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Combinatorial Enumeration in Chemistry

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1 Introduction

In the present Report we review the literature on combinatorial enumeration in chemistry published in the last two years – from June 2003 to May 2005. This represents a continuation of our reporting on advances in counting objects in chemistry since June 1999. The first Report was entitled *Enumeration in Chemistry*[1] in which we reviewed historically important enumerations, enumeration methods and the literature published between June 1999 to May 2001. The second Report was entitled *Combinatorial Enumeration in Chemistry*[2] in which we reviewed the literature published between June 2001 and May 2003 and some past achievements related to the discussed results.

As before, we will review current results and will also present the related past results to help the reader to see how the certain area of combinatorial enumeration evolved.

2 Current Results

2.1 Isomer Enumeration. – In the past two years (2003–2005) there were somewhat less reports on the enumeration of isomeric structures unlike the periods between 1999–2001 and 2001–2003.

2.1.1 Chiral Isomers of Alkanes. In a continuation of his enumerative works,[3–5] Lukovits[6] reported constructive enumeration of chiral alkanes. It should be noted that the *constructive enumeration* means counting objects by constructing each object separately using a suitable code.[7,8] In his work, Lukovits represented alkanes by chemical trees. *Chemical trees* are graph-theoretical trees[9] that represent the carbon skeleton of alkanes and in which *no* vertex has a degree greater than 4.[10] The degree of a vertex is the number of edges meeting at this vertex.[11]

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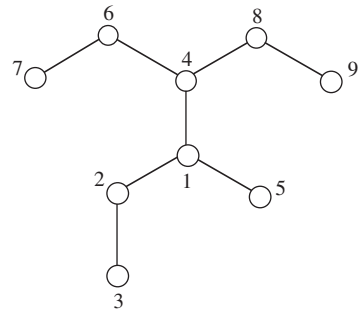
Lukovits' approach[6] is based on the *lowest degree first* (LDF) tree and the concept of canonical labeling.[12] A LDF tree is a Morgan tree (and consequently a physical tree, as well). A *physical tree*[13] is a tree obtained by assigning labels to its vertices consecutively and each vertex to be labeled must be adjacent to an already labeled vertex. Therefore, each vertex, except the vertex labeled 1, has exactly one neighbor with a lower label. Such labeling results in the vertex-adjacency matrix[10] $\boldsymbol{A}$ of a physical tree that contains only one non-zero element in each column of its upper triangle.[14] This fact allows the vertex-adjacency matrix to be replaced by the condensed representation, called the *compressed adjacency matrix* and denoted by CAM. Each digit in CAM denotes the row in the upper-half of the vertex-adjacency matrix in which digit 1 is placed. Thus CAM is a linear representation of the vertex-adjacency matrix composed of $N-1$ entries and it can be set up directly by inspecting the labeling of a physical tree. It can be also used for coding trees. Physical trees with no vertex-degree greater than 4 have been generated and enumerated using the N-tuple code.[13,15,16] An illustrative example of a physical tree representing the carbon skeleton of 3-methyl-4-ethylhexane, the upper-half of the corresponding vertex-adjacency matrix and the related CAM code is given in Figure 1.

A *Morgan-tree*, so named by Lukovits[3] in honour of H.L. Morgan, who years ago proposed an algorithm for unique labeling of chemical compounds,[17] is a physical tree in which the vertex-labeling must obey an additional restriction with respect to physical trees:[3,18] Each new label must be attached to a vertex adjacent to the vertex labeled with the lowest ordinal. The structure of the vertex-adjacency matrix belonging to a Morgan tree also allows it to be condensed to CAM. The number of Morgan trees is a small fraction of the number of physical trees. Figure 2 displays the Morgan tree representing the carbon skeleton of 3-methyl-4-ethylhexane, the upper-half of the corresponding vertex-adjacency matrix and the related CAM code.

A *LDF tree* is a tree in which a new label is attached to the vertex that has a first neighbour labeled with the lowest ordinal k and which in addition has the lowest degree of all vertices attached to the vertex labeled k. Labeling in LDF trees must start at an end-vertex. The structure of the vertex-adjacency matrix belonging to a LDF tree also allows it to be condensed to CAM. Labeling of a LDF tree is exemplified in Figure 3. This figure displays the LDF tree representing the carbon skeleton of 3-methyl-4-ethylhexane, the upper-half of the corresponding vertex-adjacency matrix and the related CAM code.

If the CAM codes of physical tree A, Morgan tree B and LDF tree C are lexicographically ordered, the obtained order is CAM(A) < CAM (B) < CAM (C). LDF trees, therefore, have the maximal lexicographical value of all CAM codes related to the same molecule; hence they are unique.

Enumeration of chiral alkanes is carried out in the following way. The computer program performing the generation procedure,[3,5,18] starts calculations by generating the LDF trees with N vertices, and then sorts out all chiral trees. To determine whether the LDF code represents a chiral tree, all vertices of degrees three or four need to be inspected. If two branches attached to these vertices are identical, the tree is *not* a chiral tree. To accomplish this task, two



A

0	1	0	1	1	0	0	0	0
	0	1	0	0	0	0	0	0
		0	0	0	0	0	0	0
			0	0	1	0	1	0
				0	0	0	0	0
					0	1	0	0
						0	0	0
							0	1
								0

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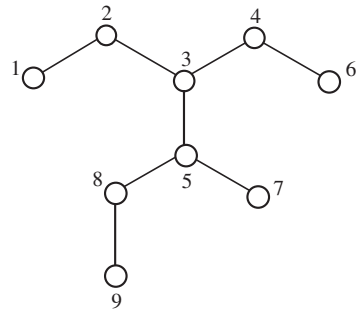
Figure 1 *Physical tree depicting the carbon skeleton of 3-methyl-4-ethylhexane, the upper-half of the corresponding vertex-adjacency matrix and the CAM code*

rules are used to delete non-chiral structures and to determine whether two branches are identical or not. For example, among the 9 heptane trees, 18 octane trees, 35 nonane trees and 75 decane trees there are 2, 5, 15 and 40 trees, respectively, possessing at least one chiral vertex. As an illustration, all chiral octane trees are given in Figure 4.

2.1.2 Counting Disconnected Structures. A great deal of research has been done on counting connected structures, *e.g.*[1,2] However, Petkovšek and Pisanski[19] presented a method, using the graph-theoretical language,[9–11] for enumerating disconnected graphs (structures) with a given number vertices if the number of connected graphs is known. They have also shown that the method can be used in reverse direction, that is, if the numbers of *all* structures are known, the number of connected structures can be readily determined. Their method can be summarized as follows. If $F(x)$ is the generating function of the



B

0	1	0	0	0	0	0	0	0
	0	1	0	0	0	0	0	0
		0	1	1	0	0	0	0
			0	0	1	0	0	0
				0	0	1	1	0
					0	0	0	0
						0	0	0
							0	1
								0

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Figure 2 *Morgan tree depicting the carbon skeleton of 3-methyl-4-ethylhexane, the upper-half of the corresponding vertex-adjacency matrix and the CAM code*

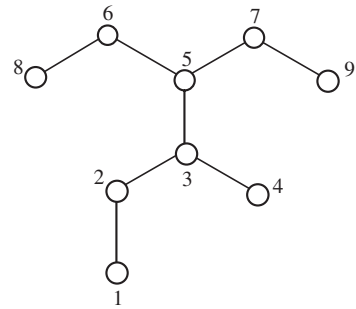
counting sequence of connected graphs, then the corresponding generation function $G(x)$ of the counting sequence of all graphs is given by:[20]

$$G(x) = \exp \sum_{k \geq 1} F(x^k)/k \tag{1}$$

Applying a variant of the Möbius inversion to equation (1), it is possible to express $F(x)$ in terms of $G(x)$:

$$F(x) = \sum_{k \geq 1} [\mu(x)/k] \log G(x^k) \tag{2}$$

where μ stands for the Möbius function.[20]



C

0	1	0	0	0	0	0	0	0
	0	1	0	0	0	0	0	0
		0	1	1	0	0	0	0
			0	0	0	0	0	0
				0	1	1	0	0
					0	0	1	0
						0	0	1
							0	0
								0

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Figure 3 *LDF tree depicting the carbon skeleton of 3-methyl-4-ethylhexane, the upper-half of the corresponding vertex-adjacency matrix and the CAM code*

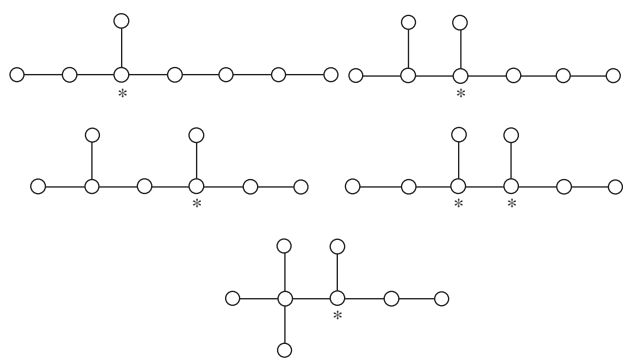


Figure 4 *All chiral octane trees. Asterisks denote chiral vertices*

An illustrative example is given below. The number of connected simple graphs (that is, graphs without loops and multiple edges)[11] with N vertices is given by:

$$F(x) = x + x^2 + 2x^3 + 6x^4 + 21x^5 + 112x^6 + 853x^7 + 11117x^8 + 261080x^9 + 11716571x^{10} + 1006700565x^{11} + \ldots \quad (3)$$

and the number of all simple graphs with N vertices is given by:

$$G(x) = x + 2x^2 + 4x^3 + 11x^4 + 34x^5 + 156x^6 + 1044x^7 + 12346x^8 + 274668x^9 + 12005168x^{10} + 1018997864x^{11} + \ldots \quad (4)$$

while the corresponding sequence of disconnected simple graphs is:

0, 1, 2, 5, 13, 44, 191, 1229, 13588, 288597, 12297299, . . . (5)

Figure 5 gives as an example *all* simple graphs with *five* vertices.

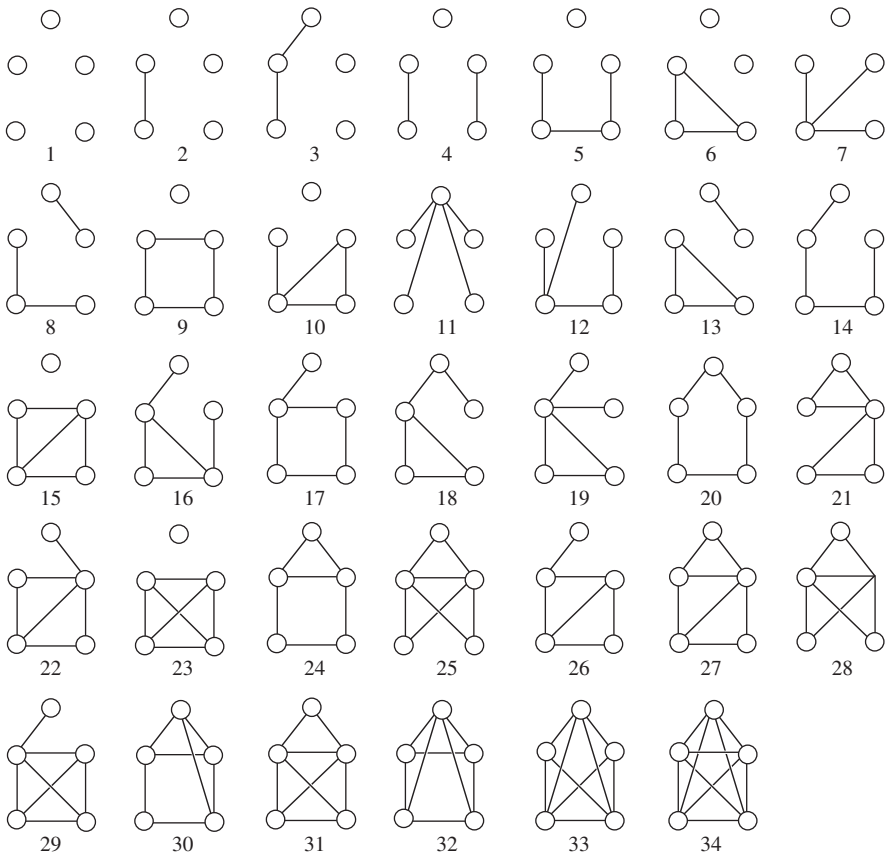


Figure 5 *All simple graphs with five vertices*

Numbers given above in (3) and (4) can be checked in the *On-Line Encyclopedia of Integer Sequences* – see sequences A001349 (3) and A000088 (4). This *Encyclopedia* is a marvellous, free of charge, source of a great many integer sequences published electronically by Neil J.A. Sloane in 2005 at the address http://www.research.att.com/njas/sequence/. It should be appreciated by all those who do combinatorial enumeration or any other research in which there is need for integer sequences. The number of all connected and all simple graphs with up to nine vertices can be also found in the book *Graphical Enumeration* by Harary and Palmer.[21] However, the number of all simple graphs with nine vertices (308708) in Harary's masterpiece *Graph Theory*[9] must be a misprint since the correct number is 274668.

2.1.3 Isomeric Fullerenes. Fullerenes C_N are carbon cages built from fused pentagons and hexagons. With increasing the value of N, the number of possible fullerenes increases considerably. The smallest fullerene is C_{20} (there was a recent report on the existence of this fullerene)[22] and C_{22} fullerene is not possible. In the mentioned *On-Line Encyclopedia of Integer Sequences*, the following numbers of isomeric fullerenes are given starting with C_{20} and increasing the subscript by 2 – see sequence A007894:

$$1, 0, 1, 1\ , 2, 3, 6, 6, 15, 17, 40, 45, 89, 116, 199, 271, 437, 580, 924, 1205, 1812, 2385, \ \ldots \quad (6)$$

These numbers have been known for some time, *e.g.*[23–28] Nevertheless, enumeration of fullerenes, notably higher fullerenes with $N > 100$ is still being pursued. Thus, Livshits and Lozovik[29] introduced the *cut-and-unfold* approach to fullerene enumeration. Their approach combines the formalism of a fullerene graph cut-and-fold onto a planar triangular lattice and a topological description of closed quasi-2D clusters. The authors have tested their approach against the available data[27] and enumerated fullerenes for $100 \leq N \leq 110$ (see Table 1) and fullerenes that satisfy the isolated pentagon rule (IPR)[30,31] for $102 \leq N \leq 150$ (see Table 2). The IPR predicts fullerenes with all the pentagons isolated by hexagons to be more stable than those with abutted pentagons.

Table 1 *Fullerene-numbers (FN) for $100 \leq N \leq 110$ obtained by the cut-and-unfold approach. These results are taken from ref. 29*

N	*FN*
100	285 914[a]
102	341 658[a]
104	419 013[a]
106	497 529
108	604 217
110	713 319

[a] Numbers labeled by *a* are also given in the *On-Line Encyclopedia of Integer Sequences*.

Table 2 *Numbers of isolated-pentagon fullerenes (NIPF) for 102 ≤ N ≤ 150 obtained by the cut-and-unfold approach. These results are taken from ref. 29*

N	*NIPF*
102	616
104	823
106	1233
108	1799
110	2355
112	3342
114	4468
116	6063
118	8148
120	10774
122	13977
124	18769
126	23589
128	30683
130	39393
132	49878
134	62372
136	79362
138	98541
140	12354
142	151201
144	186611
146	225245
148	277930
150	335569

Buckminsterfullerene, the C_{60} isomer,[32] is the smallest possible fullerene that obeys the IPR and the most stable one among the 1812 cages with 60 carbon atoms.[33,34]

2.1.4 Mathematical Models of Isomerism. Papers in this area are highly mathematical and often difficult to read. Here we report on publications by Iliev, Fujita and Balasubramanian that have appeared in the last few years.

Lunn and Senior[35] proposed many years ago a mathematical model of isomerism in organic chemistry which Iliev generalized in recent years.[36–38] Lunn and Senior considered three types of isomerism: (i) univalent substitution isomerism (positional isomerism), (ii) skeletal (structural) isomerism and (iii) enantiomorphism. *Univalent substitution isomerism* is the relationship existing between any two compounds A_1 and A_2 with the same empirical formula in case that structural formula of A_1 can be converted into that of A_2 by a permutation of the univalent substituents without disturbing the skeleton. Then the molecules A_1 and A_2 are said to be *univalent substitution isomers*. For example, 1-chloropropane and 2-chloropropane are univalent substitution (positional) isomers. *Skeletal isomers* are any two compounds A_1 and A_2 with

the same empirical formula that differ in the connectivity (Lunn and Senior used the older term connexity) relations within their respective structures. Or in other words, *skeletal isomerism* is the relationship that exists between compound A_1 and the isomeric compound A_2 if the skeleton of A_1 cannot be converted into that of A_2 without disturbing its skeleton. Then the molecules A_1 and A_2 are said to be skeletal isomers. For example, butane and isobutane are skeletal isomers. *Enantiomorphism* or optical isomerism is a special form of stereoisomerism. A pair of molecules is defined as enantiomeric if one molecule in the pair is not a superimposable mirror image of the other.

Substitution isomerism, structural isomerism and stereoisomerism define three equivalence relations on the set T_λ of all structural formulas $A = (A_1, A_2, \ldots)$ with a fixed empirical formula, skeleton and with d univalent substituents. On the other hand, the symmetric group S_d and any of its subgroups acts naturally on the set T_λ. The basic idea of the Lunn-Senior model is that one can obtain these equivalence relations by means of the action of three permutation groups G, G′, G″ $\leq S_d$, respectively, and G is not generally the 3-dimensional symmetry group of the molecule. Thus, Lunn and Senior[35] supposed that the number of orbits constitutes the upper boundaries of the number of isomers obtained by the experiment (though the computed and experimental values often coincide). In his first paper (part I),[36] Iliev defined precisely the set where the above groups act (structural formulas are identified with the tabloids with d nodes) and introduced a partial order that models the substitution reactions between isomers. This partial order can be used for prediction of certain substitution reactions and for proving the impossibility of such reactions. For any permutation group $W \leq S_d$ (W could be, for example, any of G, G′ or G″) and for any one-dimensional character χ of W, Iliev defined W-orbits with a special maximum property, which in the case $W = G'$ and χ is the two-valued character with kernel G $\leq$ G′, specializes to the chirality. Thereby Iliev was also able to get a type property[35] of the molecule under consideration. Note that the type properties of the molecule do not depend on the nature of the univalent substituents. Moreover, Iliev established a formula for counting these special W-orbits. Thus, in particular, one obtains the well-known inventory of the enantiomorphous pairs. In case that χ is the unit character of W, one gets a formula for counting all W-orbits. Iliev also generalized the formula obtained by Ruch *et al.*[39] for the number of isomers corresponding to a given partition of d. In addition, the results of Ruch *et al.*[39] which relates the dominance order between partitions and the existence of chiral pairs is reached as a consequence of a much more general statement.

Iliev devoted the second part[38] of his generalization of the Lunn-Senior mathematical model of isomerism to identification of the isomers of a given molecule with their structural formulas on the basis of their substitution reactions. A classical prototype of this identification is the Körner scheme of substitution reactions[40] between the three di-substituted and the three tri-substituted homogeneous products of benzene, which allows all these products to be identified as ortho, meta, para, vicinal, asymmetric, symmetric, respectively, in agreement with the combinatorics of the substituent positions on the six-membered ring.

