a circle – irrelevant bonds being ignored. Gordon and Davison[68] point to the work of Klement, and it appears that additional reference to this earlier work is in place – particularly in view of the revival of interest in VB calculations.[69]

THE HÜCKEL METHOD AND THE RESONANCE THEORY

Another interesting and intriguing paper, concerning both the MO method and VB calculations, which it appears has not received sufficient attention is due to Heilbronner.[70] It is entitled: *»On a graph-theoretical connections between the Hückel MO* *method and the formalism of the resonance theory«* (translated from German). Here, the author was concerned with the inverse of Hückel matrix, and was able to show, on the example of naphthalene, that the inverse of the Hückel matrix and its elements are related to certain valence structures of particular skeletal fragments. A rule can be formulated that gives the elements of the inverse as:

$$A_{ij}^{-1} = \frac{[(-1)_{ij}^{p} \cdot k_{ij}]}{K} \tag{7}$$

where p_{ij} is the number of double bonds on the shortest path between vertices i and j, k_{ij} is the number of unexcited valence structures for the molecular residual obtained by excising atom i and j and bonds incident to them, while K is the number of (unexcited) Kekulé valence structures of the molecule. Let us adopt a common numbering for naphthalene (the same as used by Heilbronner) and illustrate the derivation of element $A_{1,6}^{-1}$ (incidentally, by oversight, this particular element has been omitted in Heilbronner's exposition):

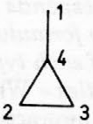


$k_{1,6} = 1 \quad p_{1,6} = 0 \quad A_{1,6}^{-1} = 1/3$

K=3 for naphthalene

(In his exposition, Heilbronner used a slightly different notation). It is evident that the corresponding residuals of the structure, when centres i and j are excited, may be viewed as the so-called ionic valence structures, in which charges + or – are associated with the i, j pairs. How general is the outlined scheme has not been investigated, except for the obvious condition on the existence of A^{-1}, *i.e.*, that the determinant of the adjacency matrix be different from zero. The latter is also a condition for the appearance of NBMO's (non-bonding molecular orbitals), the subject which has received due attention in the literature.[71]

In this connection it is somewhat disappointing to find that, whilst the Hückel matrix, and in the recent years its identical image, the adjacency matrix have played an important role in discussions of the properties of conjugated systems,[72] there has hardly been any mention of A^{-1}.[73] One can expect a correction in the near future, in particular since evaluation of the elements of A^{-1} can be obtained also in a somewhat less lengthy procedure using the well-known property of the adjacency matrix, namely that it satisfies the characteristic polynomial.[74] We will illustrate this on a simple graph, shown below, whose characteristic polynomial is:[75]



$$P(x) = x^4 - 4x^2 - 2x + 1$$

The corresponding adjacency matrix (for the assumed numbering of vertices[76]) and its powers are:

$$\boldsymbol{A}=\begin{bmatrix}0&0&0&1\\0&0&1&1\\0&1&0&1\\1&1&1&0\end{bmatrix}\quad \boldsymbol{A}^2=\begin{bmatrix}1&1&1&0\\1&2&1&1\\1&1&2&1\\0&1&1&3\end{bmatrix}\quad \boldsymbol{A}^3=\begin{bmatrix}0&1&1&0\\1&2&3&4\\1&3&2&4\\3&4&4&3\end{bmatrix}\quad \boldsymbol{A}^4=\begin{bmatrix}3&4&4&2\\4&7&6&6\\4&6&7&6\\2&6&6&11\end{bmatrix}$$

The various powers of $\boldsymbol{A}$ can also be directly constructed as their corresponding elements have a simple physical interpretation:[77] They represent the number of paths between atoms i and j of the length l, where l is the power of the matrix. One can now simply verify that, substituting the corresponding matrices in the characteristic polynomial, and performing the necessary arithmetic, we obtain $P(\boldsymbol{A}) = 0$. Hence, by multiplying the expression by $\boldsymbol{A}^{-1}$, we derive the identity: $\boldsymbol{A}^{-1}(\boldsymbol{A}^4 - 4\boldsymbol{A}^2 - 2\boldsymbol{A} + \boldsymbol{I}) = 0$ (where 1 has to be replaced with the unity matrix), or $\boldsymbol{A}^{-1} = -\boldsymbol{A}^3 + 4\boldsymbol{A} + 2\boldsymbol{I}$ giving,

$$\boldsymbol{A}^2=\begin{bmatrix}2&-1&-1&+1\\-1&0&+1&0\\-1&+1&0&0\\+1&0&0&0\end{bmatrix}$$

Now, one can again use the structural interpretation of these elements, as suggested by Heilbronner, and verify that the matrix has the correct form.

WHELAND'S ENUMERATION SCHEME

Isomer enumerations are generally considered as the beginning of graph-theoretical applications in chemistry. The subject has a long history: we have already reviewed its very beginning in an earlier section. A nice review of the subject, with extensive coverage of the literature, has been given by Rouvray.[2] Recent reviews of the subject, with special emphasis on computational advances in isomer enumeration, are books on the computational chemical graph theory by Knop and co-workers.[11,78]

The enumeration theorem by Pólya[79] is generally taken to be the most notable advance in the field. However, it appears that the work of Wheland[66] is not commonly mentioned when enumerations are considered, although he independently considered counting polynomials (named since as the Wheland polynomials[80]) for the purpose of enumerations of valence structures and may, thus, have been the first to do that. Wheland's paper appeared in the same year that Pólya published his first paper[81] and preceded several other papers of Pólya published in chemical journals.[82] Let us quote from Wheland: *»The general procedure will be to associate with each molecule, or grouping of atoms, a polynomial of the form:*

$$k_0 + k_1z + k_2z^2 + k_3z^3 + \dots + k_nz^n \tag{8}$$

where $\mathrm{k_i}$ *is the number of structures of the* i*-th degree of excitation and z is simply a parameter. Obviously, finding the polynomial which corresponds to a given molecule is completely equivalent to solving the problem as originally formulated* (i.e., *by writing down all the structures, and by determining the number of each type by actual count), since the coefficients* $\mathrm{k_i}$ *are themselves the desired quantities.«* Wheland fully appreciated the importance of polynomial forms, by pointing to unpracticality of the pedestrian structure count, which already for $n = 14$ atoms leads to 429 forms to be enlisted! Wheland also considered special cases of chain and ring structures and derived the corresponding recursive formulae. For the case of a chain of length $2n$, we have:

$$C_n = C_{n-1} + z \sum_{i=2}^{n} C_{n-i}\, C_{i-1} \tag{9}$$

and the first few Wheland polynomials for chains with $2n$ carbon atoms are of the form:

$$\begin{aligned}
&C_1 = 1\\
&C_2 = 1 + z\\
&C_3 + 1 + 3z + z^2\\
&C_4 = 1 + 6z + 6z^2 + z^3\\
&C_5 = 1 + 10z + 20z^2 + 10z^3 + z^4
\end{aligned}$$

