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SOME CHEMICAL APPLICATIONS OF GRAPH THEORY

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1. Introduction

This will be a very personal account of some chemical applications of graph theory, namely those of interest to the present author. During the University (1949 - 1953) and Ph. D. years (1953 - 1958) with C.D. Nenitzescu, I gave much attention to the problem of aromaticity, which became enhanced by the discovery of a new synthesis of pyrylium salts[1] which are benzenes with the highest possible single perturbation, namely an O^+ heteroatom; on the experimental side I predicted as early as 1955 some of the boron-containing aromatics (brilliantly developed subsequently by M.J.S. Dewar[2]), and synthesized boroxaropyrylium [3] in a later research on heterocyclic organoboron compounds.[4]

2. Aromatic compounds

On the theoretical side, I attempted a complete systematization of all-possible monocyclic aromatic compounds consisting of First-Row elements.[5] By grouping the atoms forming the

aromatic ring into three groups, X, Y, and Z according to whether the number of pi-electrons in their p_z-orbital was 2, 1, or 0 (Pauli's principle excludes other possibilities), the problem was decomposed into two partial ones: a table of possible atoms or atom groups, and an algebraic-combinatorial problem of constructing all possible m-membered $X_xY_yZ_z$ rings satisfying the equations (the second one being the expression of the Hückel rule) :

$$m = x + y + z$$
$$4n + 2 = 2x + y$$

For each algebraic solution, a combinatorial problem arises of finding the number of isomers. In collaboration with S. Teleman,[5] a formula for this number of isomers was found. This was in fact the first graph-theorectical problem I was confronted with, though at that time I was unaware that "I was speaking in prose without knowing it". In graph theory this "necklace problem" (the enumeration of isomeric necklaces consisting from beads of different colour) is elegantly solved by applying Pólya's counting theorem. This was done later,[6] in collaboration with F. Harary.+

+ In the same paper,[5] Pólya's formula was extendended to bicyclic systems. However, as observed independently,[7] the extension leads to erroneous results in the case of the naphthalene skeleton: Pólya's formula gives 329 isomers $r^6s^2t^2$ and 807 $r^4s^4t^2$, whereas actual counting yields 330 isomers $r^6s^2t^2$ and 810 isomers $r^4s^4t^2$. No reasonable explanation was yet found for this discrepancy.

An extension of these ideas arose when imposing adjacency restrictions such as not allowing adjacent Z-type atoms, or both Z-type and X-type atoms.[5] The mathematical treatment becomes much more involved, but was solved recently by Lloyd.[8] This purely topological approach to encompassing monocyclic aromatics was refined by assigning electronegativity values to each atom type, leading to an overall "aromaticity constant" of the ring[9,10] which provides a semi-quantitative measure of the stability and reactivity of the ring, allowing a more exact definition of π-excessive, π-deficient and π-equivalent aromatic heterocycles.[11] Interestingly, Y-type atoms are the same ones which can form triple bonds, and this systematization allowed the prediction,[12] later verified,[13] of a missing molecule with triple bond, namely the dication O_2^{2+}.

3. Pólya's theorem

Another straightforward chemical application of the celebrated Pólya's theorem is to enumerate isotope-isomers. Again, an extension of Pólya's formula was necessary when two labels may be attached to the same vertex of the graph (i.e. carbon and hydrogen labelling).
The column "Textbook Errors" of J.Chem.Educ. recently featured a paper on the number of substituted porphyrin isomers.[16] The paper had itself an error as noted independently,[7,17,18] which can easily be corrected by application of Pólya's counting theorem.[19]

Other recent applications of Pólya's theorem for organic and inorganic isomer enumeration appeared recently.[20,21]

4. The interplay between chemistry and graph theory

One of the three sources of graph theory was organic chemistry, through Sylvester's and especially Cayley's attempts to enumerate alkanes (the other two origins being mathematics through Euler and Jordan, and electrical networks through Kirchhoff).[22] Just before Mendeleev's and Kekulé's discoveries, Auguste Comte could state that "all attempts to bring chemical questions into the domain of mathematics must be regarded as profoundly irrational and antipathetic to the nature of these phenomena". However,only few years later (in 1878) Sylvester could write "By the new atomic theory, I mean that sublime invention of Kekulé which stands to the old in a somewhat similar relation as the astronomy of Kepler to Ptolemy's, or the System of Nature of Darwin to that of Linnaeus. Like the latter, it lies outside of the immediate sphere of energetics, basing its laws on pure relations of form, and like the former as perfected by Newton, these laws admit of exact arithmetical definitions" ...". There is a wealth of untapped mathematical potential contained in the patient and long investigations of our chemist fellows".