In his pioneering work, Körner was concerned with the dibromo- and tribromo-benzenes.[40] A few words about now almost forgotten Körner are in order. Wilhelm Guglielmo Körner (1839–1925) was a student of Friedrich August Kekulé (1824–1896) and professor of chemistry at the University of Milan. He devised one of the chemical proofs of the equivalence of the six hydrogen atoms of benzene and was the first to propose the accepted formula for pyridine. It should be noted that the problem of assigning structures to isomeric benzene derivatives was known as orientation in the benzene nucleus. This was solved in two ways; one way is known as the Körner absolute method (the Körner scheme of substitution reactions) and the other as the interconversion method.[41] Illiev developed the algebraic approach within the framework of the Lunn-Senior model that allows for all couples of isomers that can and that cannot be distinguished by means of substitution reactions to be found. He also introduced distinguishability by means of characters, proved that the enantiomers cannot be distinguish either by substitution reactions or by characters and discussed the examples of ethylene, benzene and cyclopropane.

In a related paper, Iliev[37] considered organic compounds with one monosubstituted and at least three di-substituted homogeneous derivatives. Examples of molecules studied were benzene and cyclopropane. The Lunn–Senior permutation groups of substitutional isomerism of these compounds were described and upper bounds of the numbers of their di-substituted and trisubstituted homogeneous derivatives were found. Lists of the possible simple substitution reactions among di-substituted homogeneous derivatives, di-substituted heterogeneous and tri-substituted homogeneous derivatives were given. Substitution reactions were found that allowed some derivatives to be identified by their structural formulas.

Very active in devising mathematical models of isomerism is Shinsaku Fujita. His aim is to restructure stereochemistry by clarifying ambiguous concepts. Fujita's efforts in the past were directed toward defining precisely the basic stereochemical concepts: *chirality* and *stereogenicity*,[42,43] since in many textbooks the difference between these two fundamental concepts was not fully demonstrated, *e.g.*[44,45] Stereochemistry is concerned with at least two aspects of organic molecules: One is the *geometric* aspect known as chirality and the other is the *nomenclature* aspect called stereogenicity. The geometrical aspect was studied by point groups which are well-suited to treat continuous objects. But point groups are unsuitable for treating those stereochemical problems which are characterized by a discrete nature, such as isomer classification and combinatorial enumeration. Stereogenicity was related to the *RS*-nomeclature,[46–48] where the permutability of ligands determines the *R*- and *S*-descriptors. Such permutability was treated by permutation groups, which appear to be insufficient to treat chirality.[49] In order to discuss chirality and stereogenicity from a common point, Fujita[43] introduced the concept of stereoisomeric groups, which is a combination between the coset representation of point groups and permutation groups. He then proposed the concepts of *holantimers* and *stereoisograms* and concluded that *RS*-stereogenicity is more useful than stereogenicity in discussing the *R,S*-nomeclature.[50] Above we stated when two

molecules make an enantiomeric pair. Additionally, two molecules can be defined to be enantiomeric as follows. When a molecule is regarded as a skeleton with ligands, its mirror image comprises the corresponding mirror skeleton and the corresponding ligands of opposite chirality. On the other hand, two molecules based on the same skeleton are defined as being *holantimeric* if the chirality of each ligand in one molecule of the pair is changed into opposite chirality to give the other molecule based on that same skeleton. These two molecules are then said to be holantimers. Roots of the terms *holantimers* and *holantimeric*, proposed by Fujita, are Greek words *holo* or *hol* meaning *whole* or *entire*, and *anti* meaning *opposite to*. Fujita introduced the concept of *stereoisogram* in order to correlate a set of stereoisomers based on holantimeric and enantiomeric relationships. The term *stereoisogram* results from combining the terms *stereoisomer* and *isogram*. Stereogenicity, characterized by a stereoisogram and called *RS*-stereogenicity, has been identified as a property that should be correlated with chirality.

The above concepts were applied to tetrahedral organic molecules and to square-planar inorganic complexes.[50,51] Fujita earlier[52] enumerated tetrahedral molecules with various substituents with respect to their molecular formulas and their point-group symmetries. He also classified them in terms of permutation-group symmetries in addition to point-group symmetries.[49] Using the concepts of holantimers and stereoisograms, Fujita[50] examined all the enumerated tetrahedral molecules and found that their stereoisograms can be classified into five stereogenecity types: Type I (chiral/*RS*-stereogenic), Type II (chiral/*RS*-astereogenic), Type III (chiral/*RS*-stereogenic), Type IV (achiral/*RS*-astereogenic) and Type V (achiral/*RS*-stereogenic). The stereoisograms of square-planar complexes were classified into two types: Type II and Type IV. These are called *RS*-stereogenicity types since each depends on whether it can be specified by the *RS*-nomeclature or not. Later Fujita[53] was able to give a proof for the existence of five stereogenecity types that was based on the existence of five factor groups derived from *RS*-stereoisomeric groups. In the same paper, Fujita also put the concepts of holantimers and stereoisograms on the firm mathematical basis.

However, further questions emerged from this work on the relationship between stereogenicity and chirality,[50,51] *i.e.*, how stereogenicity and *RS*-stereogenicity (or stereoisomeric groups and *R,S*-stereoisomeric groups) differ and what happens if they are identical. Since these questions remained after his approach was applied to tetrahedral molecules, Fujita applied his approach to other types of molecules. In a two-part series of papers[54,55] he studied allene derivatives and square-planar complexes in more detail. In the first part,[54] Fujita, like in the case of tetrahedral molecules, discussed chirality, *R,S*-stereogenicity, stereogenicity and skeletal isomerism of allene derivatives using his terminology for groups (point groups, *R,S*-permutation groups, *R,S*-stereoisomeric groups and isoskeletal groups) and for isomers (enantiomers, holantimers, *R,S*-diastereomers, diastereomers and isoskeletal isomers). In the case of allene derivatives, Fujita established that *R,S*-stereoisomeric groups coincide with stereoisomeric groups so that diastereomers are identical with

R,S-diastereomers. In this first paper of the series,[54] Fujita also proposed the concept of *stereoisogram set* to discuss the relationship between (R,S-)diastereomers and isoskeletal isomers. Each stereoisogram set for allene derivatives contains three stereoisograms to represent isoskeletal isomerism and each of these stereoisograms was classified into five stereogenicity types (Types I–V). Combination of these stereogenicity types can be used to characterize the isomerism of allene derivatives. Fujita[54] also discussed the case of the tetrahedral skeleton, for which he found the following hierarchy of groups: point groups $\subset$ *R,S*-stereoisomeric groups = stereoisomeric groups = isoskeletal groups.

In the second part,[55] Fujita found the following hierarchy of groups for square-planar complexes: point groups = *R,S*-stereoisomeric groups $\subset$ stereoisomeric groups = isoskeletal groups. It appears that the *R,S*-nomenclature is not applicable to square-planar complexes because *R,S*-stereoisomeric groups coincide with point groups, so that all square-planar complexes are determined to be *R,S*-astereogenic. Further, there exist no isoskeletal isomers for square-planar complexes, because isoskeletal groups coincide with stereoisomeric groups. In order to discuss stereogenicity, Fujita proposed the concept of *extended stereoisogram*, which contains three degenerate stereoisograms. Applying this concept, square-planar complexes were classified into types (Types II-II-II, IV-IV-IV, *etc*.) on the basis of relevant stereoisograms (Types I–V). The meaning of the number *three* of degenerate stereoisograms in an extended stereoisogram is that square-planar complexes cannot be named by a dichromous nomenclature like *R,S*-nomenclature or *E*/*Z*-nomeclature.

Fujita[56] also discussed the *E*/*Z*-nomenclature for ethylene derivatives using group-theoretical arguments. He comprehensively discussed chirality, *R,S*-stereogenicity, stereogenicity and isoskeletal isomerism for ethylene derivatives by considering point groups, *R,S*-stereoisomeric groups, stereoisomeric groups and isoskeletal groups. He selected ethylene derivatives as a typical example of general cases in which stereoisomeric groups should be considered in addition to *R,S*-stereoisomeric groups. He established that the *R,S*-stereoisomeric groups for ethylene derivatives do not coincide with their stereoisomeric groups, so that diastereomers (*E*/*Z*-isomers) are not identical with *R,S*-diastereomers. In order to consider the relationships amongst *R,S*-diastereomers, *m*-diastereomers (cis/trans-isomers) and isoskeletal isomers, Fujita utilized the concepts of extended stereoisograms and extended stereoisogram sets. Using these concepts, Fujita classified ethylene derivatives into Types II-II/II-II/II-II, IV-IV/IV-IV/IV-IV, *etc*. on the basis of relevant stereoisograms (Types I-V). Fujita concluded that the stereoisomerism of ethylene derivatives should be treated in terms of *m*-diastereomers characterized by *E*/*Z*-nomeclature and not to be treated in terms of *R,S*-diastereomers characterized by *R,S*-nomenclature.

In a separate paper, Fujita jointly with Sherif El-Basil[57] used the concept of doubly-colored graphs to visualize the abstract concepts such as subductions of coset representations, double cosets, and unit-subduced-cycle-indices,[58] which had been mathematically formulated in the framework of coset algebraic theory developed by Fujita.[42]

In another two-part series,[59,60] Fujita presented the stereochemical extension of the Pólya theorem.[61] In the first part,[59] he points out that the Pólya theorem is concerned with graphs and not with molecules although the key paper of Pólya[61] contains also chemical compounds in the title: *Kombinatorische Anzahlbestimmungen für Gruppen, Graphen and chemische Verbindungen* (translated later into English as *Combinatorial Enumeration of Groups, Graphs, and Chemical Compounds*). The basic assumption was that chemical compounds can be regarded as kinds of graphs. Although this assumption works in many cases, there are problems when the Pólya theorem is applied to chiral/achiral ligands. Fujita set a task to correct this situation. In the past, several approaches were proposed to treat the chirality/achirality of ligands. Hässelbarth and Ruch[39,62–64] reported an approach based on double cosets of permutation groups, whilst Fujita[42] proposed the unit-subduced-cycle-index approach. In this approach, the author has shown that the sphericity of an orbit is important to stereochemical discussion when taking account of chirality/achirality of ligands[49,65] and that the chirality fittingness due to sphericity produces the unit-subduced-cycle-index with the chirality fittingness that can be applied to combinatorial enumerations.[66]

In this work,[59] Fujita reexamined the original definition of the sphericity concept in terms of conjugacy classes so that the Pólya theorem could be substantially extended in combination with the sphericity concept. To take account of chiral ligands together with achiral ligands, permutations of the coset representations for cyclic subgroups have been classified into proper and improper elements. This has resulted in classifying the *k*-cycle contained in each permutation as an enantiospheric, homospheric or hermispheric cycle. Sphericity indices were then defined according to the enantiospheric, homospheric or hermispheric character of each *k*-cycle. Now, using sphericity indices, cycle indices with chirality fittingness have replaced the Pólya cycle indices. The use of cycle indices with chirality fittingness to enumerate stereoisomers with chiral and achiral ligands has been illustrated on allene derivatives.

In the second part of the series,[60] Fujita proposed a proligand approach to enumerate nonrigid isomers. The proligand approach is based on the concepts of proligand and promolecule[52] and it takes into consideration both chiral and achiral (pro)ligands. Fujita used the extended sphericity indices of *k*-cycles, which were also been defined according to the enantiospheric, homospheric or hermispheric character of each *k*-cycle. Then, as before, the cycle indices with chirality fittingness have been defined so as to enumerate nonrigid stereoisomers with chiral and achiral ligands. The proligand approach was applied to tetramethylmethane and compared to the Pólya approach with the conclusion that the Pólya theorem is applicable to graphs and his (Fujita's) approach to nonrigid molecules.

Balasubramanian[67] reported all irreducible representations of the octahedral (cubic) symmetry for vertex-, face- and edge-colorings of a pair of closely related Platonic bodies, the octahedron and its dual the cube using multinomial combinatorics. Combinatorial tables for all irreducible representations and all multinomial partitions were constructed and visualized by the Young tableaux.

These enumerations constitute multinomial expansions of character-based cycle index polynomials and grow in combinatorial complexity as a function of vertex- or edge-coloring partitions. It should be noted that the Pólya combinatorial theory of enumeration[61] provides the generating function for multinomial expansion in terms of the ordinary cycle index of a group which is the sum of all orbits of permutation of a group when it acts on a given set divided by the order of the group. Several authors have independently generalized the cycle index, *e.g.*[68–70] Balasubramanian has not only generalized the cycle index, which he called the generalized character cycle index, but also provided a physical and geometric interpretation of the numbers generated.[67,71,72]

Balasubramanian[73,74] also carried out combinatorial and group-theoretical analyses of a $C_{48}N_{12}$ dodecaazafullerene. The IUPAC name of this compound is rather unwieldy (8,13,18,23,26,29,32,35,40,45,50)-dodeca[60-S_6]fullerene. Balasubramanian[75] found earlier that there are 233,227,974,475 possible isomers of this compound. Many of these isomers are not expected to have much of the life-time, since if two nitrogen atoms are adjacent in an isomer, there will be nitrogen-nitrogen repulsion that would destabilize the structure. Balasubramanian[73] presented the correlation table of the rotational levels of $C_{48}N_{12}$ into the S_6 group and also its induction into the I_h parent group. He predicted the properties of the ^3A_u, ^3E_g, and ^3E_u excited states of $C_{48}N_{12}$ that lie 1.9 eV above the ^1A_g ground state and also predicted that the ^3E_g and ^3E_u states would undergo the Jahn-Teller distortion into chiral structures with no symmetry and an achiral structure with C_1 symmetry. In a related paper, Balasubramanian[74] presented the nuclear spin statistics of $C_{48}N_{12}$: the nuclear spin multiplets and statistical weights of ^{14}N spin-1 bosons, and the ^{13}C nuclear spin species and spin statistical weights of $^{13}C_{48}N_{12}$.

Balasubramanian[76] also considered combinatorial and group-theoretical analysis of three $C_{60}H_{36}$ isomers. The first paper on $C_{60}H_{36}$ appeared in 1990, in which Haufler *et al.*[77] demonstrated the formation of $C_{60}H_{36}$ through low-temperature Birch reduction of C_{60} and since that time $C_{60}H_{36}$ has been studied by a number of authors. Balasubramanian[75] predicted in 1991 that there were over 600 trillion isomers including chiral isomers of $C_{60}H_{36}$ (the exact number of isomers being 600,873,146,368,170). Among them, there are only four T isomers without chirality (or eight isomers with chirality), 31280 C_3 isomers[78] whilst the majority of $C_{60}H_{36}$ isomers belong to the C_1 group. The current report by Balasubramanian was stimulated by a recent paper of Gakh *et al.*[79] in which the authors presented NMR spectra of three isomers of $C_{60}H_{36}$ obtained using the high temperature hydrogenation reaction of C_{60}. Balasubramanian obtained the generating functions for nuclear spin species of protons and ^{13}C nuclei. Special cases of generating functions produce the NMR spectral patterns. The predicted NMR results for the three $C_{60}H_{36}$ isomers with C_1, C_3 and T symmetries agreed with the experimental results. Balasubramanian also predicted the ESR hyperfine patterns of radicals obtained from the three $C_{60}H_{36}$ isomers and gave complete tables of the nuclear spin species of these isomers.

Balasubramanian[80] additionally prepared a nice and very informative author's review on the applications of enumerative combinatorics to chemistry and spectroscopy for a special issue of *Advances in Quantum Chemistry*, dedicated to Chemical Graph Theory (guest editor: D.J. Klein). The author first presented the essence of enumerative combinatorics by means of the Pólya theorem,[61] generalization of the Pólya theorem to all irreducible representations,[81–83] the de Bruijn[84,85] extension of the Pólya theorem and the Balasubramanian generalization of the de Bruijn extension to all characters of any finite permutation group.[86] He then showed how these techniques can produce full multinomial combinatorics of all irreducible representations of any group. As an illustration, he used octahedral (cubic) and icosahedral symmetries as a function of partitions for vertex-, face- and edge-coloring. He has also given full combinatorial tables for all irreducible representations and all multinomial representations. Application was illustrated on fullerenes. This Balasubramanian's review may be regarded as a sequel to his 1985 review[87] which followed the path set by Rouvray's early review on enumeration in chemistry.[88]

2.1.5 Stereoisomers of Oligoinositols. In our last Report,[2] we presented enumerative works on oligoinositols by Dolhaine *et al.*[89,90] and by Dolhaine and Hönig.[91,92] The problem of counting oligoinositols was started by the question posed by Hudlicky *et al.*[93] These authors wondered how many stereoisomers exist of diinositols (**b**) and triinositols (**c**) existed. See the considered oligoinositols in their Haworth projections in Figure 6.

Stereoisomerism of **a**–**e** is due to tetrahedral stereocenters (chiral centers). The number of stereoisomers depends on the possibilities of distributing C–O bonds above and below the average planes of the cyclohexane rings. Because of the rapid interconversion of conformers, each cyclohexane ring can be schematized by a planar hexagon (see Figure 6). Since the considered oligoinositols exhibit high constitutional symmetry, many conformers are identical; thus the number of distinct stereoisomers is much less than 2^c, where c is the number of chiral centers.

Hudlicky *et al.*[93] gave two answers to their question for **b**: $2^{12} = 4096$ stereoisomers (theoretical result) and 990 stereoisomers (true result). The authors did not explain how they reached the latter number. Dolhaine *et al.*[89] obtained 528 as the number of stereoisomers of **b** by applying their program ISOMERS. In one of the two subsequent papers, Dolhaine and Hönig[92] published tables of oligoinositol isomers up to tetramers. But, they did *not* answer the question regarding the number of stereoisomers of **c**. They produced, however, the number of all stereoisomeric linear triinositols, *i.e.*, the sum of stereoisomers enumerations for **c** and its constitutional isomers **d** and ***e***. They also asked about the number of achiral stereoisomers among all stereoisomeric diinositols and triinositols and treated this problem by inspecting many thousands of stereoisomers.

