Bull. Chem. Soc. Jpn., 76, 2233–2252 (2003)

Accounts

From How to Why. Graph-Theoretical Verification of Quantum-Mechanical Aspects of π-Electron Behaviors in Conjugated Systems

Haruo Hosoya

Ochanomizu University, Bunkyo-ku, Tokyo 112-8610

Received June 20, 2003; E-mail: hosoya@is.ocha.ac.jp

A number of empirically known rules of the π-electronic stability of conjugated hydrocarbon molecules caused by their topological structure were analyzed for the first time systematically with the graph-theoretical molecular orbital theory developed by the author's group. The main tool in this analysis is the topological index (or Z index) proposed by the present author for characterizing the topological nature of the structural formula of a hydrocarbon molecule, coupled with the perturbation theory of the Hückel molecular orbital method proposed by Coulson and Longuet-Higgins. A mathematical foundation was given to the global quantum-mechanical aspects of π-electron behaviors in conjugated systems and also to the diagrammatic recipe of the classical organic electron theory proposed by Robinson and Ingold. Through this analysis the specific "How" obtained by quantum chemical calculations is now explained by mathematically reasonable "Why".

Thanks to the rapid and deep progress in quantum-chemical calculations one can now quite easily obtain detailed quantum-mechanical aspects of static properties and dynamic behaviors of molecules and molecular assemblies.[1] The accuracy attained may vary from case to case depending on the complexity of the system concerned, and in many cases the calculated results are in accordance with the experimentally obtained facts. However, the more sophisticated the adopted theoretical tools become, the more difficult it is to extract any causality from the compiled results of calculation. Detailed results obtained from huge and sophisticated ab initio calculation would become just a record of experimentally observed facts, unless the proper analysis based on the first principles is supplemented.

On the other hand, if π-electronic behavior in conjugated hydrocarbons is involved, one can scan a wide range with the crude Hückel molecular orbital (HMO) theory and can draw some perspective view of the behavior of electrons in organic compounds, especially conjugated polyenes and benzenoid hydrocarbons.[2–4] In this sense, analysis of conjugated π-electronic systems is the most fundamental problem in the development of theoretical chemistry. However, even in HMO method it is usually quite difficult to explain why such results came out.

In 1971 the present author proposed the "topological index Z" for characterizing the topological property of the carbon atom skeletons of saturated hydrocarbon molecules,[5] and showed its potential use in coding and classification of the structure of organic molecules[6] and also suggested its graph-theoretical application.[7] After some success in thermodynamic study in the author's group,[5,8] the Z index[9] was found to have an unexpectedly good correlation with the conventional HMO method.[11] Then, global understanding of the π-electronic structure of conjugated systems was obtained by combining this graph-theoretical idea with the perturbation technique developed by Coulson's group.[12,13] Further, mathematical proof of the Hückel rule was developed to the extended Hückel rule for polycyclic systems,[12] and some mathematical relations among HMO method, resonance theory, and graph theory were established.[13] This theory was further extended to the electronic structure of infinitely large networks toward graphite.[14–19] By using these graph-theoretical techniques, one could clarify that the π-electronic properties of infinitely large networks are already imprinted in the topology of the small units.[16] These studies were supported by several new graph-theoretical techniques developed in the author's group, such as the operator technique for systematic derivation of recursion formulas.[20–22] Very recently the present author succeeded in establishing a mathematical foundation for the diagrammatic recipe of the old organic electron theory proposed by Robinson and Ingold[23–26] by using the graph-theoretical MO method.[27]

The aim of the present paper is to unify and reconstruct all the graph-theoretical molecular orbital theory developed in the author's group not only for the static but also for the dynamic behavior of π-electrons in conjugated systems. However, because of the limits of space, only small molecules are treated in this paper, where the author has avoided providing detailed presentations of the theory, but has tried to describe the flow of logic and the reasons why the calculated results came out. Then, by the analysis of graph-theoretical molecular orbital theory the specific "How" obtained by quantum chemical calculation is explained by mathematically acceptable "Why". To write such a paper for conveying the essence of this theory is a duty of a theorist; similarly it is the duty of the experimentalists to read this paper and realize the theory.