It is interesting to note the form of the recursion expression, the difference of two successive terms having a biquadratic form and, as a result, the coefficients appear symmetrically. The recursion for the Wheland polynomial of a ring with $2n$ carbon atoms can be conveniently written using the expression for chains:

$$R_n = C_n + (1-z)\, C_{n-1} \tag{10}$$

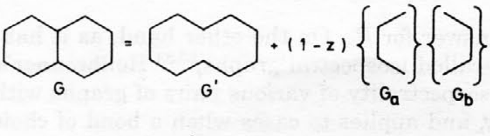
and the first few Wheland polynomials for rings are of the form:

$$\begin{aligned}
&R_2 = 2\\
&R_3 = 2 + 2z\\
&R_4 = 2 + 8z + 4z^2\\
&R_5 = 2 + 15z + 20z^2 + 5z^3
\end{aligned}$$

The above results have been derived from a direct analysis of these relatively simple structures. So, in a way, they are straightforward, *once the concept of polynomial representation has been conceived*. Another remarkable idea that followed is the consideration of associating the corresponding figure with such polynomials. This allows a comparison of two structurally related figures, in particular if they differ in the presence or absence of a single bond. For such cases, Wheland finds a general rule: (we use slightly different terminology and symbols): If a graph G differs from a second graph G' by having a single additional edge, and if this edge, together with its end vertices, divides G into two parts, G_a and G_b, then:

$$G = G' + (1-z)\, G_a\, G_b \tag{11}$$

Applying the above process to naphthalene, one obtains:



$$= R_5 + (1-z)(C_2)^2 = 3 + 16z + 19z^2 + 4z^3$$

In continuation of his analysis, Wheland gives the results, polynomials, for several more complex structures, including a number of condensed polynuclear aromatic hydrocarbons. Thus, for anthracene and phenanthrene, we have the following Wheland polynomials:

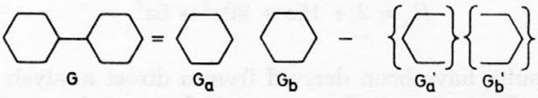
$$W(\text{anthracene}) = 4 + 48z + 150z^2 + 163z^3 + 58z^4 + 6z^5$$
$$W(\text{phenanthrene}) = 5 + 47z + 148z^2 + 165z^3 + 59z^4 + 5z^5$$

One can immediately verify our previous statement that the total number of valence structures, given by the sum of all the coefficients in the enumeration polynomial, is the same for systems with the same number of carbon atoms.

Decomposition of a graph into smaller fragments, as illustrated in the case of naphthalene, very much reminds one of the expansion of a secular determinant of a Hückel system. Heilbronner revived a useful partitioning,[50] which can be formulated in a rule (he called it the composition principle) of remarkable similarity to Wheland's rule previously given as: If there is an edge that divides G (a molecule) into two parts, G_a and G_b, then the characteristic polynomial of G can be written in terms of the characteristic polynomials of parts as:

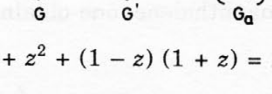
$$P(G) = P(G_a)\, P(G_b) - P(G'_a)\, P(G'_b) \tag{12}$$

where G' indicates graphs in which edges adjacent to the initial edge (a,b), which separate the graph into two parts (and corresponding vertices) are removed. Application of this procedure to biphenyl yields:



$$P(G) = x^{12} - 13x^{10} + 62x^8 - 138x^6 + 153x^4 - 81x^2 + 16$$

It seems that there are some not yet fully illuminated interesting aspects of these (and related) expressions which require further elaboration. For instance, is it essential that in Wheland's scheme, as stated, the *graph is divided into two parts* when the edge together with its end vertices is erased? On a simple example of a benzene ring, we see that the scheme works well, although the above conditions are not met:



$$= 1 + 3z + z^2 + (1 - z)\,(1 + z) = 2 + 3z = R_3$$

giving the correct answer for R_3. On the other hand, as it has been illustrated in a discussion of the so-called isospectral graphs,[53,83] Heilbronner's partitioning scheme (used to prove the isospectrality of various pairs of graphs with arbitrary residuals) has a wider validity, and applies to cases when a bond of choice (a,b) does not necessarily fragment the graph into two parts. The validity of such extensions has been verified[6,84] in proving that systems like these will necessarily have all eigenvalues (within the Hückel method) identical.

Before concluding this section, let us mention that Wheland's enumeration scheme reveals another side of the intriguing relationship between the VB method, *i.e.,* calculations with valence structures, and the MO method. Here, manipulating the *valence structures*, we arrive at *polynomial expressions* that have some similarity – *in their construction from fragments* – that is also typical of *characteristic polynomials.* In the previous section, we have seen the opposite in Heilbronner's construction of $\mathbf{A}^{-1}$, *i.e.,* manipulating the eigenvalue MO problem, we arrived at some information on valence structures. However, we have not found a direct connection with Wheland's scheme, more a kind of similarity in formalism. This reminds one of a comparison of bond orders, as defined by Pauling[85] and as defined by Coulson.[86] The former are derived from valence structures, the latter from coefficients of molecular orbitals – and although of fundamentally different starting points, they are more or less of comparable use (or limited use) when bond lengths are closely examined.[87] Some interrelation could be expected and, in 1958, relatively late in view of the then great popularity of Hückel's method and the long history of both VB and MO calculations. Ham, Ruedenberg and Platt[88] established a close and simple connection between the interdependence of VB and MO bond orders. This particular result deserves some attention but, since it is sufficiently well-known and occasionally referred to,[47] we will not elaborate it here.

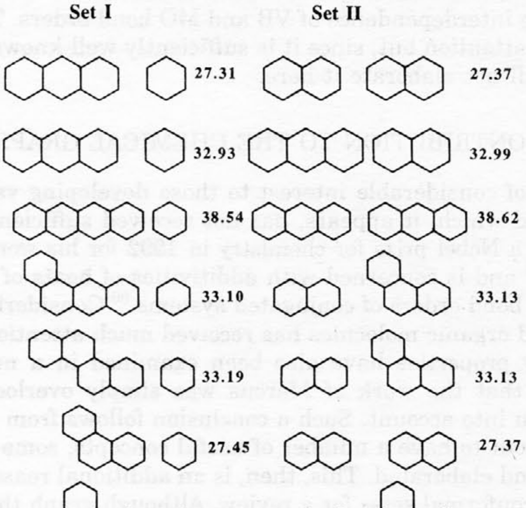
MARCUS' CONTRIBUTION TO THE CHEMICAL GRAPH THEORY

Another paper of considerable interest to those developing various graph-theoretical schemes, and which, it appears, has not received sufficient attention is due to Marcus (who got a Nobel prize for chemistry in 1992 for his work on the theory of electron transfer),[89] and is concerned with additivities of heats of combustion, resonance energies and bond orders of conjugated systems.[90] Considering that the graph theory of conjugated organic molecules has received much attention[1,4,11,57-59,91,92] and also that additivity properties have also been examined in a number of publications,[93] it appears that the work of Marcus was simply overlooked, rather than knowingly not taken into account. Such a conclusion follows from the content of the paper, which turns out to have a number of useful concepts, some of which could be further developed and elaborated. This, then, is an additional reason for singling out Marcus' notion of »conformal sets« for a review. Although graph theory is not explicitly mentioned in this work, it is evident that concepts and their implementation are very much part of the standard graph-theoretical lore. Thus, Marcus considers self-returning walks, emphasizes the nearest-neighbour relationship (adjacency), uses the characteristic polynomials, and of course, the important part of his analysis is *to count* numbers of self-returning random walks.