Rücker *et al.*[94] provided the answer. These authors used three methods to count the stereoisomers of oligoinositols: (i) Manual exhaustive construction of all stereoisomers, (ii) Counting without construction by using the

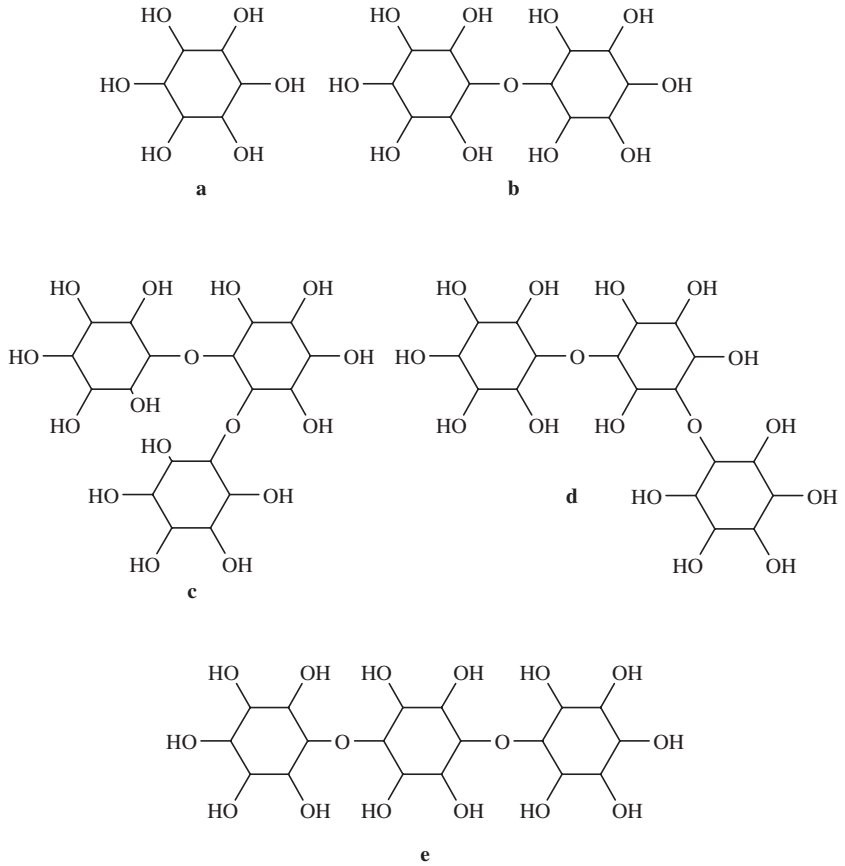


Figure 6 *Considered diinositols and triinositols in their Haworth projections*

Cauchy-Frobenius lemma (or the Burnside lemma)[95] and (iii) Application of the computer program MOLGEN 3.5.[96–99] Actually, the paper of Rücker *et al.*[94] aimed to show the potential of constructive enumeration for problems with up to a certain level of complexity, especially if it can be helped by symmetry arguments. The other two methods are used to support and check the results obtained by manual enumeration. Rücker *et al.*[94] obtained the following results: (1) There are 9 monoinositols (**a**) and 7 are achiral, (2) there are 528 diinositols (**b**) and 48 are achiral (Dolhaine *et al.*[89] give 48 in their 1999 paper whilst in the second[92] of their 2002 papers Dolhaine and Hönig give 46 as the number of achiral isomers of **b**) and (3) there are 82176 triinositols (**c**–**e**) with only a small fraction of isomers being achiral (768). All three counting methods used produced the same stereoisomer counts, but the differentiation between chiral and achiral stereisomers was not implemented in the version of MOLGEN employed in the paper.

2.2 Kekulé Structures. – Kekulé structures are still attracting attention of chemists and mathematicians. In the language of mathematics, Kekulé structures are often called *perfect matchings*.[100–103] Matching theory is a well-developed part of graph theory,[100] but it is still of interest,[104–107] especially in the theory of benzenoid hydrocarbons, *e.g.*[108–112] The importance of Kekulé structures, among other concepts, in the graph-theoretically formulated electronic-structure theory was recently discussed by Klein.[113] Kekulé structures are essential in the conjugated-circuit model of aromaticity[114–116] and in the Simpson-Herndon variant[117,118] of the valence-bond resonance theory.[119] It should be also noted that a widely used topological index,[120,121] called the *Hosoya index*,[10] is based on matchings in a molecular graph.[122] Similarly, the key concept in the topological resonance energy (TRE) is the *matching polynomial*.[123–126] The TRE is still used in assessing the aromatic character of conjugated systems, in recent years especially of fullerenes, *e.g.*[127] It should also be noted that the absolute value of the constant coefficient in the matching polynomial yields the number of Kekulé structures of a given conjugated system. Balasubramanian,[128] for example, calculated matching polynomials of fullerenes C_{20}–C_{50} and thus also produced their *K*-numbers. His results were, for example, utilized by Torrens in his work on structural properties of fullerenes.[129–134]

2.2.1 Benzenoid Hydrocarbons. Došlić[135] reported counting Kekulé structures in benzenoid parallelograms and triangular benzenoids using an approach based on the theory of lattice animals and lattice paths. A *lattice animal* is a 1-connected collection of congruent regular polygons arranged in a plane such that two polygons are either completely disjoint or have a common edge. A benzenoid in the parallelogram-like shape, called the *benzenoid parallelogram*, $B_{m,n}$, consists of $m \times n$ hexagons, arranged in m rows, each row containing n hexagons, shifted by half a hexagon to the right from the row immediately below. A *triangular benzenoid* T_m consists of m rows with the number of hexagons in each row decreasing by one from the lowest to one hexagon in the uppermost row, each row shifted by one and a half hexagon to the right from the row immediately below.

Došlić[135] proved that there is a one-to-one correspondence between the number of Kekulé structures in a benzenoid parallelogram and the number of all square-lattice paths from (0,0) to (n,m) with steps (1,0) and (0,1). As illustrative examples we give all Kekulé structures of anthanthrene in Figure 7 and the corresponding square-lattice paths in Figure 8.

A consequence of the above correspondence is the exact formula for counting the number of Kekulé structures K of benzenoid parallelograms:

$$K(B_{m,n}) = K_{m,n} = \binom{m+n}{n} = \binom{m+n}{m} = \frac{(m+n)!}{m!n!} \tag{7}$$

The same result was obtained by Gordon and Davison[136] in 1952, but it was derived in a less formal way than by Došlić. The application of equation (7) is shown in Figure 9.

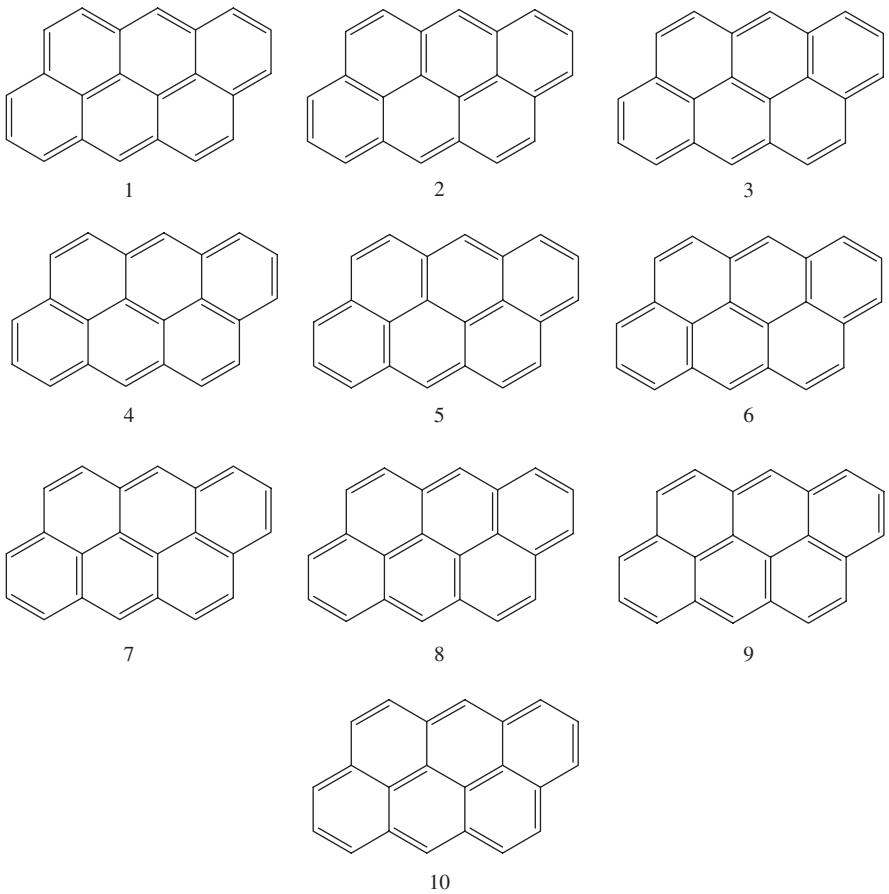


Figure 7 *Kekulé structures of anthanthrene*

The same formula as (7) was also given by Yen[137] in 1971. In his paper, Yen considered the parallelogram-shaped, the symmetric-circular-shaped, the rectangular-shaped and the skew-strip-shaped benzenoid hydrocarbons. Došlić did not refer to Yen's results.

Gordon and Davison[136] initiated the path counting method. In the *path counting method* the number of Kekulé structures K of a benzenoid B is equal to the number of the mutually self-avoiding directed peak-to-valley paths:[138,139]

$$K = \det |\boldsymbol{P}| \tag{8}$$

where $\boldsymbol{P}$ is a matrix whose elements $(\boldsymbol{P})_{ij}$ represent counts of self-avoiding paths in B starting at peak(s) and ending at valley(s). A *peak* is a vertex on the upper perimeter of B that lies above its adjacent vertices, whilst a valley is a vertex lying below its nearest neighbors on the lower perimeter of B. The peaks and valleys must match if the K-number is to be non-zero. Identification of peaks

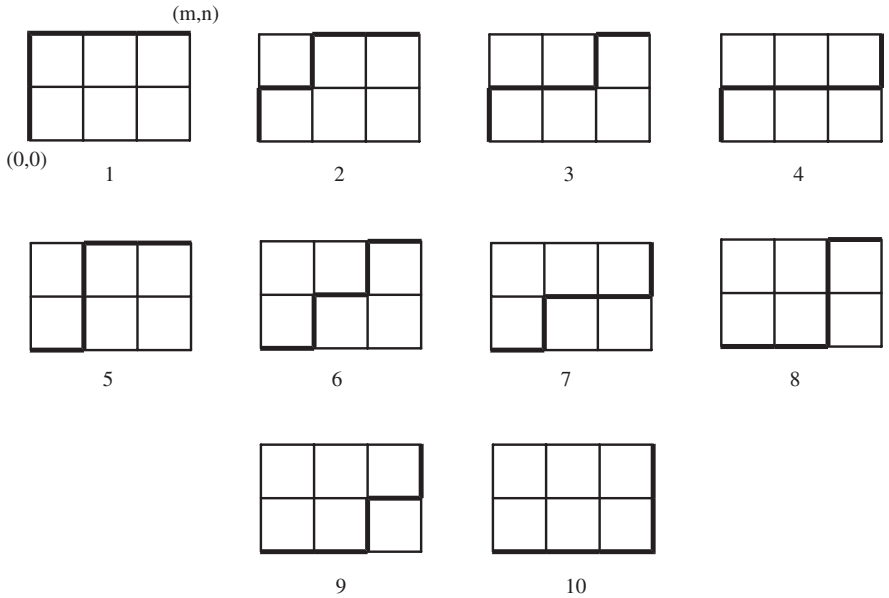
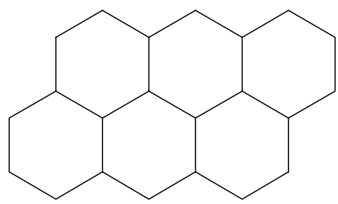


Figure 8 *Paths on the square-lattice corresponding to Kekulé structures of anthanthrene*



B_{23}

$$K_{2,3} = \binom{2+3}{3} = 10$$

Figure 9 *Counting Kekulé structures of anthanthrene by using equation (7)*

and valleys depends on the orientation of a benzenoid. For convenience, the north-south orientation[140] is used. The *K*-number is, of course, invariant to the orientation of the benzenoid. For example, anthanthrene considered in Figures 6 and 8, has three peaks and three valleys.

The use of equation (8) depends on the enumeration of paths connecting peaks and valleys. A very efficient and elegant enumeration method is founded on the *Pascal recurrence algorithm* based on the Pascal triangle.[141] As an illustrative example, we give in Figure 10 the application of the Pascal recurrence algorithm and the use of equation (8).

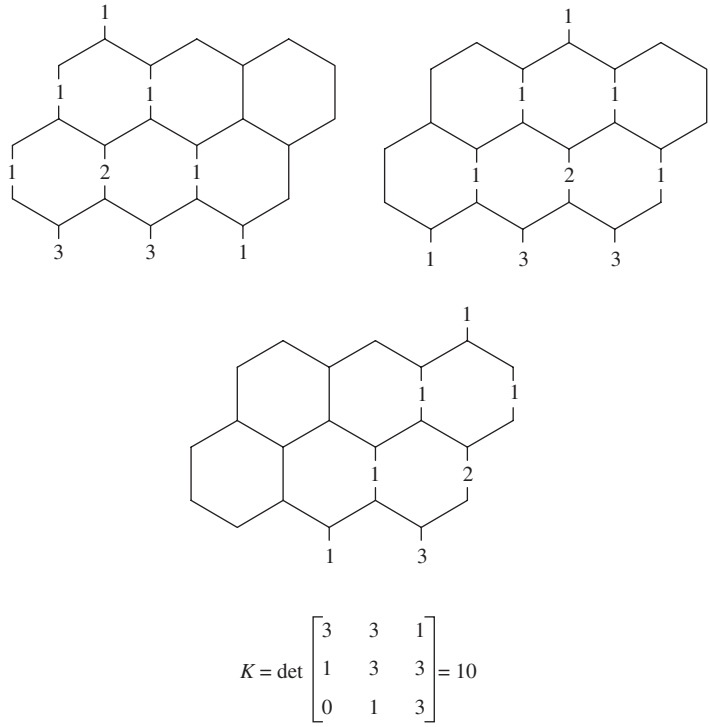


Figure 10 *Counting Kekulé structures of anthanthrene by applying the Pascal recurrence algorithm*[141]

Therefore, both approaches, the Pascal recurrence algorithm and the approach based on counting the square-lattice paths are similar. However, the Pascal recurrence algorithm is applicable to a wider range of benzenoids and not only to benzenoid parallelograms.

The counting formula for the Kekulé structures of triangular benzenoids is rather simple:[135]

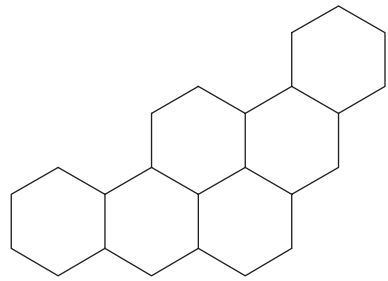
$$K(T_m) = K_m = C_{m+1} \tag{9}$$

where C_{m+1} is the $(m+1)$ *Catalan number*.[142,143] An illustrative example is shown in Figure 11.

The Catalan numbers C_N (rarely called *Segner numbers* after Johann Andreas von Segner (1704–1777))[144] can also be found in the *On-Line Encyclopedia of Integer Sequences*-see sequence A000108: 1, 1, 2, 5, 14, 42, 132, 429, 1430, ... or they can be generated using the following formula:

$$C_N = 2N!/N!\,(N+1)! \tag{10}$$

The Catalan numbers could have also been called the Euler numbers because they were discovered by Leonhard Euler (1707–1783) for counting



$K_3 = C_4 = 14$

Figure 11 *Counting Kekulé structures of dibenzo[a,i]pyrene by using equation (9)*

triangulations. A triangulation of an *N*-gon is a division of its inside into triangles. For example, a pentagon has five different triangulations. Von Segner was also involved in counting triangulations. Nevertheless, Catalan numbers are named after Eugene Charles Catalan (1814–1894), who rediscovered these numbers in connection with a different problem, that is, he solved the question: In how many ways can the product $x_1x_2 \ldots x_N$ be parenthesized? The term Segner number is ocassionally encountered. *e.g.*, in the *On-Line Encyclopedia of Integer Sequences*.

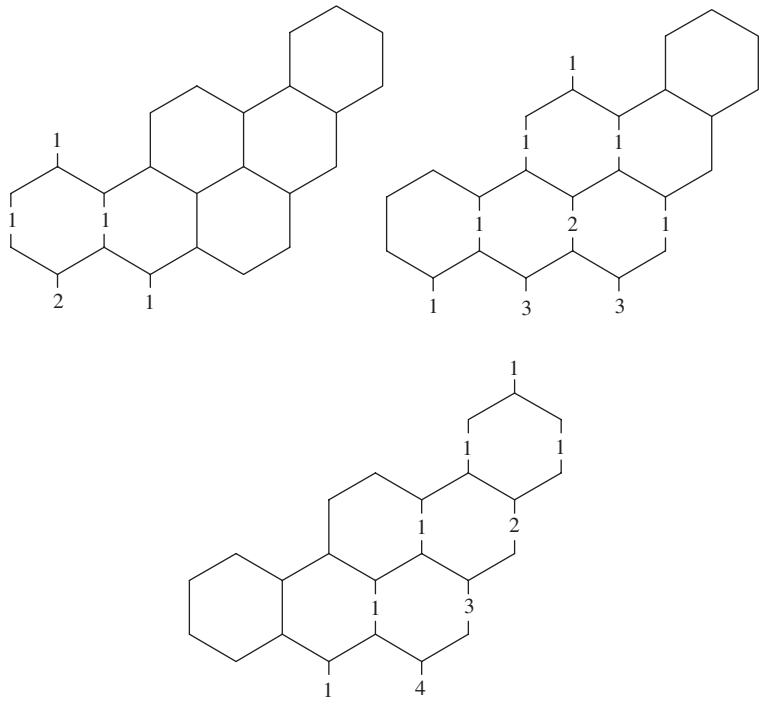
The Pascal recurrence algorithm is also applicable to triangular benzenoids, see Figure 12.

Karimi *et al.*[145] also proposed a counting method based on peaks and valleys. These authors transformed benzenoid parallelograms into square-meshes (tilted by 45 degrees square-lattices) and established that there is a one-to-one correspondence between Kekulé structures and descending paths from the top to the bottom of a square-mesh. They also generalized their counting approach to non-parallelogram benzenoids using the idea of *diminished square-mesh* which is obtained as a result of deleting one or more submeshes from a given square-mesh. In their paper, Karimi *et al.*[145] did not refer to the Pascal recurrence algorithm[141] which represents a simpler way of counting peak-to-valley paths.

A variant of the path-counting method, called the reduced graph approach,[146] was based on the idea of transforming the hexagonal network into the trigonal network and counting paths connecting peaks and valleys (though these terms were not used).[147,148] This approach was neglected by both Došlić[135] and Karimi *et al.*[145] though it preceded their reports by more than twenty years.

Došlić[135] also overlooked a more recent paper by Lukovits[149] on the resonance energy in graphite. In his paper, Lukovits calculated the number of Kekulé structures $K_{m,n}$ in the (m,n) parallelogram-shaped graphite sheets using the following recursive equation:

$$K_{m,n} = K_{m-1,n} + \mathrm{K}_{m,n-1} \tag{11}$$



$$K(T_3) = \begin{bmatrix} 2 & 1 & 0 \\ 1 & 3 & 3 \\ 0 & 1 & 4 \end{bmatrix} = 14$$

Figure 12 *Counting Kekulé structures of dibenzo[a,i]pyrene by applying the Pascal recurrence algorithm*[141]

Lukovits has also shown that equation (11) is just another way of expressing equation (7).