1. Problems to Be Solved

Let us focus our attention on the static distribution and dynamic flow or transfer of π-electrons in conjugated systems. In Fig. 1 are summarized several fundamental rules regarding the behaviors of π-electrons in conjugated systems, which a majority of (organic) chemists are daily using in interpreting and designing the syntheses and reactions of organic compounds. A theory in mathematics is constructed or proved by axioms or more fundamental theories. Of course, no theory in chemistry has ever been constructed so rigorously as in mathematics, but it sometimes happens that when some hypothesis is gradually supported by a pile of experimental facts, it suddenly jumps up to become a theory within the community of chemists even without any rigorous proof.

The "atomic hypothesis" raised by Dalton, Avogadro, Cannizzaro, and others has now been established as the atomic theory or atomic reality owing to the firm development of quantum mechanics and quantitative experiments. However, regarding the properties of electrons in molecules a proof for the widely accepted rules such as those given in Fig. 1 has rarely been documented. Thus, if the society of chemists wants to insist on its raison d'être in this modern age among the science community, those rules or theorems should be given some logical support, if not a complete proof or justification, which can logically be understood by theorists in other fields of science. Otherwise chemistry and chemical logic would be isolated in science as only a community where jargons, ciphers, and weird logic prevail.

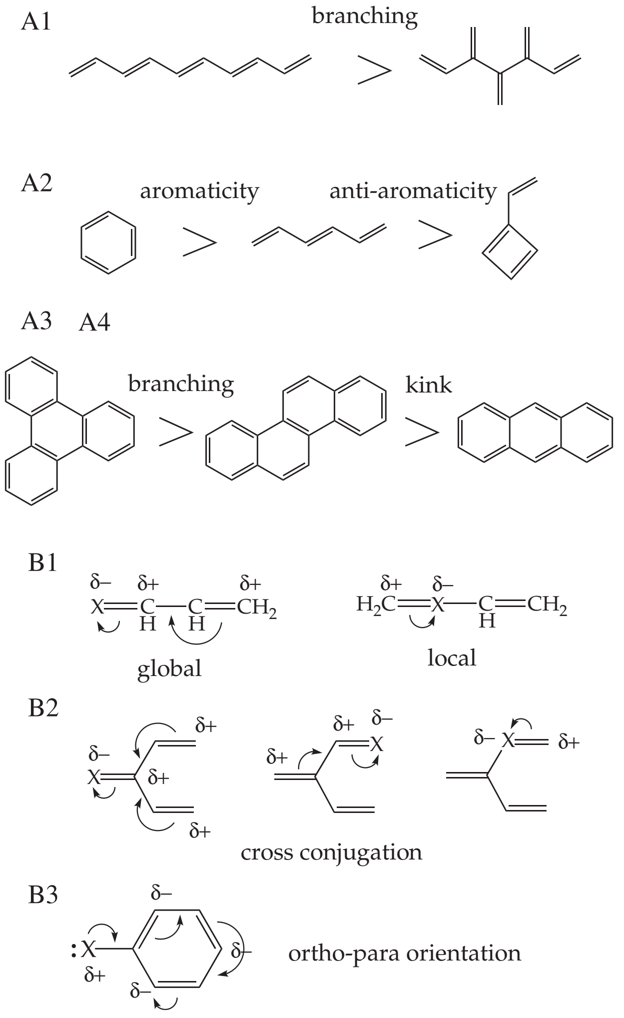


Fig. 1. Working hypotheses or general rules for the behavior of π-electrons in conjugated systems.

Now let us check the rules in Fig. 1 one by one.

A) Static Distribution of π-Electrons

A1 Polyenic branching (Destabilization (D))

Among the isomeric conjugated alkenes, the branchless linear polyene is the most stable; with the increase of branching, stability decreases down to the "comb polyene".[15] This has empirically been known but not widely recognized.

A2 $(4n+2)$- and $(4n)$-cyclization (Stabilization (S) and D)

This is widely known as the Hückel's $(4n+2)$-rule,[2] but actually is misunderstood and overused by a majority of organic chemists. Hückel treated only monocyclic conjugated systems. Correct extension to polycyclic systems will be explained later in this paper.

A3 Benzenoid kinking (S)

The relative stability of phenanthrene over anthracene has been explained by the difference in the number of Kekulé structures. The explanation was polished by Clar with the difference in the number of resonant "aromatic sextets".[28] Thus among the isomeric benzenoid hydrocarbons without any hexagonal branching, the linear polyacene is the most unstable and the zigzag one is the most stable.