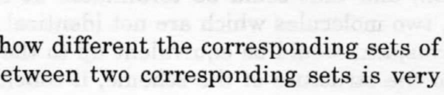
The basic task that Marcus considers is the problem of additivity of certain molecular properties but, in contrast to the usual approach to such questions, when one tries to recognize the kind of different contributions involved (*c.f.,* schemes for additivity of heats of atomizations[94]), one is more interested in a scheme that would resemble an expansion, and that could be terminated at some appropriate stage. Thus, in this scheme, two molecules which are not identical may appear having the same contributing terms, *i.e.,* would be equivalent up to the point of termination of the expansion. Due to the structure of the scheme, if conclusions from the derived additivity do not sufficiently approach the experimental results, one can continue the process by considering higher terms of the expansion, which will have a better resolution among closely related structures.

Let us follow Marcus and define *conformal* sets (in somewhat more general terms). A conformal set consists of one or more conjugated systems satisfying the following conditions (1) Compounds have an even number of electrons; (2) Elements of the set have the same number of n-step self-returning walks of the same quality; and (3) Systems with zero eigenvalue are excluded. An n-step self-returning random walk in a molecule is a walk from one neighbouring atom to another neighbouring atom, which begins and ends on the same atom, and during which one may pass a particular atom several times. The quality of a walk requires atoms to be chemically similar (*i.e,* atoms are of the same element and are in fairly similar nearest-neighbour environment).

The essence of the scheme is condition (2), the remaining conditions are introduced to exclude compounds, like radicals or fused ring systems, which are not aromatic in character. Examples of benzenoid systems on which Marcus illustrates the additivity of Hückel π-electron energies (energy units in terms of β) are given below:



The comparison includes also some nonbenzenoid systems, such as the pair azulene – naphthalene:



When one realizes how different the corresponding sets of eigenvalues could be, the agreement found between two corresponding sets is very good. Because of the diversity of eigenvalues, as Marcus remarks, conformal sets cannot be expected to provide a basis for discussions of spectral transitions.

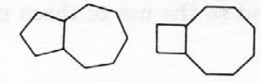
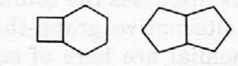
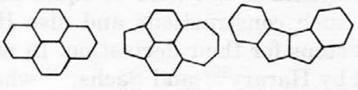
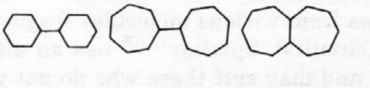
There are a few remarks worth making at this point regarding the above comparisons. Firstly, in a few instances the same set appears twice, indicating more than two conformal sets. The sets are constructed in the simplest way by using a classification of π bond types into (m,n) types:

$$(2,2)\ (2,3) \text{ and } (3,3)$$

where m,n represent the valency of carbon atoms in molecular graphs when hydrogens are suppressed. A classification of CC aromatic bonds in various (m,n) types was already considered some thirty years ago by Hartmann[95] and, more recently, by Randić[96] in an attempt to characterize molecular branching. A summary of bond types for a few smaller benzenoid hydrocarbons is given below[90]:

	(2,2)	(2,3)	(3,3)	sum	ring number:
Benzene	6	0	0	6	1
Naphthalene	6	4	1	11	2
Anthracene	6	8	2	16	3
Phenanthrene	7	6	3	16	3
Tetracene	6	12	3	21	4
Benz(a)anthracene	7	10	4	21	4
Chrysene	8	8	5	21	4
Triphenylene	9	6	6	21	4

We can expand the table with a few additional compounds that better illustrate some limitations of using only (m,n) bond types and the necessity of stipulations (1) and (3). We have, for example:

	(2,2)	(2,3)	(3,3)
	6	4	1
	4	4	1
	6	8	5
	8	4	1

Thus, considerably different structures may have the same distribution of bond types, as it is well-illustrated above in the last case of biphenyl, sesquifulvalene and heptalene. However, some other factors may be operative in these structures and decrease the expected similarity of the considered properties. For instance, sesquifulvalene will show marked asymmetry of charges with an appreciable dipole moment, which is absent in the other two structures. Further, biphenyl is alternant whereas heptalene and sesquifulvalene are non-alternant systems and so, in the former, the π-charge is uniformly distributed on all atoms, which is not the case of the latter. Heptalene, however, is excluded from the comparison by condition (3), since one of its eigenvalues is zero and cannot be aromatic. But chemical experience also suggests that biphenyl and sesquifulvalene are not so remarkably similar, which may call for consideration of another constraint – that alternants and non-alternants should not be combined. However, there is some danger that, by enlarging such additional conditions, we may exclude comparisons that are desirable. For instance, pyrene and azupyrene have the same bond distribution (6,8,5), one being alternant, the other non-alternant – but in this case a comparison is useful, and the compounds indeed show a remarkable (taking into account their structural differences) similarity. On the other hand, we have two non-alternants: acenaphthylene and as-indacene having the same bond types (5,6,3), but expected to be remarkably different (in fact, as-indacene has not yet been synthesized, showing some unusual properties). It may turn out that a useful discriminator for such compounds are the conjugated circuits[97] – a concept found useful for characterization of all kinds of conjugated systems[98] and, especially, carbon cages named fullerenes.[99] Conjugated circuits are those circuits in a Kekulé valence structure of a molecule in which there is a regular alternation of CC single and double bonds. Such circuits are necessarily even, but may be of $(4n + 2)$ or $4n$ size. The two different types of conjugated circuits can be associated with the opposing and competing molecular features, the former typifying the stable aromatic character of a system, the latter being responsible for antiaromatic characteristics. Depending on the number of conjugated circuits present in the set of Kekulé valence structures of each type, the molecule can show predominantly aromatic or non-aromatic properties. On these grounds, one may expect similarities between pyrene and azupyrene, despite the latter being non-alternant, while acenaphthylene and as-indacene belong to different classes.

As, the (m,n) bond types take into account only the presence of the next nearest neighbours, they correspond to an analysis in which only *four* self-returning walks have been considered. In some instances, this is not sufficient and one has to count six self-returning walks. The self-returning walks can be related to the coefficients of the characteristic polynomials[100] and so the use of these polynomials is a convenient search for conformity.