2.2.2 Algebraic Kekulé Structures. Randić[115,150] introduced a novel description of Kekulé structures by replacing their standard representation, which he called *geometric* Kekulé structures, by what he called *algebraic* (numerical) representation. The algebraic Kekulé structures are constructed in the following way: Each double bond in a geometric Kekulé structure gets weight 2 for two π–electrons making up the double bond and if the double bond is shared by two rings, it gets the weight of only 1. Then the numbers assigned to bonds in each ring of a polycyclic conjugated system are added up. Hence, every geometric Kekulé structure gives rise to a numerical Kekulé structure that

can simply be encoded by a linear sequence of numbers. The algebraic Kekulé structure can be generated for any class of conjugated systems, *i.e.*, conjugated (alternant, nonalternant, coronoids, *etc.*) hydrocarbons or heterosystems possessing geometric Kekulé structures.[151–158] As an example, the geometric Kekulé structures and the corresponding algebraic Kekulé structures of chrysene are given in Figures 13 and 14.

Geometric Kekulé structures provide a linear code for Kekulé structures. For example, we give below the codes for chrysene Kekulé structures. They are listed in the lexicographic order:

4 6 2 6
4 6 3 5
5 3 6 4
5 4 3 6
5 4 4 5
6 2 6 4
6 3 3 6
6 3 4 5

Gutman *et al.*[159] proved that cata-condensed benzenoids (catafusenes) have a one-to-one correspondence between geometric and algebraic Kekulé structures and that peri-condensed benzenoids (perifusenes) and corona-condensed benzenoids (coronafusenes) do not satisfy this rule. Vukičević *et al.*[160] proved the theorem on the necessary and sufficient conditions for the algebraic Kekulé structure of a perifusene or coronafusene to correspond to more than one geometric Kekulé structure. Pyrene is the simplest example of a perifusene in which two distinct geometric Kekulé structures correspond to the same algebraic Kekulé structure 5 3 3 5 (this coding of algebraic Kekulé structures of perifusene is based on the Wiswesser coding system for benzenoids).[16,153,161]

2.2.3 Fullerenes. In a series of papers,[129–134] Torrens used a set of structural parameters of fullerenes reflecting the presence of contiguous pentagons to study their periodic properties. The parameters he considered are the number of edges common to two pentagons p, the number of vertices common to three pentagons q, the number of pairs of nonadjacent pentagon edges shared between two other pentagons r and ratios q/p and r/p. He correlated $ln\ K$, $ln(per\ \boldsymbol{A})$ and $ln(per\ \boldsymbol{A})/ln\ K$ with parameters p, q, r, q/p and r/p. In doing this, Torrens really continued earlier efforts of Cash.[162,163] The values of K, $per\ \boldsymbol{A}$ and $ln(per\ \boldsymbol{A})/ln\ K$, p, q, r, q/p and r/p for fullerenes with a given symmetry from C_{20} to C_{44} are presented in Table 3. For obvious reasons, the IPR fullerenes have zero values for parameters p, q, and r. For example, buckminsterfullerene possesses the following values $K = 12500$, $per\ \boldsymbol{A} = 395{,}974{,}320$, $ln(per\ \boldsymbol{A})/ln\ K = 2.0986$, $p = 0$, $q = 0$ and $r = 0$.

Torrens also listed the numbers of Kekulé structures of some larger IPR fullerenes with icosahedral symmetry, *e.g.*, C_{80}: 140,625; C_{180}: 1,389,029,765,625; C_{240}: 21,587,074,966,666,816.

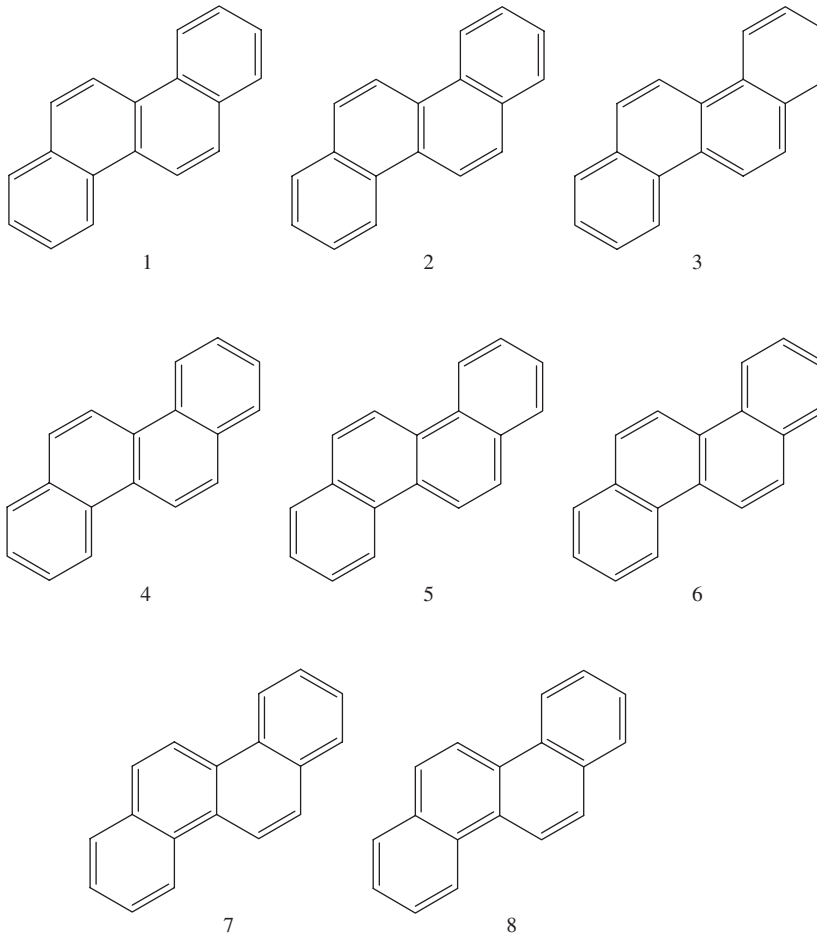


Figure 13 *Geometric Kekulé structures of chrysene*

Torrens reported several correlations between ln K, $ln(per\ \boldsymbol{A})$ and $ln(per\ \boldsymbol{A})/ln\ K$ and p, q, r, q/p and r/p. We selected the following:

$$ln\ K = 10.2 - 0.407\,p + 0.238\,q + 0.792\,q/p + 0.320\,r/p$$
$$n = 28 \qquad R = 0.931 \qquad S = 0.339 \qquad F = 28.7 \tag{12}$$

$$ln(per\ \boldsymbol{A}) = 20.2 - 0.660\,p + 0.383\,q$$
$$n = 29 \qquad R = 0.949 \qquad S = 0.757 \qquad F = 118.5 \tag{13}$$

$$ln(per\ 2A)/ln\ K = 1.88 + 0.0361\,p - 0.0490\,q + 0.00953\,r + 0.0497\,q/p - 0.2.53\,r/p$$
$$n = 28 \qquad R = 0.941 \qquad S = 0.019 \qquad F = 34.2 \tag{14}$$

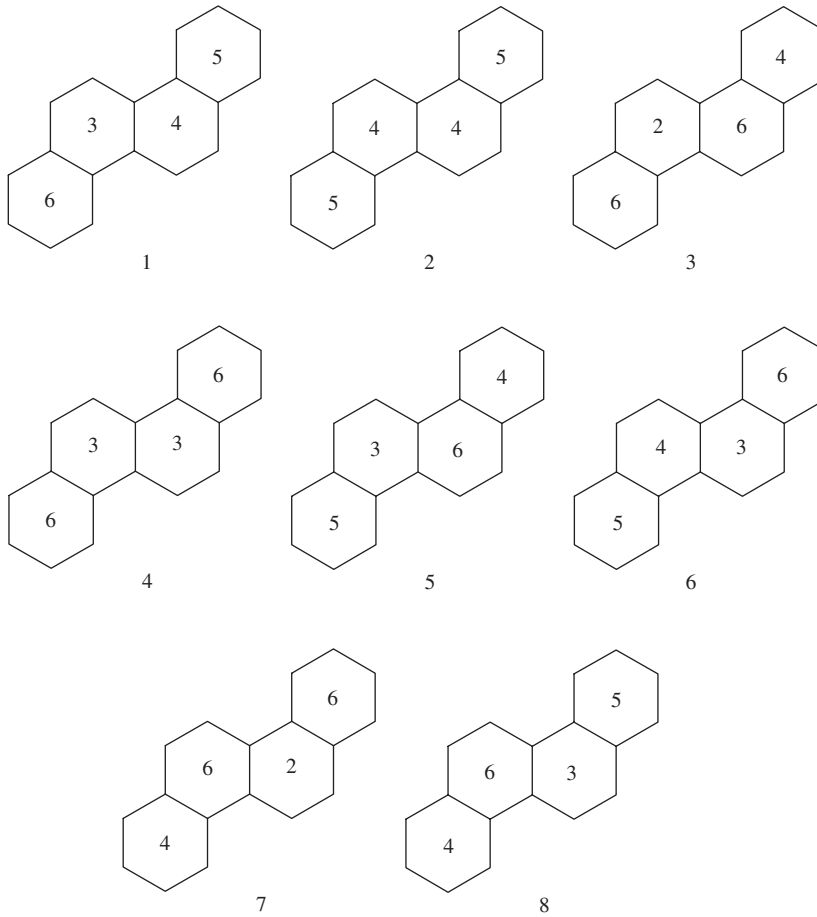


Figure 14 *Algebraic Kekulé structures of chrysene*

where n is the number of fullerenes considered, R is the correlation coefficient, S is the standard error of estimate and F is the result of Fisher's test. In the case of equation (13), the parameters of C_{60} were included in the correlation. We repeated the correlation between $ln(per\ A)$ for C_{20}–C_{44}, without including C_{60}, and their structural parameters, using the CROMRsel procedure.[164–167] CROMRsel is a multivariate procedure that has been designed to select the best possible model among the set of models obtained for a given number of descriptors, the criterion being the standard error of estimate. The quality of the CROMRsel models is expressed by fitted (descriptive) statistical parameters: the correlation coefficient (R_{fit}), the standard error of estimate (S_{fit}) and Fisher's test (F). The models are also cross(internally)-validated by a leave-one-out procedure. Statistical parameters for the cross-validated models are symbolized by R_{cv} and S_{cv}, where subscript cv denotes the cross-validation. The

Table 3 *The values of K, per(**A**), ln[per(**A**)]/ln K, p, q, and r parameters for fullerenes from C_{20} to C_{44} of a given symmetry. These results are taken from refs. 131–134*

Fullerene	K^a	*per* (**A**)^a	*ln[per(**A**)]/ ln K*	*p*	*q*	*r*	*q/p*	*r/p*
C_{20} (I_h)	36	1392	2.0199	30	20	30	0.6667	1.0000
C_{24} (D_{6d})	54	4692	2.1192	24	12	36	0.5000	1.5000
C_{26} (D_{3h})	63	8553	2.1853	21	8	30	0.3810	1.4286
C_{28} (T_d)	75	15705	2.2378	18	4	24	0.2222	1.3333
C_{28} (D_2)	90	16196	2.1540	20	8	24	0.4000	1.2000
C_{30} (C_{2v}) I	107	29621	2.2034	17	4	20	0.2353	1.1765
C_{30} (C_{2v}) II	117	30053	2.1651	18	6	20	0.3333	1.1111
C_{30} (D_{5h})	151	31945	2.0672	20	10	20	0.5000	1.0000
C_{32} (D_3)	144	55140	2.1968	15	2	18	0.1333	1.2000
C_{32} (C_2) I	151	55705	2.1780	16	4	16	0.2500	1.0000
C_{32} (C_2) II	168	57092	2.1375	17	6	16	0.3529	0.9412
C_{32} (D_2)	184	58384	2.1045	18	8	15	0.4444	0.8333
C_{34} (C_{3v})	195	103665	2.1902	15	3	15	0.2000	1.0000
C_{34} (C_s)	196	104484	2.1896	15	3	16	0.2000	1.0667
C_{34} (C_2) I	204	103544	2.1714	14	2	14	0.1429	1.0000
C_{34} (C_2) II	212	107720	2.1632	17	6	16	0.3529	0.9412
C_{36} (D_{6h})	272	192528	2.1706	12	0	12	0.0000	1.0000
C_{36} (D_{2d})	288	192720	2.1489	12	0	12	0.0000	1.0000
C_{36} (C_{2v})	312	197340	2.1231	13	2	10	0.1538	0.7692
C_{36} (D_{3h})	364	207924	2.0764	15	6	6	0.4000	0.4000
C_{38} (C_{2v})	360	366820	2.1768	14	2	14	0.1429	1.0000
C_{38} (C_{3v})	378	363300	2.1572	12	1	9	0.0833	0.7500
C_{38} (D_{3h})	456	411768	2.1116	18	8	18	0.4444	1.0000
C_{40} (D_{5d}) I	562	515781	2.0775	10	0	10	0.0000	1.0000
C_{40} (T_d)	576	704640	2.1185	12	4	0	0.3333	0.0000
C_{40} (D_{5d}) II	701	803177	2.0750	20	10	20	0.5000	1.0000
C_{44} (T)	864	2478744	2.1775	12	4	0	0.3333	0.0000
C_{44} (D_{3h})	960	2436480	2.1416	9	2	0	0.2222	0.0000

[a] Torrens, according to his e-mail to N.T. of April 19, 2005, calculated *per A* with programs provided by Dr. Gordon G. Cash (Office of Pollution Prevention and Toxics Risk Assessment Division, U.S. Environmental Protection Agency, Washington, USA) – the latest program is described in G. Delic and G.G. Cash, *Comput. Phys. Commun.*, 2000, **124**, 315. He translated these programs from C-language into Fortran. In the e-mail of April 25, 2005, Torrens stated that he took the fullerene *K*-numbers from the literature, *e.g.*, K. Balasubramanian, *J. Chem. Inf. Comput. Sci.*, 1994, **34**, 421 and H.-Y. Zhu and D.J. Klein, *J. Mol. Struct.* (*Theochem*), 1995, *338*, 11.

obtained regression equation is:

$$\begin{aligned} ln(per\ \boldsymbol{A}) =& 20.9(\pm 1.0) - 0.722(\pm 0.089)\, p + 0.437(\pm 0.091)\, q \\ n =& 28 \quad R_{fit} = 0.911 \quad R_{cv} = 0.880 \\ S_{fit}(n-I-1) =& 0.76 \quad S_{cv}(n-I-1) = 0.87 \quad F = 60.6 \end{aligned} \tag{15}$$

where *I* is the number of descriptors used in the regression. We did this because it is not clear why Torrens included buckminsterfullerene in getting the regression equation (13), unless he wanted to obtain the statistical parameters

comparable to equations (12) and (14), which appears to be the case. When we used C_{60} parameters in the regression, we reproduced his results for fitted statistical parameters (he made no cross-validation of his models): $n = 29$, $R_{fit} = 0.948$, $R_{cv} = 0.932$, S_{fit} $(n-I-1) = 0.757$, $S_{cv}(n-I-1) = 0.873$, $F = 118.5$.

The principal component analysis of the structural parameters, supported by the cluster analysis, classified fullerenes into five groups. The periodic table of fullerenes was built on the structural parameters, the principal component analysis and the cluster analysis. The conclusion reached by Torrens is that the preriodicity of fullerene properties is *not* general. Torrens[168–171] also studied the periodic properties of carbon nanotubes as well.

Jiang *et al.*[172] studied the relationship between the permanent of the vertex-adjacency matrix of fullerenes and their structural parameters p, q and r, but also introduced a set of additional structural parameters because, as stated above, p, q and r are zero for the IPR fullerenes. The new structural parameters that count contiguous hexagons are denoted by u, v and w. The u and v enumerate, respectively, the number of edges common to two hexagons and the number of vertices common to three hexagons. The third parameter w enumerates the number of pairs of nonadjacent hexagon edges shared with other two hexagons. Using the stepwise regression, the best correlation between $ln(per\ \boldsymbol{A})$ and parameters p, q, r, u, v and w for the same set of fullerenes, including C_{60} used by Torrens, is obtained as follows:

$$\begin{gathered} ln(per\ \boldsymbol{A}) = 13.28 - 0.20\,p + 0.22\,u \\ n = 29 \quad R = 1.000 \quad S = 0.016 \quad F = 28300 \end{gathered} \tag{16}$$

where *per* $\boldsymbol{A}$ was calculated with their own algorithm.[173] This is a very good correlation, which indicates that only two parameters, p and u, can give almost full information on $ln(per\ \boldsymbol{A})$. We repeated as above the correlation between $ln(per\ \boldsymbol{A})$ for C_{20}–C_{44}, without including C_{60}, and the same set of structural parameters, using the CROMRsel procedure.[164–167] The obtained regression equation is a very good one:

$$\begin{aligned} ln(per\ 2A) =& 13.207(\pm 0.054) - 0.1971(\pm 0.0027)\,p + 0.2165(\pm 0.0022)\,u \\ n =& 28 \quad R_{fit} = 0.9996 \quad R_{cv} = 0.9994 \\ S_{fit}(n-I-1) =& 0.054 \quad S_{cv}(n-I-1) = 0.062 \quad F = 14255 \end{aligned} \tag{17}$$

We also repeated their calculations for C_{20}–C_{44} including C_{60} and statistical parameters, but did not reproduce results of Jiang *et al.*[172]: $n = 29$, $R_{fit} = 0.9997$, $R_{cv} = 0.9997$, S_{fit} $(n-I-1) = 0.055$, $S_{cv}(n-I-1) = 0.062$, $F = 24792$.

2.2.4 Buckminsterfullerene. Vukičević and Randić[174] examined the 12,500 Kekulé structures of buckminsterfullerene (this number was first obtained by Klein *et al.*[175] using the transfer-matrix method) and were able to classify them according to the different innate degree of freedom that they possess. The *innate degree of freedom* or, for short, the *degree of freedom* (*df*) of a Kekulé

structure is the smallest possible number of carbon-carbon double bonds that, when selected, determine the locations of all the remaining carbon-carbon double bonds.[176,177] Vukičević and Randić[174] developed a computational algorithm for finding degrees of freedom and applied it to 12,500 Kekulé structures of buckminsterfullerene. The results they obtained are given in Table 4.

Kekulé structures of buckminsterfullerene belong to six classes. Only one Kekulé structures of buckminsterfullerene possesses the highest degree of freedom ($df = 10$). This is the Kekulé structure in which the carbon-carbon double bonds are exocyclic to pentagons.[178] There are two distinct, that is symmetry non-equivalent, Kekulé structures with $df = 9$ – one appearing 20 times and the other 60 times. The base numbers in the last column of Table 4 indicate how often distinct Kekulé structures occur – their numbers are given as exponents. For example, 23 over 120 (see the first base number and its exponent in the third row of the last column) means that 23 of 47 distinct Kekulé structures with $df = 7$ occur 120 times. The summation of exponents gives the total number of distinct Kekulé structures whilst the multiplication of exponents by base numbers gives the total number of structures with a given degree of freedom. The sum of the numbers in the second column in Table 4 gives 158 distinct Kekulé structures. This number agrees with earlier findings of Babić and Trinajstić,[179] who reported (in 1994) the frequency of occurrence of these 158 distinct Kekulé structures among 12,500 Kekulé structures of buckminsterfullerene, which is identical with the decomposition presented in the last row and the last column of Table 4. These authors considered the combinatorial assembling of fullerenes from identical fragments using symmetry arguments.