A4 Benzenoid branching (S)

Among the tetrabenzenoids (tetrahexes), triphenylene is the most stable due to its "fully benzenoid" character; it is composed of only aromatic sextet hexagons but without any isolated double bond (according to Clar).[28]

B) Dynamical Flow or Transfer of π-Electrons

B1 Resonance effects (Global and Local)

If the terminal carbon atom in a long, conjugated molecule is substituted by an electron attractive or repulsive atom, global electron flow is observed, while if the substitution occurs at an inner site, the electron flow is limited only to the one side of the π-electron system, as in Fig. 1-B1, and sometime just local perturbation is attained. Very fortunately the old organic electron theory can "predict" quite easily the above properties, but almost no justification of this diagrammatic recipe has been presented.[29]

B2 Cross conjugations (Global and Local)

As seen in Fig. 1, whether the range of perturbation by substitution to a cross conjugated system is global or local can be predicted diagrammatically by the site of substitution.

B3 *Ortho–para* orientation effect

As is well known, the *ortho–para* orientation for the ionic substitution of benzene derivatives such as aniline and phenol is quite easily predicted from the structural formula using the diagrammatic recipe proposed by Robinson and Ingold. Theoretical calculations, from accurate to rough ones, have been performed extensively for individual cases. In most cases the obtained results support the organic electron theory, but almost no general justification has been reported.

Lewis and Langmuir introduced the octet theory of valency,[30,31] and Robinson and Ingold proposed their organic electron theory before the birth of quantum theory; thus their theories are based on some vague assumptions using funny but attractive diagrams. These pioneering chemists, however, did not know anything about the essential nature of the electron and its dual property, but their incantation is still charming a majority of chemists in modern times. Although a physicist (Hückel) later succeeded in explaining the extraordinary stability of benzene by the so-called HMO method using quantum mechanics,[2] his theory is not properly understood by organic chemists.

As has often been stated in this paper, this situation is not healthy in the community of chemists who are going to develop further the modern science based on the accumulated information and technique concerning the huge number of chemical substances.

Before going into the main stream of this paper, a brief comment is necessary on Clar's "aromatic sextet theory".[28] Although Rules A3 and A4 can be applied only to catacondensed aromatic hydrocarbons, Clar could extend his theory to the general polycyclic aromatic hydrocarbons (PCAHs) including pericondensed ones. Though the recipe is quite empirical, he devised a mathematically meaningful recipe for drawing circles representing the aromatic sextets on the component benzene rings; by using a few rules, such as A3, A4, and some others, one can predict the local aromatic character and global stability of PCAHs quite easily but accurately. However, the majority of organic chemists are still sticking to the meaningless usage of circles in hexagons of PCAHs as Robinson proposed. For example, for representing the carbon atom skeleton of phenanthrene molecule, Clar's formula **1** can easily (i) count the number of π-electrons ($2 \times 6 + 2 = 14$), (ii) predict the olefinic character of the extruding CC bond in the central hexagon, and (iii) show the global stability of this molecule over anthracene (due to the difference in the number of resonant sextets), while Robinson's convention **2** fails to predict any useful information on the ground state of benzenoid molecules (Chart 1). Later in this paper a modern interpretation of Clar's theory will be briefly explained.

2. Graph Theory and Hückel MO

2.1. Graph Theory in Chemistry.[32–41] For chemists the structural formula is a useful and powerful tool for recognizing and discussing the structure of chemical substances, especially of organic compounds. Further, in the cases where no confusion might occur regarding the structure of the compounds one may reduce the atomic symbol other than hydrogen into a point, or a vertex, and wipe out hydrogens, whose number attached to a heavier atom can automatically be recovered by assuming the standard valency number. Then a benzene molecule can simply be reduced to a hexagon with three alternately arranged double bonds. Further, those double bonds may be deleted leaving a hexagon. This diagram is nothing else but what mathematicians call and use as a hexagonal "graph".

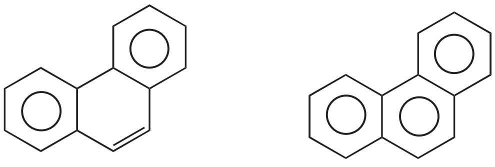

1 **2**

Chart 1.

Note that a hexagonal graph can be derived from the structural formulas of other compounds, such as cyclohexane, or cyclohexene. Thus due caution is necessary for the cases where more than two compounds with the same molecular skeleton are treated in the same analysis.