Nowadays, when graph theory possesses a powerful arsenal

of concepts, methods and theorems, it can provide in reverse a considerable help to solve chemical problems.
Graph theory is an essential tool for definition, systematization and enumeration of chemical compounds. In addition, it helps for codification and nomenclature purposes. The interplay between chemistry and graph theory continues, however because some problems posed by chemistry are unsolved graph-theoretical problems, as will be shown in the sequel.

5. Teaching rigorous chemistry

The time is ripe for chemistry to become more than a collection of compounds, properties and reactions, namely a coherent unique logical system. Attempts towards an axiomatic approach to chemistry have already been made.[23-26]
More critical is the spirit of chemical textbooks, which is far removed from the rigor prevailing in mathematical textbooks.
The fact that there exist two isomers C_4H_{10} and three isomers C_5H_{12} should be correlated with the mathematical demonstration that there can only exist two and three non-isomorphic trees with four vertices; analogously, the existence of two and only two isomers C_2H_6O should be correlated with the existence of only two non-isomorphic chains C-O-C and C-C-O.

6. Valenes and cubic graphs.

Valence isomers of annulenes (for short these will be called n-valenes) are hydrocarbons with formula $(CH)_n$, with n being an even number. Benzene is one of the 6-valenes, cyclooctatetraene is one of the 8-valenes. Historically, the first valene which was not a cyclopolyene is the "Nenitzescu hydrocarbon" $(CH)_{10}$. This field became an exciting one after the discovery of the fluctuating properties of bullvalene $(CH)_{10}$, and after the syntheses of 6-valenes: Dewar-benzene, benzvalene, benzprismane, bis(cyclopropenyl).[+]

On realizing that all formulas of valenes are cubic (i.e. regular graphs of degree three) or trivalent multigraphs, and that their enumeration was an unsolved problem of graph theory in 1966[27] (recently an unpublished solution was found by R.W. Robinson[28]), an algorithm was developed[29] for constructing these graphs. The numbers of possible n-valenes are presented in table 1 for n = 4-12.[30]

+ These, with benzene, are the only possible planar (in the graph-theoretical sense) cubic graphs with six vertices. Nonplanar graphs like the diagonal Claus formula for benzene (Thomsen graph) cannot exist as stable molecules and are not counted in table 1.

T a b l e 1. Possible and known (1974) n-valenes $(CH)_n$

n	4	6	8	10	12
Possible	2	5	17	71	357
Known[a]	2[b]	5	10	23	10

[a] At the end of 1974, ignoring geometrical isomerism

[b] Unstable molecules

Two striking facts emerge from this table : the number of possible n-valenes increases very rapidly with n, and soon most of the possible n-valenes will be prepared.

A graph-theoretical definition[31-33] of n-valenes can be given based on the idea of cubic graphs. So far, since the systematic IUPAC (Bayer) nomenclature system for these polycyclic systems is very cumbersome, most of the n-valenes were given trivial names. However, tabel 1 clearly shows the necessity of devising a systematic naming system instead of trivial names. One such proposal is a code giving in order:

- n^+
- the number of double bonds (circuits with two vertices)
- " " " three-circuits (cyclopropane rings)
- " " " four-circuits (cyclobutane rings)
- a serial number s which is 1 unless there exist more than two valenes with identical quadruplets of the previous numbers. In the latter case, s takes integer values starting with 1, ordering these valenes according to the increasing number of 5-circuits (and

additional criteria such as 6-circuits when the numbers of 5-circuits are identical).

7. Valene derivatives

Heteroanalogues of valenes, such as valence isomers of furan whose graphs contain vertices of degree two (instead of all degrees equal to three as in valenes) can also be encompassed by means of cubic graphs, namely general cubic graphs which may also possess loops.[34] A vertex of degree two then results if one loop and its point are removed. Homovalenes, e.g. valence isomers of tropylidene or cyclopentadiene, are found by the same procedure: numerical results are presented in table 2.[35]

Table 2. Planar general cubic graphs with one loop

n[a]	3	5	7	9	11
Possible	1	4	18	96	502

[a] The number of vertices remaining after removing the loop-point.