In a subsequent paper, Vukičević and Randić in collaboration with Sir Harold W. Kroto[180] catalogued all 158 distinct Kekulé structures producing the *Atlas of Kekulé Structures of Buckminsterfullerene*. Everything they did with

Table 4 *The degrees of freedom (df) of distinct Kekulé structures (KS) of buckminsterfullerene, their frequence of occurrence and their partition. These results are taken from ref. 174*

df	*Distinct KS*	*Total number of KS*	*Partition of KS and their multiplicity*
5	36	3170	$120^{19} + 60^{13} + 40 + 30 + 20^{2}$
6	39	3116	$120^{18} + 60^{13} + 30^{5} + 10^{2} + 6$
7	47	4060	$120^{23} + 60^{19} + 40^{2} + 30^{2} + 20$
8	33	2073	$120^{10} + 60^{9} + 40^{4} + 30^{3} + 20^{2} + 12 + 10^{2} + 6 + 5$
9	2	80	$60 + 20$
10	1	1	1
Total	158	12500	$120^{70} + 60^{55} + 40^{7} + 30^{11} + 20^{6} + 12 + 10^{4} + 6^{2} + 5 + 1$

the Kekulé structures of buckminsterfullerene, they also collected in an author's review.[181] In that review, they discussed the hidden treasures of Kekulé structures (*e.g.*, degrees of freedom, conjugated circuits, geometric *versus* algebraic Kekulé structures), Clar structures of buckminsterfullerene, enumeration of conjugated circuits, selected mathematical properties of Kekulé structures and in the Appendix they presented the computational algorithm in pseudocode.

2.2.5 Nanotubes. Lukovits and Janežić[182] reported the number of Kekulé structures in polyphenanthrenes (the zigzag shaped benzenoid chains), $(1,1)_n$ armchair-type carbon nanotubes and extended $(1,1)_n$ nanotubes. The lower index denotes the number of hexagons layers in a nanotube. A $(n,n)_1$ nanotube that contains a single-hexagon-layer is called the nanoribbon. They enumerated the Kekulé structures in polyphenanthrenes in terms of the number of hexagons h using the Gordon-Davison method,[136] which can be summarized by a simple counting formula:[183]

$$K(h) = K(h-1) + \mathrm{K}(h-2) \tag{18}$$

with $\mathrm{K}(-2) = 0$ and $\mathrm{K}(-1) = 1$(by definition).

Lukovits and Janežič[182] generated the number of Kekulé structures of $(1,1)_n$ armchair-type carbon nanotubes using the following recurrence equation:[184]

$$K(1,1)_n = 3\ K(1,1)_{n-1} - K(1,1)_{n-2} \tag{19}$$

with $K(1,1)_{-1} = 1$ and $K(1,1)_0 = 2$, whilst $n =$ the naphthalene unit. They also generated the number of Kekulé structures of extended $(1,1)_n$ nanotubes by means of:

$$K^*(1,1)_n = K(1,1)_n - K^*(1,1)_{n-1} \tag{20}$$

with $K^*(1,1)_{-1} = 1$ and $K^*(1,1)_0 = 3$. The numbers of Kekulé structures in polyphenanthrenes, $(1,1)_n$ armchair-type carbon nanotubes and extended $(1,1)_n$ nanotubes are given in Table 5.

From Table 5, one can see that the Kekulé structures in polyphenanthrenes, $(1,1)_n$ armchair-type carbon nanotubes and in extended $(1,1)_n$ nanotubes are related by the following equalities:

$$K(2h = n) = K^*(1,1)_{n-1} \tag{21}$$

$$K(2h + 1 = n + 1) = K(1,1)_n \tag{22}$$

The K-numbers are used to generate the conjugated circuits (see later text) that were used to calculate the resonance energies of nanotubes.

Equation (18) is a *Fibonacci-type* recurrence relationship[185,186] and the K-numbers for polyphenanthrenes are the *Fibonacci numbers*.[142,143,187] The Fibonacci numbers can also be found in the *On-Line Encyclopedia of Integer Sequences* – see sequence A000045: 0, 1, 1, 2, 3, 5, 8, 13, 21, 34, 55, 89, 144, 233, 377, 610, … The Fibonacci numbers were named after the Italian

Table 5 *The number of Kekulé structures in polyphenanthrenes K(h) in terms of the number of hexagons h, the number of Kekulé structures in $(1,1)_n$ nanotubes $K(1,1)_n$ and in extended $(1,1)_n$ nanotubes $K^*(1,1)_n$ in terms of napthalene units n (n = 2h). These results are taken from ref. 182*

h(n)	*K(h)*	$K(1,1)_n$	$K^*(1,1)_n$
−2 (−1)	0	1	5
−1	1		
0 (0)	1	2	3
1	2		
2 (1)	3	5	8
3	5		
4 (2)	8	13	21
5	13		
6 (3)	21	34	55
7	34		
8 (4)	55	49	144
9	89		
10 (5)	144	233	377
11	233		
12 (6)	377	324	987
13	610		
14 (7)	987	1597	2584
15	1597		
16 (8)	2584	4181	6785
17	4181		
18 (9)	6785	10946	17711
19	10946		
20 (10)	17711	28657	46368
21	28657		
22 (11)	46368	75025	121393
23	75025		
24 (12)	121393	196418	317811

mathematician Fibonacci (c.1175–c.1250), also known as Leonardo da (of) Pisa or Leonardo Pisano. The use of the subriquet Fibonacci, a contraction of filius Bonacci, son of Bonaccio, for Leonardo Pisano was introduced in 1838 by the mathematical historian Guillaume Libri. There is no evidence that Leonardo referred to himself as Fibonacci or was ever called so by his contemporaries. He actually called himself Leonardo Pisano Bigollo. No one has been able to trace the origin of Bigollo in his name, but it has been speculated that he called himself Bigollo (ignorant peasant) to differentiate himself, who never attended university, from the pretentious ignorant academics of those days. Additionally, his father's name was not Bonaccio: His name was Guglielmo. The problem that gave rise to the Fibonacci series was specified by Leonardo Pisano in his book *Liber Abaci* (*The Book of Abacus*, published in 1202), there serving as a model for breeding rabbits. The Fibonacci rabbit population model is perhaps the first study in mathematical biology, many centuries before the emergence of mathematical biology as a part of biological science.

2.2.6 Enumeration of Kekulé and Longer Range Resonance Valence Bond Structures. Cai *et al.*[188] proposed a novel procedure for counting Kekulé structures and longer range resonance valence bond (VB) structures (excited VB structures) that find use in the VB theory. Kekulé structures and their numbers are denoted by K, whilst two kinds of longer range resonance VB structures and their numbers are denoted by S_3 (singly-excited VB structures) and $D_{3,3}$ (doubly-excited VB structures), where the suffixes indicate the number of bonds between two through the ring(s) connected sites. This notation is used by Flocke and Schmalz[189] and they also found, in their VB calculations on the singlet ground states of fullerenes from C_{20} to C_{60}, that the most important excited structures in this case are S_3 and $D_{3,3}$. As examples, we give one Kekulé structure and one S_3 structure of benzene and one $D_{3,3}$ structure of naphthalene in Figure 15.

The procedure for counting S_3 and $D_{3,3}$ is based on the *extended vertex-adjacency matrix* and the *adjacency bonding array*. The extended vertex-adjacency matrix of a Kekulé structure contains elements 1 or 2 depending on the single or double bond between carbon atoms in the Kekulé structure and it is called *extended* because of the added column and row in which elements are set to 1 or 0 depending whether the carbon atom in the Kekulé structure is connected to the hydrogen bond or not. For example, the extended vertex-adjacency matrix for the Kekulé structure of benzene (see Figure 15) is:

$$
\begin{array}{c} j/i \\ 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \end{array}
\begin{array}{c}
\begin{array}{ccccccc} 1 & 2 & 3 & 4 & 5 & 6 & 7 \end{array} \\
\left[\begin{array}{ccccccc}
0 & 1 & 0 & 0 & 0 & 2 & 1 \\
1 & 0 & 2 & 0 & 0 & 0 & 1 \\
0 & 2 & 0 & 1 & 0 & 0 & 1 \\
0 & 0 & 1 & 0 & 2 & 0 & 1 \\
0 & 0 & 0 & 2 & 0 & 1 & 1 \\
2 & 0 & 0 & 0 & 1 & 0 & 1 \\
1 & 1 & 1 & 1 & 1 & 1 & 0
\end{array}\right]
\end{array}
$$

Since this matrix is a sparse matrix, it is not economical to be explicitly used in computer programming. In order to save computer memory, the authors used the technique of the *bond list*, which encodes the position and the value of the non-zero elements in the upper-triangle (or lower-triangle) of the matrix. Thus, each member in the bond list is coded by $(i, j, [\boldsymbol{A}]_{ij})$, with i and j referring

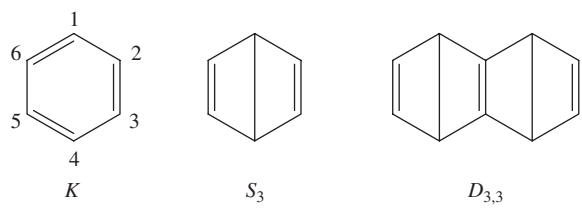


Figure 15 *Labeled Kekulé structure K, S_3 structure of benzene, and $D_{3,3}$ structure of naphthalene*

to the position and $[\boldsymbol{A}]_{ij}$ to the value of the non-zero matrix element. The bond list for the Kekulé structure of benzene, whose extended vertex-adjacency matrix is given above, is (1,2,1), (1,6,2), (1,7,1), (2,3,2), (2,7,1), (3,4,1), (3,7,1), (4,5,2), (4,7,1), (5,6,1), (5,7,1), (6,7,1).

The next step was the introduction of the adjacency bonding array. The adjacency bonding array is based on the concept of quadrivalence of carbon. The skeleton (hydrogen atoms included) of a conjugated molecule provides 3 valences and a Kekulé structure or a higher VB structure contributes the fourth valence. Then, a 2-dimensional array $a[N][3]$ (in the C-language) is used to store the atom connectivity of the molecular skeleton, which the authors call the skeleton adjacency bonding array: $a[i][k]$, $k = 0,1,2$ registers adjacent atoms (0 for a hydrogen atom) of the i-th carbon atom C_i. An additional array $K[N]$, which is referred to as a Kekulé or a higher VB adjacency bonding array, is required for notation of each Kekulé or higher VB structure. $K[i]$ records the atom paired with C_i in the Kekulé structure or higher VB structures. The Kekulé structure of benzene from Figure 15 is denoted by:

$$a[6][3] = \begin{bmatrix} 0 & 2 & 6 \\ 0 & 1 & 3 \\ 0 & 2 & 4 \\ 0 & 3 & 5 \\ 0 & 4 & 6 \\ 0 & 5 & 1 \end{bmatrix} \quad \text{combined with } K[6] = \begin{bmatrix} 6 \\ 3 \\ 2 \\ 5 \\ 4 \\ 1 \end{bmatrix} \tag{23}$$

The arrays $a[N][3]$ and $K[N]$ are also sometimes called connection matrices and are defined as

$$C(i,c) = \begin{cases} i_c \equiv c^{\text{th}} \text{ site to which site } i \text{ is attached, } c \le d, \ c = 1,2,3 \\ 0 \quad \text{when } c < d_i \le 3 \end{cases} \tag{24}$$

$$K(i) \equiv \text{j for } \{i,j\} \in \text{ Kekulé structure under consideration} \tag{25}$$

Since the skeleton adjacency array is the same for all the Kekulé and higher resonance VB structures in one molecule, it is only needed to save a one-dimensional array $K[N]$ for each structure.

Based on the adjacency bonding arrays, Cai *et al.*[188] developed very efficient algorithms for the systematic search for K, S_3 and $D_{3,3}$ structures. These authors listed in their paper K, $K + S_3$ and $K + S_3 + D_{3,3}$ numbers for 72 selected conjugated molecules.

In Table 6, we present the K, $K + S_3$ and $K + S_3 + D_{3,3}$ numbers of several conjugated molecules taken from Table 3 from the paper by Cai *et al.*[188]

2.3 Walks. – The definitions of walks and random walks are given in a number of mathematical texts, *e.g.*[9,11,103,190,191] Here we briefly repeat these definitions. A *walk* in a (molecular) graph G is an alternating sequence of vertices and edges of G, such that each edge e begins and ends with the vertices

Table 6 *K, S_3 and $D_{3,3}$ numbers for several conjugated molecules taken from Cai et al.*[188]

Conjugated molecule	*K*	$K + S_3$	$K + S_3 + D_{3,3}$
Benzene	2	5	
Naphthalene	3	17	39
Pyrene	6	62	301
Triphenylene	9	84	411
Perylene	9	117	722
Chrysene	9	121	747
Anthanthrene	10	162	1209
Benzo[*ghi*]perylene	14	204	1449
Benzo[*e*]anthanthrene	19	333	2827
Coronene	20	332	2690
Dibenzo[*bc*,*ef*]coronene	30	702	7711
Ovalene	50	1210	14181
Quaterrylene	81	2241	30492
Buckminsterfullerene	1250	722300	20633840

immediately preceding and following *e* in the sequence. The *length* of a walk is the number of edges in it. Repetition of vertices and edges is allowed in a walk.

Simple random walks probabilistically grown step by step on a graph are distinguished from walk enumerations and associated equipoise random walks. A *random walk* in a (molecular) graph is naturally designated by a probability measure, of which there are at least two natural intrinsic ones. The first is the probability measure that entails starting walks from each vertex with equal probability and subsequent steps are such that each neighboring vertex is stepped to with equal probability, so that the probability of stepping from vertex *i* to vertex *j* is $1/di$, where *di* is the *degree* of vertex *i*. The walks of the consequently generated distribution are referred to[192] as *simple random* walks. The second is the probability measure that takes each possible walk of a given length as equally probable. These probability measures are generally quite different, though if a graph is regular (*i.e.*, having all vertices of the same degree), then these two probability measures are equivalent. The walks generated by this second probability measure are called *equipoise random* walks. Simple random walks are not much used in chemical graph theory, whereas the equipoise random walks have been used fairly frequently.[193–208] Equipoise or simple random walks have often been called just *random*, probably without recognition of the alternative type – or perhaps due to confusion of the two possibilities. Simple random walks have been used to obtain probabilistic solutions to mathematical, physical, computational or chemical problems, *e.g.*[192,209–215]

2.3.1 Enumeration of Random Walks. Counting simple random walks was reported by Klein *et al.*[216] In parallel to the generation of walks from the powers of the adjacency matrix (see, for example, our Report in ref. 2) that may be viewed as an identification of the distribution for equipoise random walks, Klein *et al.*[216] generated the distribution for simple random walks by powers of a *Markov matrix* $\boldsymbol{M}$ with elements that are probabilities for associated

individual steps:

$$(\boldsymbol{M})_{ij} = \begin{cases} 1/d_j & i \neq j \\ 0 & \text{otherwise} \end{cases} \tag{26}$$

The $(\boldsymbol{M}^l)_{ij}$ is the probability for an l-step random walk beginning at vertex j to end at vertex i.

The *random-walk count* of the length l $(rwc)_l$ at vertex i is given by:

$$(rwc)_l(i) = \sum_{j=1}^{N} (2M^l)_{ij} \tag{27}$$

If we consider only diagonal elements of matrix $\boldsymbol{M}$, $(\boldsymbol{M}^l)_{ii}$, the self-returning l-step random walk $(srrw)_l$ at vertex i is:

$$(srrw)_l\,(i) = (\boldsymbol{M}^l)_{ii} \tag{28}$$

which, of course, is the probability for a simple random walk starting at vertex i to return to i after l steps. These vertex characteristics were earlier discussed by Klein[217] in the context of the general *sum rules* for *resistance distances*,[218] though $(srrw)_l(i)$ was in his paper denoted $w_l(i)$.

Klein *et al.*[216] have also shown that the $(rwc)_l$ and $(srrw)_l$ can be computed *via* eingevalues of matrix $\boldsymbol{M}$. However, matrix $\boldsymbol{M}$ is nonsymmetric unless the graph is regular. But in the general case the eigenvalues of $\boldsymbol{M}$ are related to those of a symmetric matrix, since $\boldsymbol{M}$ can be given as:

$$\boldsymbol{M} = \boldsymbol{A}\ \boldsymbol{\Delta}^{-1} \tag{29}$$

where $\boldsymbol{A}$ is the vertex-adjacency matrix, Δ is the diagonal matrix with elements $(\boldsymbol{\Delta})_{ii} = d_i$ and $\boldsymbol{\Delta}^{-1}$ is its inverse. Matrix $\boldsymbol{M}$ can be related to an auxiliary matrix $\boldsymbol{H}$:

$$\boldsymbol{H} = \boldsymbol{\Delta}^{-1/2}\ \boldsymbol{M}\ \boldsymbol{\Delta}^{1/2} \tag{30}$$

Matrices $\boldsymbol{H}$ and $\boldsymbol{M}$ are related by a similarity transformation, so that $\boldsymbol{H}$ has the same eigenvalues as $\boldsymbol{M}$ and eigenvectors c'_r, which are simply related to those of c_r. Hence:

$$c'_{\mathrm{r}} = \boldsymbol{\Delta}^{-1/2}\ c_r \tag{31}$$

$$c_{\mathrm{r}} = \boldsymbol{\Delta}^{1/2}\ c'_r \tag{32}$$

If $\boldsymbol{A}\ \boldsymbol{\Delta}^{-1}$ is substituted for $\boldsymbol{M}$ in equation (30):

$$\boldsymbol{H} = \boldsymbol{\Delta}^{-1/2}\ \boldsymbol{A}\ \boldsymbol{\Delta}^{-1/2} \tag{33}$$

one sees that $\boldsymbol{H}$ is symmetric, whence one can use standard symmetric-matrix diagonalization routines to obtain the c_r and associated eigenvalues λ. Then:

$$(rwc)_l(i) = \sum_{r}^{N} (c_{ri} d_i^{-1/2}) \lambda_r^l \left(\sum_{j=1}^{N} c_{rj} d_j^{-1/2} \right) \tag{34}$$

where the c_{ri} are components of c_i. For $(srrw)_I(i)$, a similar expression applies with the j-sum eliminated and j set equal to i. Analogous formulas for equipose walks were reported by Rücker and Rücker[198,202–204,206,208] and have been reviewed by us in our last Report.[2] The $\boldsymbol{H}$ matrix is also related to the *connectivity index* of Randić.[219,220] The connectivity index χ is given as the half-sum of the off-diagonal elements of $\boldsymbol{H}$:

$$\chi = (1/2) \sum_{i \neq j} (2H)_{ij} \tag{35}$$

Klein *et al.*[216] have also shown that the *combinatorial Laplacian matrix L* (often called just the *Laplacian matrix*[221,222]) is related to matrix $\boldsymbol{H}$:

$$\boldsymbol{L} = \boldsymbol{\Delta} - \boldsymbol{A} = \boldsymbol{\Delta}^{-1/2} (\boldsymbol{I} - \boldsymbol{H}) \boldsymbol{\Delta}^{1/2} \tag{36}$$

The eigenvalues λ of $\boldsymbol{L}$ give the *Wiener index W* of acyclic structures:[223,224]

$$W = N \sum_{\lambda=2}^{N} 1/\lambda \tag{37}$$

When the above formula is extended to cycle-containing structures, a variant of the Wiener index[225] is obtained, which is named the *quasi-Wiener index* or *Kirchhoff index* and is usually denoted by W^*.[223,226–229]

The difference matrix $\boldsymbol{I} - \boldsymbol{H}$ is called the *normalized Laplacian matrix* $\boldsymbol{L}_{norm}$ (also sometimes called just the *Laplacian matrix*) of G and there is much theory about it.[230] The matrix $\boldsymbol{L}_{norm}$ is clearly also related to the connectivity index:

$$\chi = (1/2) \sum_{i \neq j} (L)_{norm} \tag{38}$$

2.3.2 Walks on Plerographs and Kenographs. In his paper on the mathematical theory of isomers (published in 1847), Arthur Cayley (1821–1895), a distinguished 19th century English mathematician, considered two types of molecular graphs, which he named *plerograms* and *kenograms*.[231] In modern chemical graph theory, plerograms (P) are molecular graphs in which *all* atoms are represented by vertices whilst kenograms (K) are referred to as *hydrogen-suppressed* or *hydrogen-depleted* molecular graphs.[232] In their book *Mathematical Concepts in Organic Chemistry*, Gutman and Polansky[101] used the terms *complete molecular graphs* and *skeleton graphs* for plerograms and kenograms, respectively. The term *thorn* or *thorny* graps for plerograms is also found in the literature.[233,234]

Vukičević *et al.*[235] introduced the terms *plerographs* and *kenographs* for plerograms and kenograms, respectively, because plerograms and kenograms are *graphs* rather than types of *diagrams*, and these authors also wanted to preserve the roots of Cayley's terms: *plero* (from the Greek word *pleres* = full) and *keno* (from the Greek word *kenos* = empty). Therefore, Vukičević *et al.*[235] substituted *grams* in Cayley's terms by *graphs*. Cayley could not do this because

the name *graph* was not yet adopted in 1847. Introduction of the term *graph* happened later, when one-page paper by Sylvester[236] appeared in *Nature* (in 1877), in which he introduced this term, stimulated as he stated by *chemicographs* in *Lectures notes for chemical students* (London, 1866) by Edward Frankland (1825–1899). Frankland used in his *Notes* the term *graphic-like symbolic formulae*. If *plerographs* and *kenographs* are used to represent hydrocarbons, then one may think of them as CH-graphs and C-graphs, respectively. In Figure 16, we give as an illustration the plerograph and the kenograph representing 2,3-dimethylhexane.