In graph theory[42] a graph is a mathematical object composed of *V* vertices and *E* edges. Each edge is joined between a pair of vertices. More than one edge can connect a given pair of vertices, corresponding to a multiple bond in the chemical sense; if the terminals of an edge are identical, such an edge is called a loop. A graph without a multiple edge or a loop is called a simple graph. If a pair of vertices are joined by an edge or edges, they are adjacent. An edge may or may not have an arrow or direction (See Fig. 2b). A graph with no directed edge is a non-directed graph, while a graph with at least one directed edge is a directed graph. A series of consecutive edges, v_1–v_2–$v_3 \ldots v_m$, in which all the vertices are different is a path of length $m - 1$. If v_m of this path is joined back to v_1, we have a ring or cycle of length m. A graph without a ring or cycle is a tree graph, otherwise we call a non-tree graph. If there is at least one path between any pair of vertices in a given graph, such a graph is a connected graph.

Chemical reaction networks can also be treated by using directed graphs.[43] Fruitful results have been obtained by Fujita and others[44–46] on the systematic representation and classification of organic reactions in the analysis using graph and group theories. However, in this paper these topics will not be discussed.

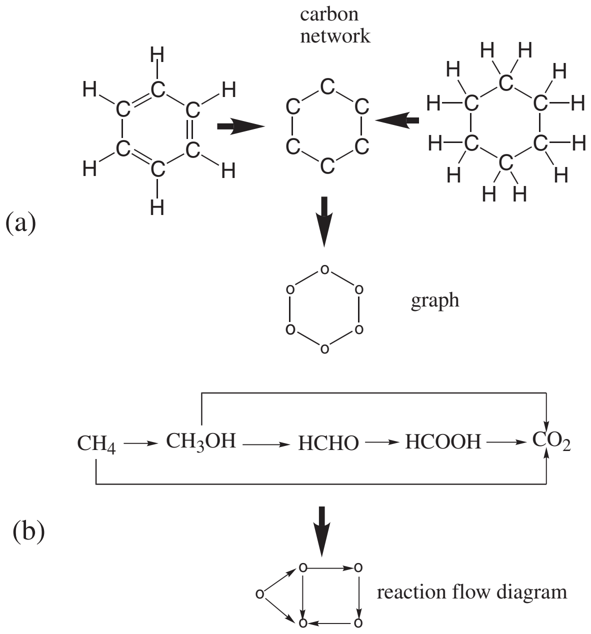
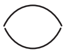
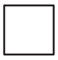
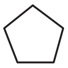
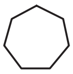
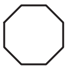


Fig. 2. Various examples of graphs used in chemistry.

Table 1. $p(\mathrm{G},k)$ and Z Values of Path Graphs, or the Carbon Atom Skeletons of Linear Polyenes or Normal Alkanes

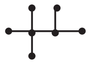
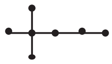
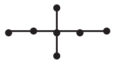
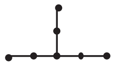
N	G	$p(\mathrm{G},k)$					Z_G
		$k=0$	1	2	3	4	
1		1					1
2		1	1				2
3		1	2				3
4		1	3	1			5
5		1	4	3			8
6		1	5	6	1		13
7		1	6	10	4		21
8		1	7	15	10	1	34
9		1	8	21	20	5	55

Table 2. $p(\mathrm{G},k)$ and Z Values of Monocyclic Graphs, or the Carbon Atom Skeletons of Cyclic Polyenes

N	G	$p(\mathrm{G},k)$					Z_G
		$k=0$	1	2	3	4	
2		1	2				3
3		1	3				4
4		1	4	2			7
5		1	5	5			11
6		1	6	9	2		18
7		1	7	14	7		29
8		1	8	20	16	2	47

Three different series of connected non-directed simple graphs are shown in Tables 1–3. Chemically relevant smaller graphs have been extensively tabulated with their characteristic quantities by the group of the author.[47–50] Table 1 gives the lower members of the path graphs in graph theory, corresponding to the networks of the carbon atom skeletons of linear polyenes or normal alkanes. The $p(\mathrm{G},k)$ number and Z index will be explained later in detail. Here just note the sequence of Z's forming the famous Fibonacci numbers. In Table 2 are given the $p(\mathrm{G},k)$ numbers and Z indices of monocyclic graphs, or the carbon atom skeletons of conjugated cyclic polyenes including benzene and cyclobutadiene. Here the Lucas series can be seen. In Table 3 the nine isomers of heptane are depicted by nine tree graphs with seven vertices.[5] Note that different numbers, Z_G, from 13 to 21 are assigned to each graph, roughly reflecting the degree of branching.