Benzoannulene valence isomers can be counted by a similar algorithm.[36] An analogous code was devised for specifying the annelation in the case of valence isomers of benzoannulenes.

If vertrices of valenes are labelled (by means of heteroatom substitution, e.g. valence isomers of pyridine, or by means of substituents, e.g. valence isomers of toluene) the number

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+ For analogous systems with heteroatoms corresponding to general cubic graphs n is followed by a digit indicating the number of loops (circuits with one vertex).

of possible isomers increases considerably. This number is found by applying Pólya's theorem, starting from the symmetry (i.e. cycle index) of each graph.[37] The analysis reveals that several valenes may possess the same cycle index. The smallest such case is of benzene and benzprismane derivatives (ignoring the stereoisomerism of the latter). This observation has a historical interest, since the controversy between Kekulé and Ladenburg around the benzene formula was based on the number of possible isomers. Many more such coisomeric graphs were found for 8-valenes and 10-valenes.[37]

Degenerate Cope rearrangements of some n-valenes like bullvalene are possible: a complete analysis of all possible cases for $n \leq 12$ was made.[38]

8. Benzenoid polycyclic hydrocarbons

Polycyclic hydrocarbons formed from n condensed benzenoid rings ("polyhexes" for short) are the most important carcinogenics; they are traditionally classified into two classes: catacondensed ("n-catafusenes") which do not have, and peri-condensed ("n-perifusenes") which do have points common to three benzenoid rings. There can exist only one 2-catafusene (naphthalene), but two 3-catafusenes (anthracene and phenanthrene) and one 3-perifusene (perinaphthenyl). By

means of the dualist graph [+] (consisting from the points corresponding to centres of hexagons, connected by lines whenever two hexagons are condensed), a new, more comprehensive definition of cata- and peri-condensation can be given: dualist graphs of catafusenes are trees, and of perifusenes contain circuits.[39] Under this definition, all n-catafusenes are isomeric. Perifusenes are more difficult to handle and their enumeration is another unsolved problem of graph theory,[27,28] called the "animal cell growth problem", in this case for hexagonal cells. Only a computer enumeration was feasible.[40] Catafusenes can, however, be enumerated by means of recurrence formulas: the formulas are simple for nonbranched systems,[39] and complicated for branched ones.[41] A numerical code expressing the topology of the catafusene was proposed[39] based on the three orientations of lines in the graphite lattice,[42] symbolized by digits 0 (for linear annelation as in anthracene), 1 or 2 (for angular annelation as in phenanthrene). Coding of a catafusene starts from a free end of the dualist graph; the smallest number formed by the n-2 digits indicating the geometry of the annelation is selected as the unique code of the n-catafusene. This code can be used in the nomenclature of catafusenes, obviating the need to coin trivial names: thus chrysene is [12] tetracatafusene, and picene is

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[+] Unlike dual graphs, in dualist graphs angles are fixed and no point corresponds to the external region.

[121] pentacatafusene.[39] Branching can be indicated by round brackets within the code,[43] e.g. triphenylene is 1 tetra-catafusene.

9. Topology of condensed polycyclic systems, resonance energies, and the Hückel rule

Interestingly, the topology of catafusenes, reflected in their code, can be directly correlated with their resonance energy, which depends linearly on the number of zeroes in the code.[44] Topological correlations had already been advocated by Sahini,[45] and more recently by Trinajstić, Gutman and coworkers.[46] The reason for these correlations lies in the fact that, as shown earlier,[47] the Hückel matrix has the same eigenvalues (i.e. the same spectrum) as the adjacency matrix of the graph. Otherwise stated, Hückel's simple MO theory is a translation of the molecular topology, for pi-electron systems, into an approximation of the Schrödinger equation. Using various short-cuts based on the Sachs theorem, Trinajstić[46] devised methods for finding eigenvalues without actually solving the secular equation.

An obvious generalization of polyhexes was to enumerate all isomeric non-benzenoid cata-condensed systems,[48] for which an analogous codification system based on their dualist graphs was proposed.