Various molecular descriptors have been computed for plerographs usually in terms of the corresponding descriptors for kenographs.[237–239] Vukičević *et al*.[235] calculated walks for plerographs and kenographs representing alkanes. In the case of alkanes, all vertices in the related kenographs correspond to carbon atoms, while in plerographs the mono-valent vertices correspond to hydrogen atoms while four-valent vertices correspond to carbon atoms.

Vukičević *et al*.[235] obtained the number of walks by the matrix multiplication, since it is well-established that the number of walks of length λ beginning at vertex i and ending at vertex j is given by the element $(\boldsymbol{A}^{\lambda})_{ij}$, the ij-element, in the λ-th power of the vertex-adjacency matrix $\boldsymbol{A}$ (see details in our previous Report[2]). They calculated walks with up to length 7 on plerographs and kenographs for octanes using a *C++* program. The obtained relationship between the number of walks in octane-plerographs $w(P)$ and the number of walks in octane-kenographs $w(K)$ is approximately linear:

$$w(P) = 26678.9 + 2.1\ w(K) \tag{39}$$

with the correlation coefficient $R = 0.995$. Therefore, if the walks are used, for example, in the structure-property-activity modeling[121] of acyclic structures, then it will be sufficient in most cases to use kenographs for representing the molecules under study. The use of plerographs would be justified only in case they provide new insights, though their use will be more time-consuming since they are more complex structures than kenographs as can be seen in Figure 16. It should also be pointed out that plerographs correspond more closely to molecular structures than kenographs.

2.3.3 Walk Counts and Zagreb Indices. Zagreb indices M_1 and M_2 have been introduced more than 30 years ago.[240] They are simply defined in terms of vertex-degrees:

$$M_1 = \sum_{\text{vertices}} d_i\, d_i \tag{40}$$

$$M_2 = \sum_{\text{edges}} d_i\, d_j \tag{41}$$

In recent years these indices have been modified[241] and their mathematical properties investigated.[242–248] Although they have initially been used to study the molecular branching,[249] they soon afterwards found application in the

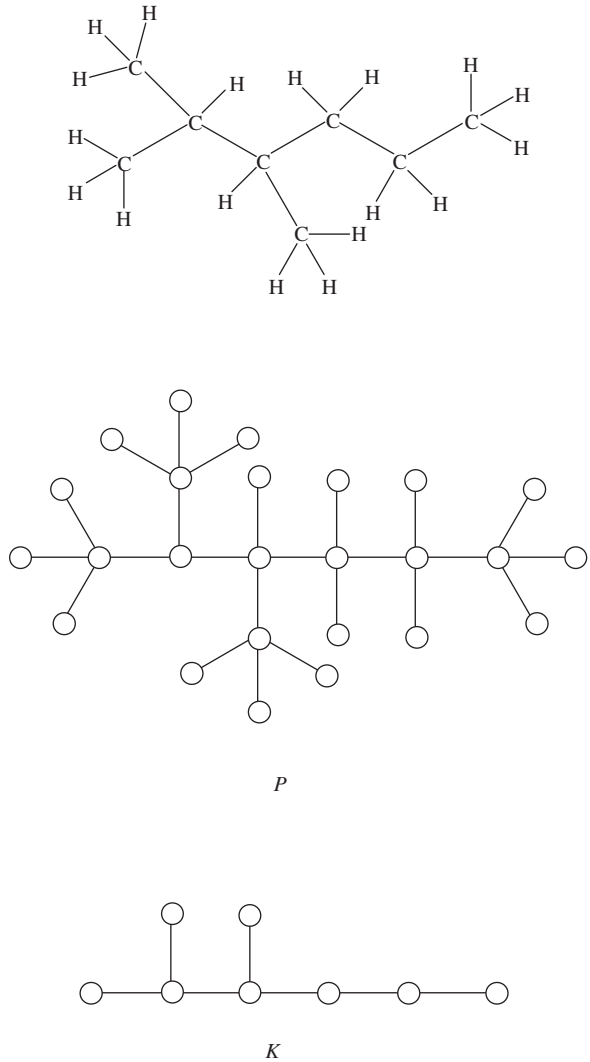


Figure 16 *Two graph-teoretical representation of 2,3-dimethylhexane: plerograph P and kenograph K*

structure-property-activity modeling, *e.g.*[121] A few years ago Gutman *et al.*[250] established the relationship between the two-step walks over all vertices in a molecular graph G, denoted by mwc_2 (*mwc* stands for *molecular walk count*) and the sum of the squares of the vertex-degrees (that is, the first Zagreb index M_1):

$$mwc_2 = \sum_{\text{vertices}} d_i\, d_i = M_1 \tag{42}$$

Now Braun *et al.*[251] established the equivalence of molecular walk count of length 3 mwc_3 and the second Zagreb index M_2 and also confirmed the above result of Gutman *et al.*[250] Using the definition of molecular walk count[252,253] (see also our second Report[2]), Braun *et al.*[251] derived the following formula:

$$mwc_3 = 2\sum_{\text{edges}} d_i\, d_j = 2M_2 \tag{43}$$

Thus, equations (42) and (43) show that both Zagreb indices may be regarded as combinatorial quantities related to simple walks on molecular graphs.

2.4 Structural Complexity. – Several papers reporting studies on the complexity of Platonic solids, Archimedean solids, fullerenes and nanotubes have appeared in the last couple of years. These are attractive structures and are of current chemical interest.

2.4.1 Platonic Solids. Because of their high symmetry-based beauty, Platonic solids attract attention not only of scientists, but also of artists.[254,255] *Platonic solids* are regular convex polyhedra and there are five of them: tetrahedron (T), cube (C), octahedron (O), icosahedron (I) and dodecahedron (D) (see their shapes in Figure 17). Note that a convex polyhedron is *regular* if all of its faces are regular polygons. A polyhedron is *convex* if every dihedral angle is less than 180°. The dihedral angle is the angle formed by two polygons joined along a common edge.

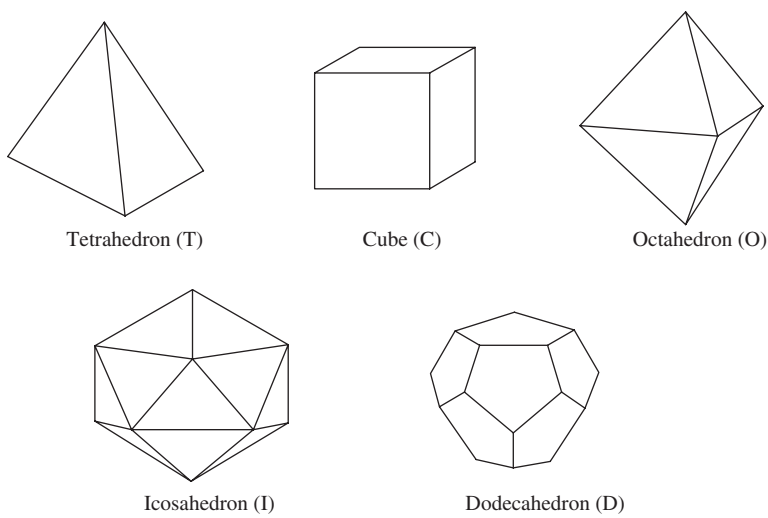


Figure 17 *The shapes of Platonic solids*

Regular convex polyhedra are called Platonic solids because they play an important role in Plato's philosophy. Plato (*ca.* 428–347), however, was not the first to write about regular polyhedra – the mathematician Theatetus (*ca.* 380 B.C.), a friend of Plato's and pupil of Socrates (*ca.* 470–399), discovered the octahedron and the icosahedron and was also the first to write about the five regular polyhedra.[256]

In chemistry, Platonic solids serve as versatile models for molecular shapes.[257–259] Among them, the tetrahedron is especially important in organic chemistry since more than 130 year ago Le Bel[260] and van't Hoff[261] used it independently to model the 3-dimensional structure of carbon compounds. The tetrahedron, the cube and the dodecahedrane are used to model three strained organic molecules: tetrahedrane C_4H_4 (some of its derivatives are known[262]), cubane C_8H_8 (prepared in 1964 by Eaton and Cole[263]) and dodecahedrane $C_{20}H_{20}$ (prepared in 1982 by Paquette *et al.*[264]). The C_{20} fullerene (still unprepared) is the unsaturated analogue of dodecahedrane.[22] Hydrocarbons modeled by the octahedron and icosahedron are not known. However, they model well inorganic compounds.[265] Thus, there are known octahedral molecules, *e.g.*, SF_6, octahedral complexes, *e.g.*, $Co(NH_3)_6{}^{+3}IrCl_6{}^{-3}$, whilst the icosahedron models boron compounds, *e.g.*, $B_{12}H_{12}{}^{2-}$.[266,267]

Bonchev[268] discussed the global, relative and local complexity of Schlegel graphs[269] representing Platonic solids by using several combinatorial measures of complexity: the total subgraph count,[270,271] overall connectivity,[272,273] overall Wiener indices[274] and total walk count.[275] We also discussed these complexity measures in our second Report.[2] Bonchev derived equations for the first several orders of global, relative and local complexity indices as functions of the number of vertices and vertex-degrees and used them to assess the complexity of the Platonic solids. The relative complexity index was defined as the ratio of the complexity index selected and its value for the complete graph having the same number of vertices as the respective Platonic solid. A simple graph is called a *complete graph* if each pair of its vertices is adjacent.[9–11] The global complexity index measures the complexity of the whole structure and the local complexity index is defined *per* vertex or *per* edge.

Bonchev[268] obtained the following *relative* complexity order of the Platonic solids in their Schlegel representation: T > O > I > C > D. Judging by this order the larger Schlegel graphs of a Platonic solid, the lesser chance for it to be close to the related complete graph. This is violated only by icosahedron, presumably because of its high local symmetry. Both kinds of *local* complexity indices (*per* vertex and *per* edge) produced the following order: I > O > D $\geq$ C $\geq$ T. The order obtained by the *global* complexity indices is: I > D > O > C > T, indicating the icosahedron as the most complex Platonic solid. This global ordering concides with orderings produced[276] by using the Bertz index[277] and the Estrada second-order edge-connectivity index.[278] The cyclomatic number also gives the same complexity order.[279] The *cyclomatic number* (or the circuit rank) μ of a polycyclic graph G[10,11] is the minimum number of edges that have to be removed from G in order to convert it into an acyclic graph. It is

given by the expression: $\mu = E - V - 1$, where E is the number of edges and V is the number of vertices of G.

In a related paper, Balaban and Bonchev[280] produced a complexity order of Platonic solids according to their sphericity expressed in terms of the solid angles of their vertices. *Sphericity* determines how closely a polyhedron, viewed as a geometrical object, approaches a sphere. One measure of sphericity is provided by the solid angle (usually given in steradians or in degrees).[281] The solid angle θ of Platonic solids may be computed as follows:

$$\sin(\delta/2) = \cos(\pi/a)/\cos(\alpha/2) \tag{44}$$

$$\theta = a\,\delta - (a-2)\pi \tag{45}$$

where δ is the dihedral angle and a is the number of edges belonging to n-gons meeting at a vertex forming equal planar angles α. For example, θ for the icosahedron ($a = 5$, $\alpha = 60^\circ$, $\delta = 138^\circ\,57'$) is 2.635 steradians or $150^\circ\,57'$. The obtained complexity order based on the solid angle is D > I > C > O > T. This order is in agreement with complexity orders of Platonic solids based on the indices derived from the resistance-distance matrix.[276,279,282]

2.4.2 Archimedean Solids. Archimedean solids[283] (also known as Archimedean bodies[284] and Archimedean polyhedra[255]) were until recently much less studied than the Platonic solids. They came into the focus of research interest after the discovery of buckminsterfullerene, a pure carbon molecule consisting of 60 atoms, and assignment of its structure as that of the truncated icosahedron.[32] As far as we know, buckminsterfullerene is the only real molecule whose structure is modeled by an Archimedean solid. Nevertheless, the Archimedean solids are occasionally studied, usually in conjunction with the Platonic solids and other polyhedra, *e.g.*[285–287]

Archimedean solids are semiregular convex polyhedra.[269] A *semiregular polyhedron* is a polyhedron whose faces are regular polygons, although not all the same, and each of whose vertices is symmetrically equivalent to every other vertex (thus, they are vertex-transitive structures). There are 13 Archimedean solids: truncated tetrahedron (TT), truncated cube (TC), truncated octahedron (TO), truncated icosahedron (TI), truncated dodecahedron (TD), cuboctahedron (CO), truncated cuboctahedron (TCO), snub cuboctahedron (SCO), rhombicuboctahedron (RCO), icosidodecahedron (ID), truncated icosidodecahedron (TID), snub icosidodecahedron (SID) and rhombicosidodecahedron (RID). Their shapes are shown in Figure 18.

The first surviving description of the Archimedean solids is that of the Greek geometer Pappus of Alexandria who lived in the fourth century (around 320).[288,289] Pappus of Alexandria attributed the invention of semiregular convex polyhedra to Archimedes (287–212 B.C.); hence, the name *Archimedean solids*. The painter-mathematicians of the Renaissance were interested in the Golden Cut and in its appearance in the Platonic solids and Archimedean solids.[254] In 1492, the Archimedean solids were rediscovered by the painter and

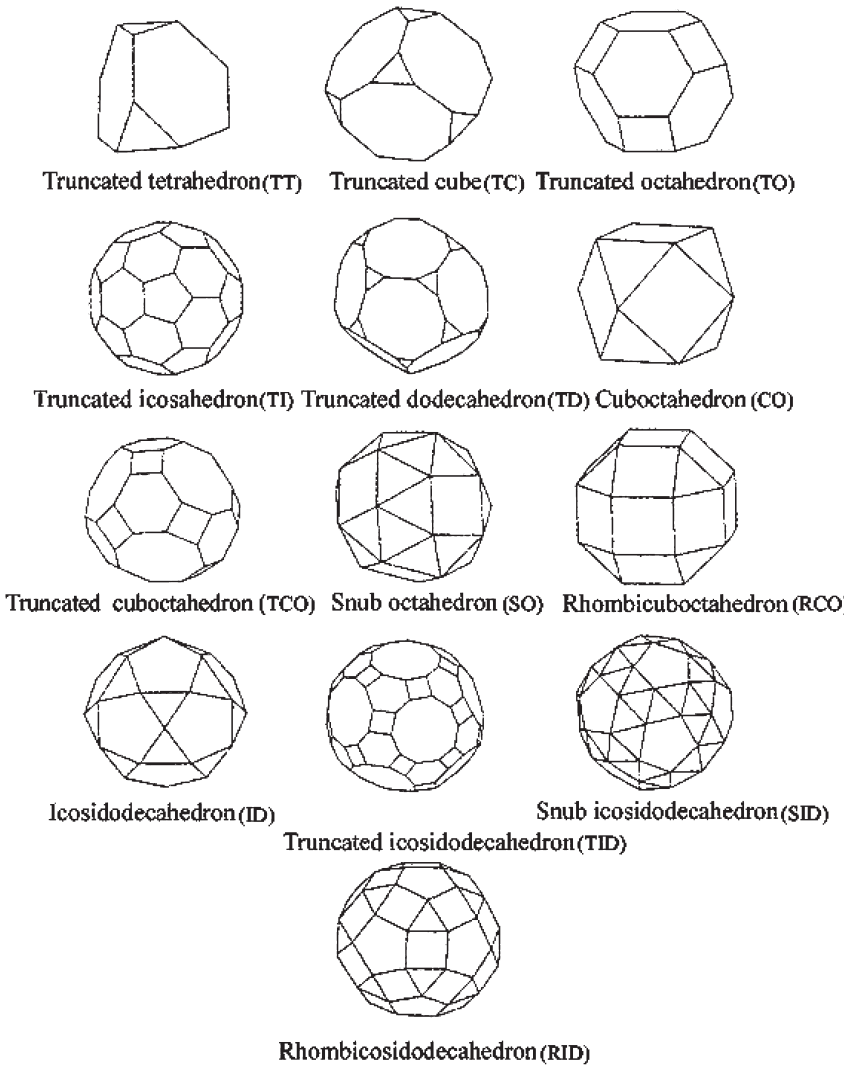


Figure 18 *The shapes of Archimedean solids*

mathematician Piero della Francesca.[290] In his masterpiece *De Divina Proportione* (1509, reproduced in 1956), Luca Pacioli examined, besides the Platonic solids, some of the Archimedean solids, in particular the cubooctahedron. But the Renaissance author who was perhaps most interested in the Archimedean solids was Daniel Barbaro, as can be seen in his book *Prattica de la Perspectiva* (1569). It was, however, Johannes Keppler (1571–1630) who catalogued the 13 Archimedean solids in 1619 and gave them their now generally accepted names.