Table 3. $p(\mathrm{G},k)$ and Z Values of Heptane Isomers

G	$p(\mathrm{G},k)$				Z_G
	$k=0$	1	2	3	
	1	6	6	0	13
	1	6	7	0	14
	1	6	8	0	15
	1	6	7	2	16
	1	6	8	2	17
	1	6	9	2	18
	1	6	9	3	19
	1	6	9	4	20
	1	6	10	4	21

Before introducing the minimum essentials of graph theory, let us introduce some historically important encounters of chemistry and mathematics. At the end of the 19th century, many chemists and mathematicians rushed into the problem of counting the number of indistinguishable graphs with a fixed number of vertices, i.e., the problem of isomer counting, and many but incomplete papers were published in Berichte and JACS.[51–53] Finally in 1936 a graph theorist Pólya was happily able to gain a new concept, or a strong mathematical tool, the "counting polynomial".[54] Namely, as hinted at by this chemical problem, the graph theory could make a great advancement by which one can quite systematically perform the enumeration of graphs by manipulating this type of polynomial. An important branch of permutation group was established in this area of mathematics. However, the mathematical meaning of isomer counting has been totally ignored by chemists for more than thirty years, since in that era, as mentioned before, revolutionary new concepts and theories were successively introduced and taken into the main stream of chemistry. Later in this paper, the usefulness and powerfulness of the counting polynomial will be explained by taking the Z index as an example.

All the methods and theories related to the counting of isomers and Kekulé structures can be attributed to graph theory. From olden times chemists themselves have thus been accustomed to do mathematical thinking but without knowing its relevance to mathematics. Now we go back to the main stream of this paper. The algebraic representation of a graph will be explained.

2.2. Adjacency Matrix and Characteristic Polynomial in HMO. For a graph **G** with N vertices, the adjacency relation among the component vertices is given by the adjacency matrix, **A**.[42] Namely, **A** is defined as an $N \times N$ symmetric matrix with elements a_{ij}

$$a_{ij} = 1 \text{ for an adjacent pair of vertices } i \text{ and } j, \\ \text{and 0 otherwise.} \tag{2.1}$$

An example is given for a square graph as

$$A = \begin{pmatrix} 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \end{pmatrix}, \tag{2.2}$$

where the four vertices are numbered circularly. Note that this algebraic representation **A** is equivalent to a geometrical object, **G**, meaning that **G** can be reproduced uniquely from **A**, and vice versa. Since **A** has the elements of order N^2, many attempts have been tried to reduce the number of digits for representing **G**.

The characteristic polynomial $\mathrm{P_G}(x)$ of **G** has been defined for this purpose as

$$\begin{aligned} \mathrm{P_G}(x) &= (-1)^N \det(\mathbf{A} - x\mathbf{E}) \\ &= \sum_{k=0}^{N} a_k x^{N-k}, \end{aligned} \tag{2.3}$$

where **E** is the $N \times N$ unit matrix and x is a scalar. For the case of a square graph we have $\mathrm{P_G}(x) = x^4 - 4x^2$. Later this polynomial will be used for explaining the instability of cyclobutadiene. Although the $\mathrm{P_G}(x)$ cannot necessarily distinguish the topological structure of a graph, it can be used for rough discrimination.

The $\mathrm{P_G}(x)$ has been defined in mathematics, but it was found to be closely related to the Hückel molecular orbital (HMO) method for analyzing the π-electronic structure of conjugated hydrocarbon molecules. According to the standard recipe, the secular determinant $\Delta(\mathcal{E})$ for the π-electrons of a molecule is written down as

$$\Delta(\mathcal{E}) = \det\{(\alpha - \mathcal{E})\mathbf{E} + \beta\mathbf{A}\}, \tag{2.4}$$

and the orbital energy $\mathcal{E}$ is to be determined to make $\Delta(\mathcal{E})$ zero.