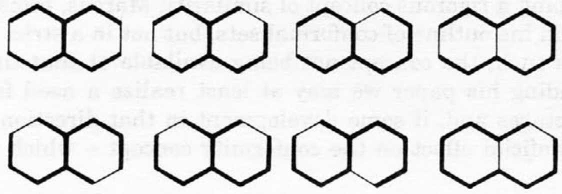
In one section of the paper, Marcus discusses the connection between secular determinants and random walks, but alternative graph-theoretical schemes for the construction of a characteristic polynomial are here of equal interest. In chemical literature, Coulson[101] considered such constructions and also Heilbronner[50,102] derived polynomials and gave some steps for their derivation. In mathematical literature, the problem was considered by Harary[103] and Sachs,[104] who derived a general expression only with contributions from various molecular fragments – consisting of isolated edges or isolated rings (circuits). Spialter[27,105] has an alternative presentation, which is sufficiently simple and may suit these who do not wish to follow more technical mathematical expositions. Similarly, Graovac *et al.*[75] developed a simple procedure, based on the Sachs theorem, for constructing characteristic polynomials of chemical graphs. Since then, a number of procedures have been published on the computation of a characteristic polynomial of a (chemical) graph, *e.g.*[106,107] It follows from the Sachs theorem that only isolated bonds and rings play an important role in the construction of the characteristic polynomial. We can see now that such components are also of interest in the count of self-returning walks, since a walk can use a closed ring to return to the starting point, or has to retract its path – but there is no need for two or more fused or connected rings.

It appears that the concept of conformity may yield additional results and may offer more, if elaborated and modified or expanded. Some preliminary results in this direction appear encouraging.[108] More recent interest in the graph theory of conjugated systems may contribute to better clarifications of the conditions imposed on comparisons of conformal sets. On the other hand, the concept of self-returning walks may be of considerable interest also in other comparisons of structures. The problem of *comparability of structures* and their *ordering* is an important subject in the graph theory as well as in its applications, such as chemistry. It is closely connected with the problem of graph isomorphism (*i.e.*, recognition of different graphs[109]). *Comparability* as such has been considered for functions (and graphs as special cases) already at the beginning of this century by Muirhead,[110] though his work has not received sufficient prominence (it is discussed in this paper later on). Muirhead proposed a rigorous definition for the *comparison* of different functions and in this way defined the term technically. There are other concepts in use in science, such as *similarity*, which still lacks a proper technical definition.[111,112] It appears that self-returning walks may provide a tool for characterizing similar environments in a graph (or molecular skeletons), and, starting from here, one may succeed in developing a rigorous concept of similarity. Marcus, himself, uses the concept of similarity in his outline of conformal sets, but not in a strict and well-defined sense – simply as such, the concept not being available at that time, as it neither is today. But, reading his paper we may at least realize a need for the concept of similarity of structures and, if some development in that direction brings results – it may have a beneficial effect on the conformity concept – which might be viewed as its precursor.

THE PROBLEM OF RING RECOGNITION

One of the most difficult problems currently unresolved in graph theory – difficult in the sense of classification of computational problems – is concerned with the search for a common fragment (in particular the maximal common fragment) among selected graphs. A special case and aspect of this problem is the search for all rings (or better to say circuits[113]) in a given polycyclic structure. If one lists all the circuits in a structure, then such a list provides a convenient basis for comparing different structures. But the *problem of recognition of rings* (and circuits) within a given chemical structure is also an important first step in the perception of the nature of the chemical structure,[114] important for the prediction of its chemical behaviour, and for inference of possible synthesis for the structure.[115] In some applications, a less ambitious task of finding only some rings or some circuits is of special interest, where the problem may be to find the smallest set of the smallest rings,[116] interesting for chemical documentation, and used in »the ring index«[117] and a conventional line notation system such as the one originated by Wiswesser.[118] In the development of programs for computer-assisted synthesis, on the other hand, one is interested in the so-called chemically significant rings,[119] or rings and circuits anticipated to be of relevance to such analysis. Finally, the concept of conjugated circuits clearly illustrates the importance, such applications as characterization of aromaticity[120] and classification of conjugated hydrocarbons,[121] of selected circuits within a particular valence structure.

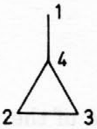
The problem of ring perception has received considerable attention and we are not going to review the subject. Some times ago, Wipke and Dyott[122] reviewed the subject and made a comparative study of the efficiency of several algorithms for ring perception, where one can find references to earlier work. Looking through their list of references, we see that a dozen papers have been concerned with the problem of finding a set of rings or circuits. Conceptually the most simple, and literally a pedestrian algorithm, is due to Corey and Wipke[123] (also considered by Tiernan in the computer science literature[124]) in which the rings are found by a »walking« algorithm. The algorithm starts from any vertex in the graph and »walks« (at random, but not repeating the steps) on the structure, keeping a record of its path and noting any branching point along the way. When the path crosses itself, a circuit (ring) has been found. The process is completed when all choices have been exhausted at all of the branching points. The above algorithm can be improved upon, *i.e.*, its efficiency can be increased, if one simultaneously considers both ends of a path at a site of ring closure, until all rings involving that ring closure have been found.[125] Another kind of algorithms make use of the concept of spanning trees, *i.e.*, acyclic subgraphs which use all the vertices of the graph, but not all the edges (in order to exclude ring closures). As an example, several spanning trees of naphthalene are shown below:



A complete list of the spanning trees of naphthalene has been given by Mallion.[126] Before briefly outlining the algorithm for the search of circuits based on the spanning trees, let us point to an essential advantage of such schemes: There is a theorem that allows deriving the number of the spanning trees in a simple manner thus, a possible error of omission can be checked. The theorem appears to be attributed to Kirchhoff who, 146 years ago, was concerned with solving equations appearing in investigations of the distribution of currents in electrical network.[127] However, it may be that the theorem as such is less ancient.[128] Be it as it may, the work of Kirchhoff preceded the earliest enumerations in chemistry by some thirty years, and may well represent the first graph-theoretical application in natural sciences – perhaps to be considered as the date of birth of the graph theory in physics (?)! The work is still of considerable interest, in particular in graph-theoretical studies of ring currents – a topic of some importance in discussions of the N.M.R. spectra of aromatic molecules.[129] It is interesting, except for the scale of the problems, that the same type of analysis that Kirchhoff used for electric circuitry (macro-world) applies to molecular ring currents (micro-world).