Rajtmajer *et al.*[291] considered the complexity of the Archimedean solids by means of four complexity indices: the index based on the concept of the augmented vertex-degree, and three indices based on the total number of walks, the total number of paths and the total number of trails. Note, a walk is a *trail* if all the edges are distinct and a *path* if all vertices are distinct.[9,11] The complexity index, based on the concept of the *augmented vertex-degree*, was recently introduced by Randić and Plavšić[292–294] and reviewed by us in our second Report on combinatorial enumeration[2] and by several other groups.[206,295] This concept is based on the notion of partial additivity of vertex-degrees. The augmented degree of a given vertex is obtained by adding to its degree, the degrees of vertices with the weight that depends on their distances from this vertex. The complexity index is then given as the sum of augmented degrees of all vertices in a structure *not* equivalent by symmetry. The greater value of the index, the greater is the complexity of the structure. Since the Archimedean solids are vertex-transitive structures, the complexity index ξ for them is identical with the augmented degree of a single vertex:

$$\xi = (AVD)_i = \sum_{i=1}^{\lambda_{\max}} d_i / 2^{\lambda(\mathrm{ij})} \tag{46}$$

where d_i is the degree of vertex i, $\lambda(ij)$ is the shortest distance in terms of the number of edges between vertices i and j, and λ_{max} is the value of the maximal shortest distance.

All the Schlegel graphs representing Archimedean solids are *regular* graphs, that is, all vertices have the same degree d. The number of walks of length q, $w(q)$, in these graphs is equal to $V d^q$. Note that the first vertex can be chosen in V ways and its each successor in the walk in d ways. Total walk counts, $twc(q)$, were calculated by summing up all walks up to a certain length q, $w(q)$:

$$twc(q) = \sum_{q} w(q) \tag{47}$$

Rajtmajer *et al.*[291] calculated the total numbers of paths and trails using their own computer program. They obtained the following ordering of the Archimedean solids by the four complexity indices:

(i) The augmented vertex-degree
TT < TC < TO < TD < TCO < TID < TI < CO < RCO < ID < RID < SCO < SID

(ii) The total number of walks with up to the length of 8
TT < TC = TO < TCO < TI = TD < CO < TID < RCO < ID < RID < SCO < SID

(iii) The total number of paths with up to the length of 8
TT < TC < TO < TD < TCO < CO < TI < TID < RCO < ID < RID < SCO < SID

(iv) The total number of trails with up to the length of 8
TT < TC < TO < TD< TCO < TI < TID < CO < RCO < ID < RID < SCO < SID

All four indices predict the truncated tetrahedron (TT), the truncated cube (TC) and the truncated octahedron (TO) as the least complex structures, and the rhombicuboctahedron (RCO), the icosidodecahedron (ID), the rhombicosidodecahedron (RID), the snub cuboctahedron (SCO) and the snub icosidodecahedron (SID) as the most complex structures among the Archimedean solids. The ordering of TI, TD, CO, TCO and TID differs from index to index. The above can be visualized by the Hasse diagram based on the partial order of the four complexity indices (see Figure 19). It should be noted that some authors consider the complexity as a partially-ordered quantity.[296–300] The Hasse diagram reflecting the partial order of indices appears to be a very useful device for appraising the structural complexity of molecules and graphs.

The diagram in Figure 19 is such that in going downward along a path from structure X to structure Y, all four indices have a smaller value for X than for Y. Furthermore, the two structures X and Y are directly linked by an edge downward from X to Y if and only if no third structure is placed by this partial ordering between X and Y.

The complexity order of Archimedean solids in terms of the solid angle of their vertices is[280] TT < CO < TC < TO < RCO < ID < TCO < TD < TCO < RID < TID. The two chiral Archimedean solids (snub octahedron, snub icosidodecahedron) were not considered. This order disagree with all four complexity given above, except in the case of the truncated tetrahedron which is predicted to be the least complex of all Archimedean solids. This discrepancy is perhaps due to different bases of the compared complexity orders; the above orders being the result of 2D representation and the Balaban-Bonchev order of 3D structure of Archimedean solids.

2.4.3 Fullerenes and Nanotubes. Randić *et al.*[301] considered the problem of evaluating the complexities of 19 lower fullerenes having from 20 to 50 carbon atoms and of buckminsterfullerene C_{60}. They selected this set of fullerenes because they had been already studied by Laidboeur *et al.*[302] who depicted all these fullerenes by means of their Schlegel graphs and denoted their symmetries. Schlegel graphs, named after the 19th century German mathematician Victor Schlegel,[303] are convenient graph-theoretical representations of fullerenes – they are planar 3-connected graphs.[269,304] In Figure 20, we give, as an example, the Schlegel graph representing buckminsterfullerene.

Randić *et al.*[301] studied the complexity of lower fullerenes by using the distance degree sequences *DDS*s for all symmetry non-equivalent vertices, the multiplicity μ of the *DDS*s, which are defined as the cardinality of each equivalence class, the augmented degrees for all vertices of different equivalence class ξ (see text above),[292–294] which represent a measure of the local

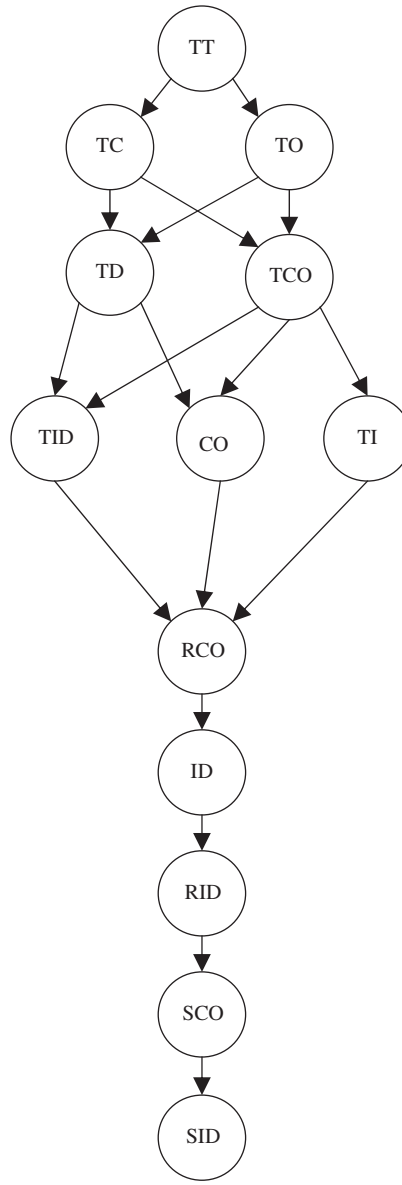
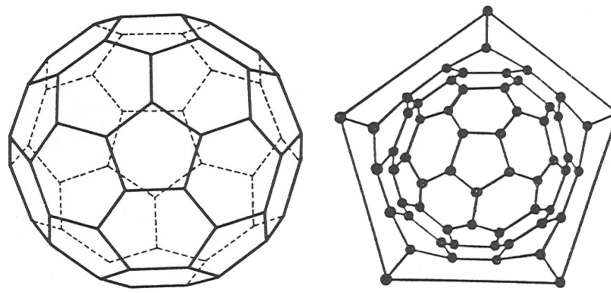


Figure 19 *The partial order by means of the Hasse diagram for Archimedean solids based on the four complexity indices*

complexity, the average value of the augmented vertex-degrees ξ_{av} and the sum of all augmented vertex-degrees as the overall complexity index $V\xi_{av}$. For illustration, we give below the values of these complexity measures for buckminsterfullerene (since we gave in Figure 20 the Schlegel graph of C_{60}, these



C_{60} Schlegel graph of C_{60}

Figure 20 *The truncated icosahedron structural model of buckminsterfullerene C_{60} and the corresponding Schlegel graph*

measures can be checked easily):

DDS :	3, 9, 18, 24, 30, 30, 24, 9, 3
μ :	60
$\xi = \xi$	18.5098
$V\xi_{av}$	1110.5880

Both ξ_{av} and $V\xi_{av}$ increase with the size of the fullerene. However, the authors considered two isomers of C_{38} (D_{3h} and C_{3v}), three isomers of C_{40} (T_d, C_{3v} and D_{5d}) and two isomers of C_{44} (T and D_{3h}) Since the augmented vertex-degree depends on the symmetry characteristics of a structure, it is expected that the indices ξ_{av} and $V\xi_{av}$ would have higher values for a less symmetric structure. Thus, C_{38} (C_{3v}) and C_{44} (D_{3h}) are predicted to be more complex than C_{38} (D_{3h}) and C_{44} (T). However, in the case of three C_{40} isomers, two isomers possessing different symmetries (T_d and C_{3v}) have identical values of ξ_{av} and $V\xi_{av}$. This is probably a coincidence, possibly as a result of the average *DDS* being the same for both fullerenes: 3.00, 9.00, 18.00, 22.50, 25.50, 22.50, 12.00, 5.40.

In the same article, Randić *et al.*[301] also considered the complexity of single-wall carbon nanotubes. These nanotubes can be constructed by rolling a long strip of a planar graphene sheet. Their properties depend on how the ends of the strip become connected. In this paper, the authors used the concept introduced by Klein *et al.*[305]: The geometry of a nanotube if defined in terms of two parameters – the *twist* t_+ and the *countertwist* t_- under the condition that t_+ must be an integer higher than, or equal to, 3, whilst t_- can have any integer value between 0 and t_+, that is, $t_- \leq t_+$. The numbers t_- and t_+ indicate how many linearly condensed hexagons in two direction diverging from one hexagon by 120° in the nanotube are involved in the repeating pattern on the nanotube until they overlap when rolling the strip. When $t_- = 0$, the nanotube is achiral and is called a zigzag nanotube whose diameter in Ångströms is approximately $0.78t_+$. When $t_+ = t_-$, the nanotube is also achiral and is called

an armchair nanotube with the diameter $0.78t_+\sqrt{3}$. When $t_+ \neq t_-$, the nanotube is chiral with the diameter $0.78(t_-^2 + t_+^2 + t_-t_+)^{1/2}$. The twist t_+ and the countertwist t_- parameters determine the helicity of nanotubes by $\sin(1 - t_-/t_+)\pi$.

The complexity of a nanotube depends on its length, diameter and helicity. The values of the ratio t_-/t_+ range from zero for the zigzag nanotubes through 0.5 for the skew nanotubes to 1 for the armchair nanotubes. Therefore, the helicity of nanotubes ranges from 0 for the zigzag and armchair nanotubes to 1 for the skew nanotubes. Hence, the skew nanotubes are more complex than either zigzag or armchair nanotubes. The key parameters for studying complexity of nanotubes are the twist t_+ and the countertwist t_- since they determine the diameter and helicity of nanotubes.

2.5 Other Enumerations. – In this section, we present combinatorial enumerations that do not fit in any of the above sections, though some are related to discussions above or in our previous Reports.[1,2]

2.5.1 The Number of Spanning Trees. Kirby *et al*.[306] put forward a theorem for counting spanning trees in general molecular graphs (that is, non-planar graphs with loops and multiple edges) with particular application to toroidal fullerenes. A spanning tree is a connected subgraph of graph G containing all vertices of G.[11] The problem of counting spanning trees goes back to the work by Kirchhoff[307] and subsequent mathematical formulations.[190] Spanning trees are used to study the complexity of reaction mechanisms,[308] of molecular graphs,[206,309,310] in calculating the magnetic properties of conjugated polycyclic molecules by means of the ring-current model within the framework of the π-electron molecular orbital theory.[311–313]

An important contribution to the enumeration of spanning trees of molecular *planar* graphs was the theorem by Gutman *et al*:[314]

$$t(G) = det\ \mathbf{D} \tag{48}$$

where $t(G)$ is the number of spanning trees and $\boldsymbol{D}$ is the difference matrix defined as follows:

$$\boldsymbol{D} = \boldsymbol{\Delta}^* - \boldsymbol{A}^* \tag{49}$$

where $\boldsymbol{A}^*$ is the vertex-adjacency matrix of an inner dual G^* of G and $\boldsymbol{\Delta}^*$ is a diagonal matrix of G^* with elements $\lambda^*(k)$, where $\lambda^*(k)$ is the size of cycle k (called the patch cycle by Kirby *et al*.[306]) in G. Matrix $\boldsymbol{D}$ may also be regarded as a *Laplacian matrix*[315–317] of the vertex-weighted inner dual G^*, the weights of vertices in G^* being equal to the sizes of cycles in the parent graph G.

An inner dual G^* of a planar polycyclic graph G is obtained by placing a vertex in each cycle of G and pairs of vertices in G* are connected if the corresponding rings in G have common edges. Examples of a graph and its inner dual are given in Figure 21.

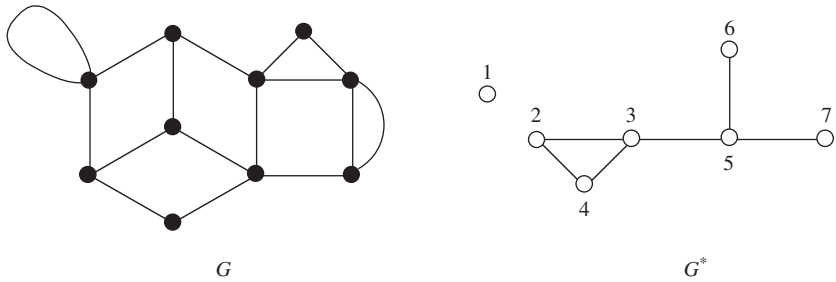


Figure 21 *Graph G and its labelled disconnected inner dual G**

The difference matrix $\boldsymbol{D}$ belonging to the inner dual G^* from Figure 21 and the corresponding number of spanning trees are given below.

$$\begin{matrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 4 & -1 & -1 & 0 & 0 & 0 \\ 0 & -1 & 4 & -1 & -1 & 0 & 0 \\ 0 & -1 & -1 & 4 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 4 & -1 & -1 \\ 0 & 0 & 0 & 0 & -1 & 3 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 2 \end{matrix}$$

$$t(G) = 860$$

The theorem stated as equation (48) is a special case of the theorem derived by Kirby *et al.*:[306]

$$t(G) = \det \boldsymbol{V}/(\det \boldsymbol{U})^2 \tag{50}$$

where the $\boldsymbol{V}$-matrix is defined as:

$$\boldsymbol{V} = \boldsymbol{Z}\boldsymbol{Z}^{\mathrm{T}} \tag{51}$$

and the $\boldsymbol{U}$-matrix is a non-singular matrix to be chosen in such a way that its determinant is 1 or some small integer. The $\boldsymbol{Z}$-matrix is the cycle-edge incidence matrix.[317,318]

The cycle-edge incidence matrix $\boldsymbol{Z}$ is a $c \times e$ matrix (c and e being the numbers of cycles and edges, respectively), which is determined by the incidences of cycles and edges in G:

$$[\boldsymbol{Z}]_{\mathrm{ij}} = \begin{cases} 1 & \text{if a cycle } i \text{ is incident with an edge } j \\ 0 & \text{otherwise} \end{cases} \tag{52}$$

Kirby *et al.*[306] considered three kinds of cycles: independent cycles, fundamental cycles and patch cycles and showed that they all produce the same

number of spanning trees. However, *det* $\boldsymbol{U}$ is equal to 1 only for the fundamental set of cycles of any graph and for patch cycles of any planargraph.

If equations (49) and (51) are applied to planar graphs and use is made of patch cycles, then:

$$\boldsymbol{V} = \boldsymbol{Z}\boldsymbol{Z}^{\mathrm{T}} = \boldsymbol{\Delta}^{*} - \boldsymbol{A}^{*} = \boldsymbol{D} \tag{53}$$

and consequently:

$$t(G) = \det \boldsymbol{V}/(\det \boldsymbol{U})^2 = det\ \boldsymbol{D} \tag{54}$$

2.5.2 The Number of Conjugated Circuits in Graphite. Lukovits[149] calculated the number of conjugated circuits in (*m*,*n*) parallelogram-shaped graphite sheets and used them to obtain the resonance energies per electron (REPE) of graphite sheets. He computed the benzene-like, the naphthalene-like and the anthracene-like conjugated circuits $[6]_{m,n}$, $[10]_{m,n}$ and $[14]_{m,n}$ for several values of *m* and *n* ($m,n \leq 6$) using the following equations:

(i) The benzene-like conjugated circuits

$$[6]_{m,n} = 2(m + n - 1)!/(m - 1)!\ (n - 1)! \tag{55}$$

or

$$[6]_{m,n} = [6]_{m,n-1} + [6]_{m-1,n} + [6]_{m-1,n}/(\mathrm{m}-1) \tag{56}$$

(ii) The naphthalene-like conjugated circuits

$$[10]_{m,n} = [6]_{m-1,n} + [6]_{m,n-1} \tag{57}$$

From equations (56) and (57) it follows that if *m* and *n* are sufficiently large, then $[6]_{m,n} = [10]_{m,n}$ in (*m*,*n*) parallelogram-shaped graphite sheets. By setting $m = n$, from equations (55), (56) and (57), Lukovits[149] obtained:

$$[10]_{n,n} = 2\{(2n - 2)!\ (2\mathrm{n} - 2)/[(n - 1)!]^2\} \tag{58}$$

(ii) The anthracene-like conjugated circuits

$$[14]_{m,n} = [6]_{m-2,n} + [6]_{m,n-2} \tag{59}$$

In any conjugated hydrocarbon *G* made up of hexagons subunits, the REPE is given by:[200,319,320]

$$\mathrm{REPE}_G = \{[6]_G\ R_6 + [10]_G\ R_{10} + [14]_G\ R_{14} + \ \ldots\}/V\ K_G \tag{60}$$

where *V* is the number of carbon atoms in *G*. For (*n*,*n*) parallelogram-shaped graphite sheets, *V* is equal to:

$$V = 2(n^2 + 2n) \tag{61}$$

Randić,[114,115] who introduced the concept of conjugated circuits, used R_{4n+2} to denote the energy contributions of the $(4n + 2)$-membered conjugated circuits to the resonance energy.

Lukovits[149] calculated the resonance energy per electron (REPE) of graphite sheets using the expression that he obtained from equations (11), (55), (58), (60) and (61):

$$[\mathrm{REPE}]_{n,n} = [n\ R_6/(2n^2 + 4n)] + \{[n^2 - n)R_{10}/[(2n - 1)\ (n^2 - 2n)]\} \qquad (62)$$

Lukovits has taken the values of the parameters $R_6 = 0.8220$ eV and $R_{10} = 0.3355$ eV from Randić *et al.*[321] The value of parameter R_{14} is rather small (0.0580 eV) and its inclusion in the REPE expression depends on the number of the anthracene-like conjugated circuits. Since Lukovits established that the number of $[14]_{m,n}$ circuits is much smaller than the number of $[10]_{m,n}$ circuits, he did not include them in the REPE calculation of graphite sheets.