It was generally assumed that the Hückel 4n + 2 pi-electron rule, strictly valid only for monocyclic aromatics, could be extended to cata-condensed systems such as naphthalene or

azulene. We showed that this tacit assumption was erroneous, and that there exist non-benzenoid cata-condesed polycyclic hydrocarbons which fulfill the Hückel rule yet lack closed electronic shells.[49] Similar conclusions were reached by other authors.[50,51]

10. Diamondoid hydrocarbons

A less obvious extension of the above ideas allows the classification, counting, codification and nomenclature of diamondoid hydrocarbons such as adamantane, diamantane and triamantane which, being completely free of steric strain, represent end-points of thermodynamically-controlled isomerizations. Just as polyhexes are portions of the graphite lattice, diamondoid hydrocarbons are portions of the diamond lattice. On raising the problem into the third dimension, four orientations of edges are possible in the diamond lattice, hence four digits (1,2,3,4) are used for coding.[53] Two classes (catamantanes and perimantanes) are similarly defined on the basis of their dualist graphs being trees or cyclic graphs, respectively. The code can be used for nomenclature purposes to distinguish between isomeric systems (three isomeric tetra-catamantanes and one tetra-perimantane which is not isomeric with the former ones, are possible).

11. Cospectral graphs

For documentation purposes, graphs representing constitutional formulas should be stored in memory banks of computers independently of conventions regarding nomenclature and of a particular

language. This is done on the basis of the adjacency matrix, usually in condensed form.[54] A search for other means of translating a graph into an information which can be more economically stored in computers led to the idea that the characteristic polynomial or the spectrum of the adjacency matrix could serve this purpose.[55] It was shown[56] by counter-examples that many cospectral graphs exist, if the graph ignores univalent atoms. It was then argued that if hydrogen atoms are also taken into account the characteristic polynomial could uniquely represent the topology of molecules.[57] Again counterexamples were given[58,59] showing that this is not true, so that by now no information short of the adjacencies can be used for storing graphs in computer memories.

12. Isoprenoid structures

The importance of the isoprene rule needs hardly be stressed for natural compound chemistry. A computer program was devised allowing, for a given graph, the recognition of its being isoprenoid or not, and all possible decompositions into isoprene submits.[60] So far the program was tested only for mono- and sesquiterpenoids (C_{10} and C_{15}). The decomposition of graphs into subgraphs (factors) of given order is a difficult problem in graph theory.

13. Enumeration and construction of all possible constitutional isomers and stereoisomers

This is a central problem in organic chemistry, and the advent of the mass spectrometer makes it necessary to devise a system enabling one to construct all constitutional formulas corresponding to the same molecular formula. For acyclic systems, Lederberg and coworkers developed the DENDRAL program,[61] but cyclic graphs were more difficult to handle. For smaller cyclic graphs, an algorithm based on graphs of degree four or less was devised.[62] Recently, Masinter, Lederberg and coworkers succeeded in elaborating a sophisticated program for the exhaustive generation of cyclic and acyclic isomers.[63]

Though graphs are topological concepts hence symbolize constitutional formulas, they may be put to use for rationalizing also stereoisomerism. After Pólya counted[64] the chiral alkanes, little progress was made until Harary and Robinson applied these ideas to planar steric trees,[65] and then to the chemically relevant problem of chiral and achiral alkanes and monosubstituted alkanes.[66]

By analogy with an algorithm for counting all conformations of macrocyclic rings superimposable on the diamond lattice,[53] all configurations of annulenes superimposable on the graphite lattice were examined.[67]

14. Infinite lattices

In all previous graphs, vertices symbolized atoms and edges symbolized covalent bonds: they should be termed constitutional graphs, because they correspond to constitutional formulas. Chemical graphs of the same type may also be infinite, as shown by the graphite and diamond lattices. Other possibilities for elementary carbon were examined, and the relative stability of the lattice was estimated: polyyne carbon (unidimensional), condensed 4 + 8 gons or 7 + 5 gons (bidimensional), truncated octahedral lattice (tridimensional).[68]

15. Reaction graphs

A quite different class of graph applications in chemistry correlates vertices in a graph with assemblies of atoms (molecules or reactive intermediates) and edges with elemetary transitions between two such assemblies (e.g. reactio steps). Such graphs should be called reaction graphs.