The theorem attributed to Kirchhoff ensures that the number of spanning trees follows from a somewhat modified adjacency matrix of the graph. The adjacency matrix of the graph is supplemented by introducing quantities d_i on its diagonal, representing the valencies of the vertices, whilst nonvanishing off-diagonal elements are given with a negative sign. Such an *augmented* matrix (also called the Kirchhoff matrix or Laplacian matrix)[130,131] has an interesting property: The absolute value of any of its minors (a subdeterminant derived by omitting one row and one column) has the same magnitude, equal to the number of the spanning trees. We illustrate this intriguing theorem on a simple graph shown below, which the reader can easily verify:

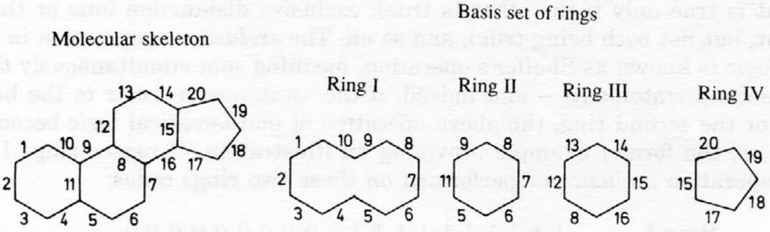
Graph Adjacency matrix Kirchhoff matrix A minor



$$\begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 1 \\ 0 & 1 & 0 & 1 \\ 1 & 1 & 1 & 0 \end{bmatrix} \quad \begin{bmatrix} 1 & 0 & 0 & -1 \\ 0 & 2 & -1 & -1 \\ 0 & -1 & 2 & -1 \\ -1 & -1 & -1 & 3 \end{bmatrix} \quad \begin{vmatrix} 0 & 0 & -1 \\ 2 & -1 & -1 \\ -1 & 2 & -1 \end{vmatrix} = |3|$$

The corresponding spanning trees are:

Bonds not contained in the spanning trees are termed *ring closure bonds*. One first select a set of *independent* circuits (not necessary the set of the smallest rings), referred to as the *fundamental* set of circuits (rings) or *basis* set of circuits (rings). Rings and bonds are then labeled, which permits their representation as a single binary code. We will illustrate this on the example discussed by Wipke and Dyott:[122]


Basis set of rings

Molecular skeleton

Ring I Ring II Ring III Ring IV

Labelling of edges is arbitrary (and not essential). The four rings making up the basis of rings, shown above, can then be represented by the following codes:

Ring I	1 1 1 1 1 1 1 1 1 1 0 0 0 0 0 0 0 0 0 0
Ring II	0 0 0 0 1 1 1 1 1 0 1 0 0 0 0 0 0 0 0 0
Ring III	0 0 0 0 0 0 0 1 0 0 0 1 1 1 1 1 0 0 0 0
Ring IV	0 0 0 0 0 0 0 0 0 0 0 0 0 0 1 0 1 1 1 1

The above codes have an important property – they permit their manipulation in the algebraic sense. Simple operations are addition and subtraction (general superpositions in physical terminology, corresponding to *union* and *intersection* in the set-theoretic terminology, respectively). Of more interest here is an operation termed *exclusive* or[132] which gives all the elements in either set, but not those present in both sets. We can formally represent this operation as a special *Boolean* arithmetic, as shown below together with more familiar addition and multiplication tables:

Addition	Multiplication	Exclusive or
$0 + 0 = 0$	$0 \cdot 0 = 0$	$0 : 0 = 0$
$0 + 1 = 1$	$0 \cdot 1 = 0$	$0 : 1 = 1$
$1 + 0 = 1$	$1 \cdot 0 = 0$	$1 : 0 = 1$
$1 + 1 = 1$	$1 \cdot 1 = 1$	$1 : 1 = 0$

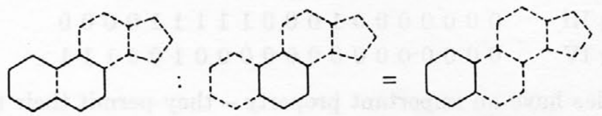
Here, we have introduced the symbol (:) for exclusive or, instead of the usually adopted symbol XOR. The above are only three out of the eight possible such arithmetic tables with symmetry requirements, *i.e.,* (A,B) giving the same results as (B,A), where A, B stand for zero or one. We can write them in a tabular form as follows:

$$\begin{array}{c|c} 0 & 0 \\ \hline 0 & 0 \end{array} \qquad \begin{array}{c|c} 1 & 0 \\ \hline 0 & 0 \end{array} \qquad \begin{array}{c|c} 0 & 0 \\ \hline 0 & 1 \end{array} \qquad \begin{array}{c|c} 1 & 0 \\ \hline 0 & 1 \end{array} \qquad \begin{array}{c|c} 0 & 1 \\ \hline 1 & 0 \end{array} \qquad \begin{array}{c|c} 1 & 1 \\ \hline 1 & 0 \end{array} \qquad \begin{array}{c|c} 0 & 1 \\ \hline 1 & 1 \end{array} \qquad \begin{array}{c|c} 1 & 1 \\ \hline 1 & 1 \end{array}$$

The *addition, multiplication* and *exclusive or* correspond to the seventh, third and the fifth cases, respectively. The above are not matrices, but tables of operations (binary operations) and may have various interpretations. For example, in the *mathematical logic*[133] concerned with the algebra of statements (judgments), we can replace *one* with *»true«* and *zero* with *»not true«* and the above binary operations correspond to: identically false (not true); conjunction (simultaneous truth of both statements); Lukasiewicz operation (neither of the two statements); equivalence (one statement is true only if the other is true); exclusive disjunction (one or the other statement, but not both being true); and so on. The *exclusive or* operation in mathematical logic is known as Sheffer's operation, meaning »not simultaneously the first and the second statement« – and indeed, if the »statements« refer to the bonds in the first or the second ring, the above operation of mathematical logic becomes our *exclusive or*, the former example providing an illustration. Consider rings I and II and the operation *exclusive or* performed on these two rings codes:

Ring I	1 1 1 1 1 1 1 1 1 1 0 0 0 0 0 0 0 0 0 0
Ring II	0 0 0 0 1 1 1 1 1 0 1 0 0 0 0 0 0 0 0 0
(I : II)	1 1 1 1 0 0 0 0 0 1 1 0 0 0 0 0 0 0 0 0

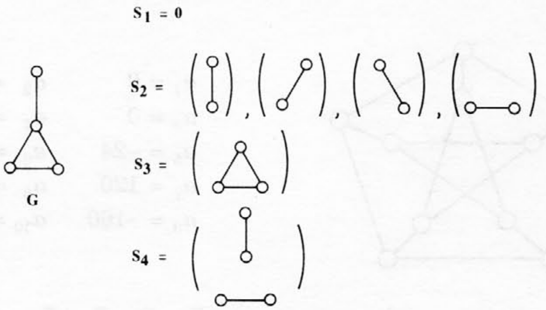
Pictorially, the above operation can be illustrated as follows:



The above discussion of the simple »walking« algorithm and the algebraic algorithm, using the concept of spanning trees and the binary operation *exclusive or*, illustrates conceptually very different approaches to finding all the circuits in a system. There is, however, yet another, one may say almost »classical« approach, which seems not to have attracted attention of those concerned with the problem. The outline of these schemes, known amongst people concerned with computer processing of structural data, was necessary in order to appreciate the distinctive flavour of more mathematical schemes associated with calculus (the attribute »classical« has been used in that sense). In our exposition, we will closely follow a work of Sachs, but several alternative and closely related schemes have been reported in the literature.[134] The basis for these methods is a connection between circuits (rings) contained in a graph and the characteristic polynomial of a graph. Sachs[104] has undertaken to illuminate the connection, and as it will be shown later on, he outlined a scheme which allows the number of circuits of different size to be derived from the information given by the characteristic polynomial. He starts by emphasizing that the characteristic polynomial represents an important invariant of a graph (which is not dependent on the adopted scheme for the numbering of vertices). Then, for the case of regular graphs (these are graphs in which all vertices have the same valency), the following statement applies:[104] Let the characteristic polynomial of a graph be $P(x) = x^k + a_1 \cdot x^{k-1} + \dots + a_k$; then the number of different circuits of size h is determined by the degree k, the maximal eigenvalue x and the first h coefficients $a_1, a_2, \dots, a_h$. In continuation, Sachs first derives a theorem which gives the form of the coefficients of the characteristic polynomials as:

$$a_i = \sum_{S \in S_i} (-1)^{n(S)} \cdot 2^{c(S)} \tag{13}$$

where the summation goes over all elements S (called elementary and basic figures or Sachs graphs[75])[135] of the set S_i with i vertices. In addition, a_0=1. Sachs graphs are those composed of either isolated edges (elementary figures) or/and isolated cycles (basic figures). The values n and c indicate, respectively, the number of components in S and the number of cycles in S. In fact, the above represent a very simple expression, and let us get familiar with it on an example. We quote a simple example from a paper by Graovac *et al.*[75] which is concerned with an application of Sachs' theorem:



Hence, the coefficients become:

$$\begin{aligned} a_1 &= 0 \\ a_2 &= (-1)^1\, 2^0 + (-1)^1\, 2^0 + (-1)^1\, 2^0 + (-1)\, 2^0 = -4 \\ a_3 &= (-1)^1\, 2^1 = -2 \\ a_4 &= (-1)^2\, 2^0 = 1 \end{aligned}$$

and the characteristic polynomial is:

$$P(x) = x^4 - 4x^2 - 2x + 1$$

(Observe that the characteristic polynomial is defined, as it is customary in mathematics, by determinant: det $|x\,I - \mathbf{A}| = 0$; not as customary in physics and chemistry: det $|\mathbf{A} - x\,\mathbf{I}| = 0$, which would change signs of all odd powers of x).

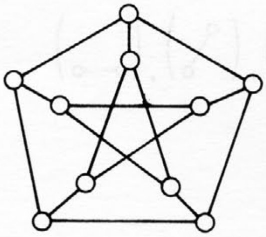
Search for an expression on the number of circuits of different size contained in the structure represents, in a way, a reversed approach. It is clear from the Sachs theorem for the coefficients that each circuit enters with a weight 2 and is combined with contribution arising from subgraphs composed of isolated bonds. Hence, if we subtract the number of such subgraphs from the corresponding coefficients, and divide the result by 2, we will obtain the number of circuits of the particular size. This is the essence of the Sachs theorem concerned with the number of circuits of a particular size in a graph, as stated below:

Theorem (Sachs[104]): Let G be a graph with the characteristic polynomial: $P(x) = x^k + a_1 x^{k-1} + \ldots + a_k$; and let b_q be the number of different linear subgraphs of G which consist precisely of q edges. Also let have:

$$\bar{a}_i = \begin{cases} a_i & \text{for odd } i \\ a_i - (-1)^q\, b_q & \text{for } i = 2q \end{cases} \tag{14}$$

Then, the following holds: The size of a circuit (t) is equal to the index of the first non-zero coefficient of $\bar{a}_1, \bar{a}_2, \ldots, \ldots$, and the number of circuits is equal to $-(1/2)\bar{a}_t$.

As an illustration, let us consider Petersen's graph,[136] which is of considerable interest in chemistry.[137] The coefficients of the characteristic polynomial are as follows:[104]



$$\begin{aligned} a_1 &= 0 & a_2 &= -15 \\ a_3 &= 0 & a_4 &= 75 \\ a_5 &= -24 & a_6 &= -165 \\ a_7 &= 120 & a_8 &= 120 \\ a_9 &= -160 & a_{10} &= 48 \end{aligned}$$

For the first four, a values, one obtains $\bar{a}_1 = \bar{a}_2 = \bar{a}_3 = \bar{a}_4 = 0$ *since* there are no rings of size smaller than five in the graph. The first non-zero coefficient $\bar{a}$ is an odd index; hence, simply $\overline{a}_5 = -24$, and the above theorem then tells us that there are 12 distinctive five membered rings (these are not difficult to identify; every vertex participates in six 5-membered rings, which makes a total of 60, but each such ring has obviously been counted five times). To continue finding larger sized circuits, it is useful to introduce additional auxiliary parameters E ($E_{i,c}$) (in Sachs' notation) and one uses the results for smaller rings (D_i). The reader is directed to Sachs' paper for more details – we quote the results only (for the Petersen graph):

i	1	2	3	4	5	6	7	8	9	10
D_i	0	0	0	0	12	10	0	15	20	–

It is interesting that the method cannot be applied to the search for *the largest circuits*, known also as Hamiltonian circuits, the search for which is still an important problem in graph theory and its applications.[138]

The characteristic polynomial gives the number of circuits, but does not indicate the circuits themselves. These, however, could be obtained if the Sachs procedure for the derivation of the coefficients is followed, although for sizable polycyclic systems, the construction of all subgraphs required for evaluation of the coefficients may be lengthy and cumbersome. Hence, the above scheme will not be of great help in actual ring perceptions, except perhaps for verifying if all the circuits of interest have been found. For an alternative derivation, with high pictorial – geometric clarity, of the coefficients of the characteristic polynomial, we mention the paper by Spialter.

THE CONCEPT OF COMPARABILITY OF GRAPHS

Finally, we would like to discuss another mathematical topic of considerable interest to those using graphs and related structures in their work. This is the topic of *comparability* of functions or graphs, a notion that we may have intuitively used in one way or another and which was considered 92 years ago by Muirhead[110] who was concerned with its rigorous formulation. The work of Muirhead is not well known, though it is properly mentioned in one of the important textbooks on mathematics, concerned with inequalities.[139] The problem arises when one needs to compare functions or two or more variables. Let us take, for the sake of illustration, two distinct qualities, such as height and weight of two persons, and let us assume that these are recruited for a job in which both of these two qualities are required, giving priority to those who are heavier and taller. So, the pair (h_i, w_i), the height and the weight, respectively, characterizes each candidate. There is no difficulty in comparing individuals for which one establishes $h_i \geq h_j$ *and* $w_i \geq w_j$, but a problem arises if $h_i > h_j$ *but* $w_i < w_j$ (or the other way around), as we have no information on the relative importance of the two parameters, h and w, which are treated as equally essential. Muirhead considered such situations, generally on the functions of many variables, and defined conditions on the parameters which, if satisfied, will tell us if two functions (graphs) are comparable (in which case, one can order them and speak of the more important, or which one precedes the other), and will also point to situations when such comparisons cannot be made. Conceptually, Muirhead's conditions are quite simple, as it will be shown shortly, and the significance of his work is that he made a rigorous algebraic formulation of the notion of *comparability*, which, prior to him, was undefined and left to intuitive characterizations.