2.5.3 The Number of Conjugated Circuits in Nanotubes. Lukovits and Janežič[182] calculated the number of conjugated circuits in armchair $(1,1)_n$ carbon nanotubes and $(n,n)_1$ nanoribbons and used them to obtain the resonance energies per electron (REPE) of these structures. For any $(1,1)_n$, nanotube, they derived the following formulae for 6- and 10-membered circuits in terms of the corresponding Kekulé structures:

$$\begin{aligned}[6](1,1)_n =& 4(K^*(1,1)_{n-2}K(1,1)_{-1} + K^*(1,1)_{n-3}K(1,1)_0 \\ &+ K^*(1,1)_{n-4}K(1,1)_1 + \ldots + K^*(1,1)_{-1}K(1,1)_{n-2} +\end{aligned} \qquad (63)$$

$$[10](1,1)_n = [6](1,1)_{n-1} \qquad (64)$$

Using data from Table 5, one can easily obtain the number of two smallest conjugated circuits of $(1,1)_n$ nanotubes.

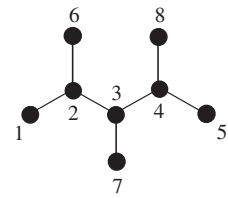
For nanoribbons, the counting formulas for 6- and 10-membered circuits are given in terms of the K-numbers of polyphenanthrenes (note that $K(2h) = K(n)_{\mathrm{ph}}$)

$$[6](n,n)_1 = 4n\ K(2n-3)_{\mathrm{ph}} \qquad (65)$$

$$[10](n,n)_1 = 4n\ K(2n-4)_{\mathrm{ph}} \qquad (66)$$

Lukovits and Janežič[182] calculated the resonance energies of armchair $(1,1)_n$ carbon nanotubes and $(n,n)_1$ nanoribbons for a given n using equation (64) and found for n very large REPE of $(1,1)_n$ nanotubes is 0.160 eV and for nanoribbons 0.142 eV. Since these values are a bit larger than REPE for buckminsterfullerene (0.12 eV),[303] Lukovits and Janežič[182] concluded that carbon nanotubes belong to the most aromatic structures.

2.5.4 Combinatorial Matrices. There are a number of combinatorial matrices available in the literature, usually used to generate graph invariants.[120,121,317] We have already mentioned some of these matrices, such as the random-walk



(i) Edge-graphical matrix ${}^{e}\boldsymbol{G}$

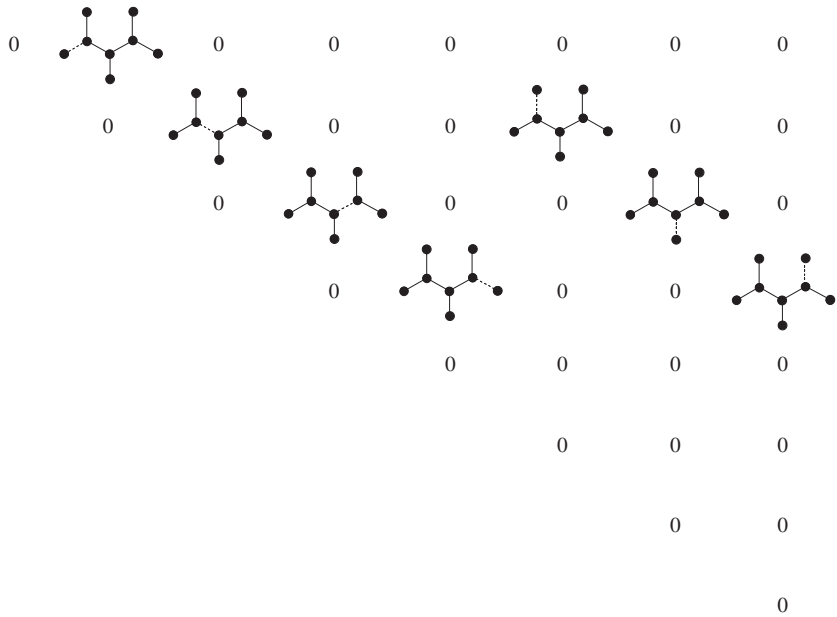


Figure 22 *Four types of graphical matrices for a tree representing the carbon skeleton of 2,3,4-trimethylpentane*

Markov matrix (section 2.3.1), the Laplacian or difference matrix (sections 2.3.1 and 2.5.1) and the incidence matrix (section 2.5.1).

Randić *et al.*[322] proposed a novel type of combinatorial matrices, which they called *graphical matrices*. They used these matrices to generate the distance-based molecular descriptors. Graphical matrices are combinatorial matrices whose elements are subgraphs of the graph rather than numbers – hence their name. Thus far, very little work has been reported on these matrices.[323] However, many combinatorial matrices,[120] such as the Wiener matrices[324–326] and the Hosoya matrices,[327] may be regarded as the numerical realizations of the corresponding graphical matrices.[317]

The advantage of a graphical matrix lies in the fact that it allows for a great many possibilities of numerical realizations. In order to obtain a numerical form of a graphical matrix, one needs to select a graph invariant

(ii) Sparse vertex-graphical matrix $^{sij}\boldsymbol{G}$

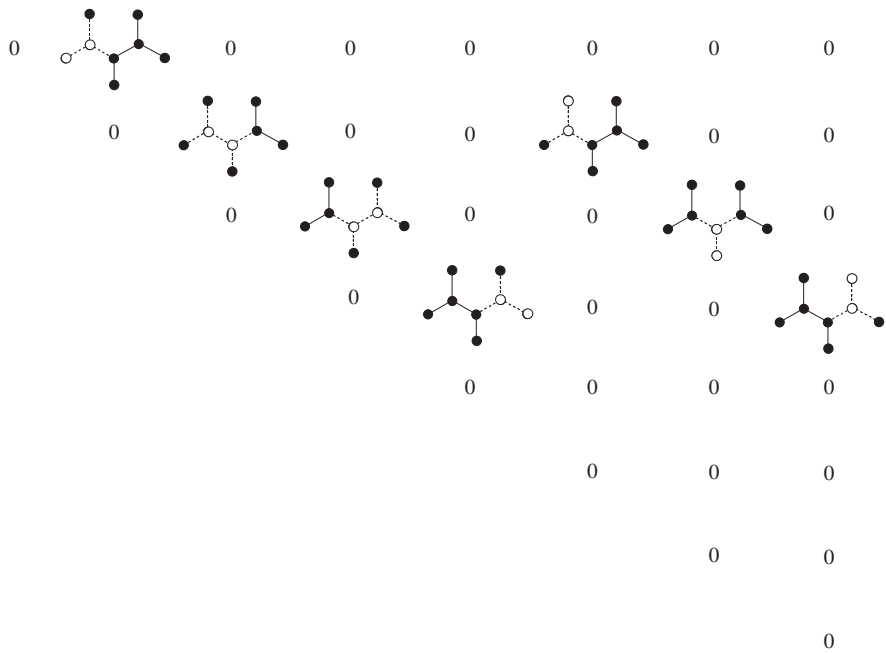


Figure 22 (continued)

and replace all the graphical elements (subgraphs of some form) by the corresponding numerical values of the selected invariant. In this way, the numerical form of the graphical matrix is established and one can select another or the same type of invariant – this time an invariant of the numerical matrix. Graph invariants generated in this way are *double invariants*[323] in view of the fact that two invariants are used in constructing a given molecular descriptor.

Nikolić *et al.*[328] classified graphical matrices $\boldsymbol{G}$ into four types-two being *sparse* matrices: (i) the *edge-graphical* matrices $^{e}\boldsymbol{G}$, (ii) the *vertex-graphical* matrices $^{sij}\boldsymbol{G}$, and two being *dense* matrices: (iii) the *path-graphical* matrices $^{p}\boldsymbol{G}$ and (iv) the *vertex-graphical* matrices $^{dij}\boldsymbol{G}$. The elements of the edge-graphical matrix $^{e}\boldsymbol{G}$ are obtained by consecutive removal of *edges* connecting vertices i and j from graph $\boldsymbol{G}$. The elements of the sparse vertex-graphical matrix $^{sij}\boldsymbol{G}$ are obtained by the consecutive removal of *adjacent* vertices i and j, and the incident edges from $\boldsymbol{G}$. The elements of the path-graphical matrices $^{p}\boldsymbol{G}$ are obtained by consecutive removal of the *paths* joining vertices i and j from G. The elements of the dense vertex-graphical matrices $^{dij}\boldsymbol{G}$ are obtained by

(iii) Path-graphical matrix $^{p}\boldsymbol{G}$

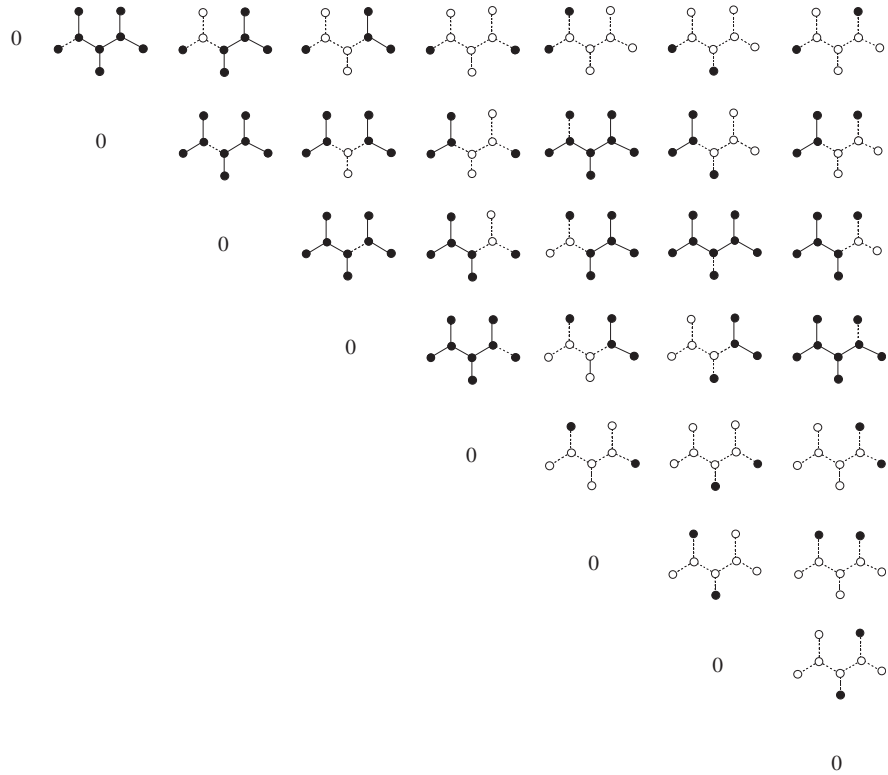


Figure 22 (continued)

removing pairs of vertices *i* and j at increasing distances from *G*. In their paper, Randić *et al.*[322] discussed only the dense vertex-graphical matrix $^{dij}\boldsymbol{G}$. In Figure 22, we give all four types of graphical matrices for 2,3,4-trimethylpentane. Since the graphical matrices are square symmetrical matrices, we give only their upper triangles.

The next step is to replace (sub)graphs with the invariants of choice. For this purpose, Randić *et al.*[322] used the Wiener index[225,329,330] and Nikolić *et al.*[328] used the Wiener index and the Hosoya index.[122] The numbers that replace the subgraphs in the graphical matrices are obtained by *summing up* their Wiener indices or their Hosoya indices. The numerical forms of four graphical matrices presented in Figure 22, obtained using the Wiener number, are given in Table 7. The summation of the matrix-elements in each matrix-triangle gives the following descriptors of 2,3,4-trimethylpentane: the *edge-Wiener-Wiener index* ^{e}WW, the sparse *vertex-Wiener-Wiener index* ^{suv}WW, the *path-Wiener-Wiener number* ^{p}WW and the dense *vertex-Wiener-Wiener index* ^{duv}WW. These numbers are also given in Table 7.

(iv) Dense vertex-graphical matrix $^{dij}\boldsymbol{G}$

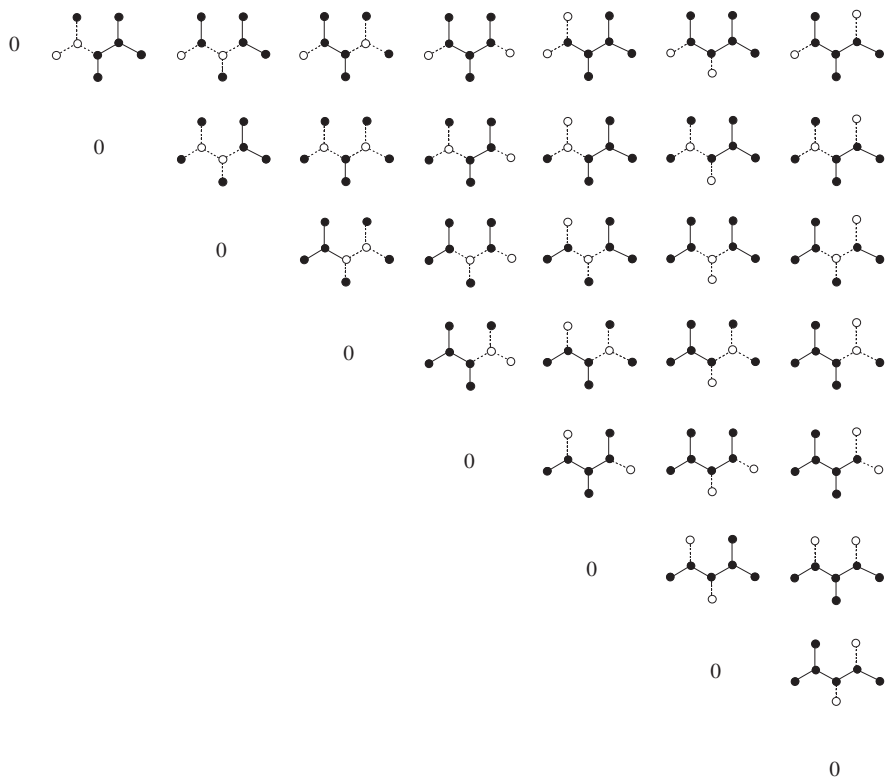


Figure 22 (continued)

It should be noted that if we replace subgraphs in the edge-Wiener matrix by *products* of the number of vertices in each subgraph, the obtained numerical matrix, called the *Wiener matrix* $\boldsymbol{W}$,[324–326] also called the edge-Wiener matrix $^{e}\boldsymbol{W}$,[120,317] gives the standard Wiener index W. Similarly, if we replace each non-zero element in the edge-Wiener matrix with its inverse value, the obtained modified edge-Wiener matrix ^{m}W gives the modified Wiener index $^{m}\boldsymbol{W}$.[331] Finally, if we replace subgraphs in the path-Wiener matrix by *products* of the numbers of vertices in each subgraph, the obtained numerical matrix $^{h}\boldsymbol{W}$ gives the *hyper-Wiener index*.[317,324,325,332] All the three results are valid *only* for acyclic graphs. Examples of the edge-Wiener matrix, the modified edge-Wiener matrix and the hyper-Wiener matrix and the corresponding indices are presented in Table 8.

3 Conclusion

In the last six years we reported on a number of novel results achieved in the combinatorial enumeration in chemistry. In the period of 1999–2001, we

Table 7 *Four Wiener-like matrices (only upper triangles are shown) of 2,3,4-trimethylpentane and their corresponding Wiener-Wiener indices*

(i) Edge-Wiener matrix ${}^{e}\boldsymbol{W}$

0	46	0	0	0	0	0	0
	0	22	0	0	46	0	0
		0	22	0	0	0	48
			0	46	0	0	46
				0	0	0	0
					0	0	0
						0	0
							0

${}^{e}WW = 276$

(ii) Sparse vertex-Wiener matrix ${}^{sij}\boldsymbol{W}$

0	18	0	0	0	0	0	0
	0	4	0	0	18	0	0
		0	4	0	0	8	0
			0	18	0	0	18
				0	0	0	0
					0	0	0
						0	0
							0

${}^{sij}WW = 88$

(iii) Path-Wiener matrix ${}^{p}\boldsymbol{W}$

0	46	18	4	0	0	0	0
	0	22	8	4	46	8	4
		0	22	18	18	48	18
			0	46	4	4	46
				0	0	0	0
					0	0	0
						0	0
							0

${}^{p}WW = 384$

(iv) Dense vertex-Wiener matrix ${}^{dij}\boldsymbol{W}$

0	18	4	10	31	29	32	21
	0	4	1	10	18	9	31
		0	4	4	5	8	5
			0	18	10	9	18
				0	31	32	29
					0	32	31
						0	32
							0

${}^{dij}WW = 496$

Table 8 *The edge-Wiener matrix ${}^{e}\boldsymbol{W}$, the modified edge-Wiener matrix ${}^{m}\boldsymbol{W}$ and the hyper-Wiener matrix ${}^{h}\boldsymbol{W}$ and the corresponding indices W, ${}^{m}W$ and ${}^{h}W$ of 2,3,4-trimethylpentane*

0	7	0	0	0	0	0	0
	0	15	0	0	7	0	0
		0	15	0	0	0	7
			0	7	0	0	7
				0	0	0	0
					0	0	0
						0	0
							0

$W = 65$

0	1/7	0	0	0	0	0	0
	0	1/15	0	0	1/7	0	0
		0	1/15	0	0	1/7	0
			0	1/7	0	0	1/7
				0	0	0	0
					0	0	0
						0	0
							0

${}^{m}W = 0.848$

0	7	5	3	1	1	1	1
	0	15	9	3	7	6	3
		0	15	5	5	7	5
			0	7	3	3	7
				0	1	1	1
					0	1	1
						0	0
							0

${}^{h}W = 122$

considered 96 papers published during these two years that were concerned with combinatorial enumerations. The next two years (2001–2003), there has been even a greater output – we considered 100 papers that have been reporting topics from the area of combinatorial enumerations in chemistry. Finally, in the last two years (2003–2005), there were 89 papers that we included in our report. But for the each period mentioned, we included in our reports a much greater number of references, since we have mentioned older results and related results

from other areas of chemistry that find useful chemical enumerations. We also considered journals that published most of combinatorial results in each period. In all three periods (1999–2001, 2001–2003, 2003–2005), the first medium for publishing combinatorial enumerations in chemistry was the *Journal of Chemical Information and Computer Sciences* (JCICS), published by the American Chemical Society. This journal since the beginning of 2005 has split into two journals – the *Journal of Chemical Information and Modeling* and the *Journal of Chemical Theory and Computation*. It is expected that the first of these two journals will inherit the tradition of JCICS and will continue to publish papers about chemical combinatorial enumerations. The next important journals for chemical combinatorics appear to be the *Journal of Mathematical Chemistry* and *MATCH Communications in Mathematical and Computer Chemistry*. Additionally, two more journals with frequent contribution to chemical enumerations were *Chemical Physics Letters* and *Croatica Chemica Acta*, published by the Croatian Chemical Society. In the period 1999–2001, a number of chemical combinatorial papers appeared in the *Bulletin of Chemical Society of Japan* and in the period just reviewed in this report (2003–2005), in the *Internet Electronic Journal of Molecular Design* (www.biochempress.com). Important contribution over the years appeared in *Nature*, the *Journal of the American Chemical Society*, the *Journal of Organic Chemistry*, I*nternational Journal of Quantum Chemistry* and *Theretical Chemistry Accounts* (formerly *Theoretica Chimica Acta*).

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