Apparently the first use of reaction graphs was for exploring 1,2-shifts in carbenium ions.[69] In the case of ethyl cations with five different substituents partitioned in two groups, with two and three substituents respectively, Wagner-Meerwein-Whitmore isomerizations lead to twenty non-isomorphic, i.e. isomeric, graphs (if the two ethyl carbons may be distinguished from one another, for instance by isotopic labelling), or to ten graphs if the two carbons are indistinguishable. The resulting reaction graphs of orders 20 and 10 respectively,

are remarkable. Both are cubic graphs. The former is the Desargues-Levi graph, and applies also to intramolecular isomerizations of five-coordinated complexes with trigonal-bipyramidal configuration (with two apical and three equatorial ligands) such as phosphoranes[70-72] or organometallic complexes.[73,74] The 10-vertex graph[75] is the Petersen graph, also called the 5-cage because it is the smallest graph of girth* five.

Intramolecular isomerizations of trigonal bipyramidal stuctures may have several modes of rearrangement,[76] each involving different mechanisms: the most plausible are the Berry pseudorotation and the turnstile rotation mechanisms.[72] The overall symmetry of the reaction graph suggests a certain codification of the twenty vertices of the graphs by using two symbols from the five substituent symbols,[77] which is closest to the notation proposed by Ugi.[78] Similar reasoning applies to intramolecular isomerizations of octahedral complexes with six different ligands; the reaction graphs are more complex, however, in this case and have 30 vertices.[79]

Various parallel and/or subsequent substitution reactions, such as successive aromatic substitutions, or solvolysis of polyhalogenated compounds, yield complex reaction graphs.[80]

Two exciting uses of reaction graphs are for (i) the planning of synthetic approaches to complex molecules starting from

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* The girth of a graph is its smallest circuit.

available synthons and using known conversions, as brilliantly demonstrated by Corey and Wipke,[81,82] and for (ii) analysis of complex reactions such as the isomerizations leading to adamantane[83] or diamantane.[84] In the latter analysis, strain energies for all species are calculated, allowing to determine the chemical structure of intermediate products and the actual pathways of the isomerization.

16. Isographic non-variants

A combination of informations provided by constitution graphs and by reaction graphs can be afforded by a third type of graphs whose vertices represent atoms in reactant and product, and whose edges represent bonds which are common to both reactant and product. Such graphs are called isographic non-variants,[85] and their main use is for the analysis of pericyclic reactions such as reactions with cyclic six-membered transition states.[86] An analogous analysis had been performed earlier by Mathieu[87] but it had not explored all possibilities, and a similar analysis was published more recently by Hendrickson.[88]

17. Mathematical excursions

As mentioned earlier, many problems raised by chemistry have yet to be solved rigorously by graph theorists. In some cases, algorithms and computer programs may be used for providing restricted numerical solutions to problems of chemical interest. In a few cases, it may be possible to uncover mathematically interesting facts starting from chemical considerations. Several new classes of graphs are derived by generalizing the

Desargues-Levi graph, and these were called "combination graphs".[89]

A very interesting class of highly symmetric graphs are the g-cages mentioned above, i.e. the smallest unitransitive cubic graphs of girth g. Tutte[90] demonstrated that there exist only five cages with g = 3,4,5,6 and 8. The 4-cage is the non-planar valence isomer of benzene, corresponding to the Claus diagonal formula; the 5-cage is the Petersen graph. If the unitransitivity restriction is removed, (3,g)-cages result. The (3,7)-cage was described by McGee.[91] A first (3,10)-cage with 70 points was obtained in 1972,[92] but two more such (3,10)-cages were recently found by W. Harries.[93] In 1973, three different (3,9)-cages with 60 vertices were known,[94] but now a total of six have been found.[95] Only one (3,11)-cage[94] with 112 vertices and one (3,12)-cage[96] with 126 vertices are known.

Valence isomers of annulenes, corresponding to cubic graphs, were the incentive to count and construct all cubic graphs with up to 10 points and all planar cubic graphs with 12 points. In a multi-author paper these graphs allowed the demonstration of theorems concerning cubic identity graphs.[97]

18. Outlook

Only few chemical applications of graph theory were discussed in the present and in a previous review.[98] Many more are discussed in an edited book due to appear at the end of 1975.[99] It is certain that graph theory has still much to offer to chemists.

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