According to Muirhead, two functions, $F_1 = F_1(v_1, v_2, \ldots, v_k)$ and $F_2 = F_2(v_1, v_2, \ldots, v_k)$, are said to be *comparable* if there is an inequality between them (either $F_1 \geq F_2$ or $F_1 \leq F_2$) valid for all the values of variables v_i in a selected interval. Thus, the function F_1 must be always larger (or smaller) than the function F_2 in the whole space interval selected for their coordinates. If one function is in some region smaller and in other larger, the functions are said not to be comparable, *i.e.*, they cannot be ordered so that one precedes the other. It should be noted that, here, the term *comparable* is a technical term, and when applicable, leads to a clear result: One function excels the other in all respects, whilst in everyday usage, the term may imply the opposite (corresponding to non-comparable function here), like two students in a class that show different abilities in two subjects, A being better in mathematics, but less proficient in a foreign language, and B showing the opposite qualities, may be comparable from the standpoint of the school, interested in their overall performance. According to Muirhead's rigorous comparison, the above case cannot be compared.

A special class of functions of more interest here are of the form:

$$v_1^{a_1} v_2^{a_2} \ldots v_k^{a_k} \tag{15}$$

where a_i are non-negative integers. For such functions, Muirhead defines a relative order by the conditions:

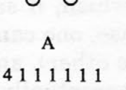
$$a'_1 + a'_2 \ldots + a'_i \geq a_1 + a_2 + \ldots + a_i \tag{16}$$

$$a'_1 + a'_2 + \ldots + a'_k = a_1 + a_2 + \ldots + a_k \tag{17}$$

where k is the number of variables and $1 < i < k$.

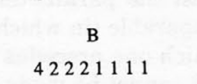
One can view the above multivariable functions as *configurations* defined on the set v_i, where the parameters a_i define a particular *population*. The above conditions then concern partial sums, and require these partial sums, corresponding to two functions, to satisfy the same inequalities (*i.e.*, one is always greater than or equal to the other). For the above inequalities, one should first order the parameters a_i in decreasing sequence, *i.e.*, $a_i > a_{i+1}$.

Let us illustrate the application of the above conditions and, for that purpose, we consider the following three graphs (taken from a discussion of molecular branching and its algebraic characterization):



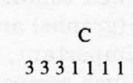
A

4 4 1 1 1 1 1 1



B

4 2 2 2 1 1 1 1



C

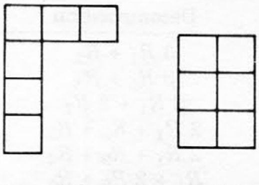
3 3 3 1 1 1 1 1

Here, we will use valencies of their vertices as parameters a_i, and wish to find out whether the graphs can be compared. For this, we need to get partial sums for each of the graphs, which then form the basis for conclusions. The corresponding partial sums are:

A	B	C
4 = 4	4 = 4	3 = 3
4 + 4 = 8	4 + 2 = 6	3 + 3 = 6
4 + 4 + 1 = 9	4 + 2 + 2 = 8	3 + 3 + 3 = 9
4 + 4 + 1 + 1 = 10	4 + 2 + 2 + 2 = 10	3 + 3 + 3 + 1 = 10
4 + 4 + 1 + 1 + 1 = 11	4 + 2 + 2 + 2 + 1 = 11	3 + 3 + 3 + 1 + 1 = 11
etc.	*etc.*	*etc.*

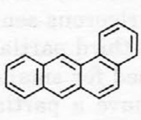
Comparing now the partial sums, we immediately see that, in the case of graphs A, B, as well as A, C, the conditions set by Muirhead are fulfilled, since in each step the partial sum of A is larger or equal to the corresponding sum for B or C. Hence, we can order the graphs in a sequence so that A precedes both B and C. However, this does not resolve the question of comparability of B and C, and, as we immediately see, the pair of structures is *not comparable* in the rigorous sense of Muirhead. Namely, in the first partial sum B precedes C, but in the third partial sum the order is *reversed*, and it is this reversal of the order established for smaller partial sums which contradicts the conditions. So, it is possible to have a partial ordering and cases for which the criteria of comparability cannot decide the issue. To come back to the example of recruitment of people of different height and weight, if we have three persons with the following measurements: A = 2.00 m and 100 kg; B = 1.80 m and 90 kg; and C = 1.75 m and 95 kg; we have a similar case, where A can be compared (in the technical sense adopted here) to B and C, while B and C cannot be compared, *i.e.*, their ordering is not legitimate.

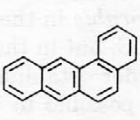
Discussion of molecular branching is an example of an application of Muirhead's scheme. In discussions of chirality functions, Ruch and Schönhofer[140] used the Young diagrams, and found it necessary to order such diagrams. Young diagrams,[141] which were introduced into mathematics the very same year that Muirhead defined comparability of functions, received a better publicity, primarily as they can be of use in discussions of permutational symmetries, being a graphical (pictorial) representation of the partition of an integer. For instance, partitions of 6 = 3 + 1 + 1 and 6 = 2 + 2 + 2 are represented by the Young diagrams as:

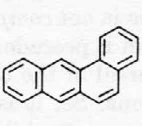


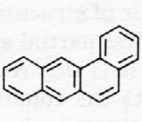
Can these partitions (diagrams) be compared in Muirhead's rigorous sense? It is easy to see that the two partitions shown cannot be compared (like the partitions corresponding to an exchange of the roles of rows and columns in the Young diagrams, *i.e.*, 6 = 4 + 1 + 1; and 6 = 3 + 3). All other partitions of 6, however, allow a comparison between themselves and with the above non-comparable cases.

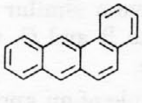
Muirhead's work deserves more attention by chemists. It is not so much that it will resolve many burning questions, since the scheme has also some limitations. It seems to us that this work will be more remembered in the future for its *initiative* step in developing a scheme that *rigorously defines an intuitive concept*, such as comparability. Chemistry has been plagued with ill-defined concepts or concepts vaguely defined, so that in the work of Muirhead we see how a rigorous definition, even if very logical and straightforward (obvious), can help to clarify the discussion in some applications. The strength of Muirhead's procedure is that it solely uses structural information (such as supplied by the data on the parameters involved). A major weakness, it appears to us, of the scheme is its rather great restrictiveness. In practical situations, we would not hesitate much in making the choice between a fellow who is 1.90 m and weights 85 kg when contrasted to another, rather short and overweight (say 1.65 m, but weighing 90 kg). In this particular case, the two variables may play a different role. In other situations, experience may suggest a relative order beyond the stage derived from Muirhead's conditions, so the scheme as such may undergo various modifications in special applications. Let us illustrate the above on a case of comparison of Kekulé valence structures of conjugated hydrocarbons. Take, for example, benzanthracene. Its seven Kekulé valence structures are:

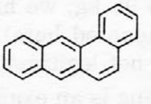

A

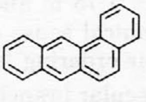

A'


B


C


D


E


F

We would like to order these structures according to their expected importance to molecular stability, as measured by their partial contributions to the resonance energy. These contributions can be estimated from information on the number of conjugated circuits present in each of the structures. These can be simply counted for the above, relatively simple, Kekulé structures and are summarized below in the tabular form:

Benzanthracene	Decomposition	Code (R_1 R_2 R_3 R_4)
A and A'	$3\,R_1 + R_2$	3 1 0 0
B	$3\,R_1 + R_3$	3 0 1 0
C	$2\,R_1 + 2\,R_2$	2 2 0 0
D	$2\,R_1 + R_2 + R_3$	2 1 1 0
E	$2\,R_1 + R_2 + R_4$	2 1 0 1
F*	$R_1 + 2\,R_2 + R_3$	1 2 1 0

(*In structure F, one also finds another R_3 conjugated circuit and R_4 circuit, but as these can be obtained by linear combination of already used circuits, they are excluded from the consideration, *i.e.*, in the last Kekulé structure of benzanthracene, not all of the six conjugated circuits are linearly independent. It should be noted that only linearly independent conjugated circuits are considered in the above).

Here, the discussion of ordering requires some modifications: First, we order the variables R_n in a sequence, *i.e.*, $R_1 > R_2 > R_3 > R_4$. The coefficients then play the role of the parameters for which we will construct partial sums:

A and A'	B	C	D	E	F
3	3	2	2	2	1
4	3	4	3	3	3
4	4	4	4	3	4
4	4	4	4	4	4

It is clear that we cannot discriminate between A and A', which have an *identical composition* of conjugated circuits. Other Kekulé structures can be compared, and the order parallels the alphabetical labels given, except that the pairs (B, C) and E, F) do not permit ordering, since the second partial sum and the third partial sum, respectively reverse the relative order established for smaller sums. Now, so far, we have not used information on the numerical values of R_n – but if we had, there would be no problem in resolving the above ambiguities. So, we see that Muirhead's rigorous test limits us in reaching the complete ordering, but, with *additional* information (not necessitated in Muirhead's scheme), we could continue the process. It appears, however, that some conclusions could be reached also from less detailed information on the type of the dependence of R_n on n (asymptotic behaviour and curvature). With such additional data, a more complete ordering can be expected, if the information can be suitably algebraically processed, and some results indicate this to be possible by considering an iterative scheme, where the partial sums derived from the Muirhead analysis are used as an input in another cycle of construction of secondary partial sums.

CONCLUDING REMARKS

Development and application of the graph theory in chemistry are neither new nor erupted in rare spurs at few periods of its, over a hundred years old history. A number of important papers have appeared during the period, although until a *more recent awareness of the subject*, as an important and growing mathematical branch, *the direct reference to graphs has not been made*. In addition, people concerned with the developments of other aspects of chemistry *have unknowingly contributed to graph-theoretical development* in chemistry. This, in particular, is the case of the early development of the valence bond method, and subsequent expansion of the molecular orbital method, in particular when confined to the Hückel scheme. In the course of the development, some of the earlier works have not found proper recognition in the more recent literature, and this is not so much surprising and does not reflect upon those involved. Papers with graph-theoretical content are frequently not labelled as such and are scattered in abundant chemical literature, usually under subjects that do not indicate their relevance to graphs. The situation is not much better today, even after *the Journal of Mathematical Chemistry* was born and is going strong. Papers with aspects of the chemical graph theory are still being scattered in many journals. But the use of the chemical graph-theoretical methods and approaches and their direct impact on solving chemical problems is nowadays very visible. Thus, the chemical graph theory is on the right path to establishing as firm place in the realm of theoretical chemistry. However, we still have to wait for a (theoretical) chemistry textbook with a chapter on chemical graph theory.

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13. As a useful indication what is covered by »non-numerical methods« we quote from the National Academy of Science document (»The Proposed National Resource for Computation in Chemistry: A User Orientied Facility«): »Non-numerical methods. This is a developing area that includes application of artificial intelligence, pattern recognition, symbol manipulation, graph theory and computer graphics«.
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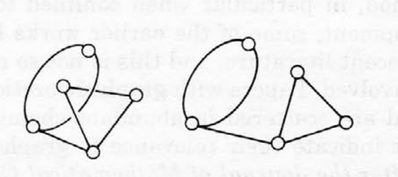
16. The difference between *topology* and *connectivity* is not always well-discriminated (in particular in chemical literature). We illustrate the distinction on an example discussed in: R. G. Bursacker and T. L. Saaty, *Finite Graphs and Networks – An Introduction with Applications* (McGraw-Hill, New York, 1965). They illustrated the above concepts on page 7 in Figure 1-2 of their book:



G_a G_b

Graphs G_a and G_b have important distinctive features from the standpoint of topology, but they are equivalent from the standpoint of graph theory, *i.e.*, G_a and G_b have different topology, but the same connectivity.

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Connecticut, 1974) E.L. Eliel concluded his closing remarks suggesting that the time has come for organic chemists to learn group theory, graph theory and set theory – indicating concern on the present situation. We could add that it would not hurt to include some mathematical logic, at least as far as binary relations go.

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SAŽETAK

Zabilješke o nekim manje poznatim ranim doprinosima kemijskoj teoriji grafova

Milan Randić i Nenad Trinajstić

Razmatrano je dvanaestak manje poznatih, ali važnih, radova za razvoj i primjenu teorije grafova u kemiji: rad Flavitzkoga (1874) o prebrojavanju izomera, Muirheadov rad (1901) o usporedivosti funkcija i Balandinov pregledni članak (1940) o primjenama teorije grafova u kemiji. Ovamo pripada i Blochov rad, u kojemu je po prvi puta uporabljen polinomni razvoj za prebrojavanje valentnih struktura poznat iz kasnijega, mnogo citiranijeg Pólyina rada i Sachsov rad u kojemu je, mnogo godina prije nego su razvijene suvremene metode prebrojavanja prstenova, prikazan način prebrojavanja prstenova u molekuli. Uz spomenute radove razmotrene su slabosti Rumerove metode prebrojavanja valentnih struktura, Heilbronnerovi radovi o Hückelovu (karakterističnom) polinomu konjugiranih sustava i o inverznoj matrici susjedstva, te rad Nobelovca Marcusa o aditivnim svojstvima molekula koji se može smatrati prethodnikom novijih radova o indekcima veza u benzenoidnim ugljikovodicima i o ulozi konjugiranih krugova u njima.