Note that the adjacency matrix appears in Eq. 2.4 owing to the nearest neighbor approximation in HMO. Then by substituting

$$\mathcal{E} = \alpha + x\beta, \tag{2.5}$$

into Eq. 2.4 one can get the same expression as Eq. 2.3. That is, solving an HMO determinant is nothing else but finding the zeros or "spectrum" of $\mathrm{P_G}(x)$.[55,56]

Nowadays even a laptop computer can quite rapidly obtain all the necessary numerical results of HMO calculation for molecules even with $N = 100$ or larger. However, in the early stage of the development of molecular orbital calculations it was a rather difficult task to expand the determinant of a given molecular skeleton into the polynomial of x for *large* molecules with only $N = 10$, and there have been proposed a number of methods for relating the coefficients $\{a_k\}$ of $\mathrm{P_G}(x)$ with the topology of the molecule. The reports of incomplete trials by the groups of Coulson,[57] Daudel,[58,59] Fukui,[60] and others have been documented.

However, before a useful theory was born, the computer technology and more sophisticated electronic theories began to make rapid progress. Although the practical necessity for the solution to this open question has faded out, its mathematical importance still does not die out.

In 1972 this problem was rigorously solved by the present author by using the theory of Z index.[61] After its publication he was informed by the Zagreb group that already in 1964 a German mathematician Sachs had obtained a neat expression for the coefficients $\{a_k\}$ of $\mathrm{P_G}(x)$ from a purely graph-theoretical stand point.[62,63] Although the Sachs theory is very elegant, it has a fatal drawback. Namely, since it has no recursion formula, it is almost unpractical to be applied to graphs even a little smaller than $N = 10$. On the other hand, several powerful recursion formulas in the Z index treatment are available, where the non-adjacent number $p(\mathrm{G}, k)$ plays a central role.

Before presenting the theory of the Z index another line of approach to the facile and systematic derivation of $\mathrm{P_G}(x)$ should be introduced here. In the cradle age of HMO theory, the pairing theorem for alternant hydrocarbons by Coulson and Rushbrooke[64] and the use of recursion formulas by Heilbronner[65] were very helpful for the researchers in this field. However, triggered by the papers published in early 1970's by the present author[5,61] and by the Zagreb group,[63] a number of interesting theories have been found and many useful techniques have been proposed by many groups of researchers. For example, they include: the transfer matrix method,[66,67] symmetrical decomposition of graphs,[37,68,69] pruning technique,[70] symmetry blocking method,[71] etc.

In this area the author's group also proposed several new methods, such as Chebyshev expansion method;[72] operator technique for efficient derivation of complicated simultaneous recursion relations;[20,73] factorization technique using the topological symmetry of highly symmetrical graphs, such as fullerenes;[74,75] another transfer matrix method for generating the Z-counting polynomial, $\mathrm{Q_G}(x)$ (vide infra), and $\mathrm{P_G}(x)$ of catacondensed benzenoid hydrocarbons;[76] the use of edge-weighted graphs for transforming $\mathrm{P_G}(x)$ to the matching polynomial, $\mathrm{M_G}(x)$ (vide infra), of polycyclic graphs;[77–80] etc. Although these topics cannot be explained in this paper, they are potentially relevant to the discussion of the main theme of this paper.

2.3. Topological Index.[9] The Z index Z_G for graph **G** is defined in three steps.[5] First, define the non-adjacent number, $p(\mathrm{G}, k)$, as the number of ways for choosing k disjoint edges from **G**, with $p(\mathrm{G},0)$ being unity for any graph. Then define the Z-counting polynomial, $\mathrm{Q_G}(x)$, by using the set of $p(\mathrm{G}, k)$ as follows:

$$\mathrm{Q_G}(x) = \sum_{k=0}^{m} p(\mathrm{G}, k)x^k, \tag{2.6}$$

where m is the maximum number of $k = [N/2]$ for **G** with N vertices. Finally the Z index is defined as the sum of all the $p(\mathrm{G}, k)$'s for **G**, or

$$Z_\mathrm{G} = \sum_{k=0}^{m} p(\mathrm{G}, k) = \mathrm{Q_G}(1). \tag{2.7}$$

In $\mathrm{Q_G}(x)$ the variable x just holds the number k and has no physico-chemical meaning, but counting polynomials like Eq. 2.6 are very useful and powerful tools for performing graph-theoretical enumeration and analysis.[81] It is to be noted here that the matching polynomial[82] (or acyclic,[83] or reference polynomial[84]), $\mathrm{M_G}(x)$, which was later proposed, has the same mathematical content as $\mathrm{Q_G}(x)$, since it is defined in terms of $p(\mathrm{G}, k)$ and can simply be transformed into $\mathrm{Q_G}(x)$. Namely,

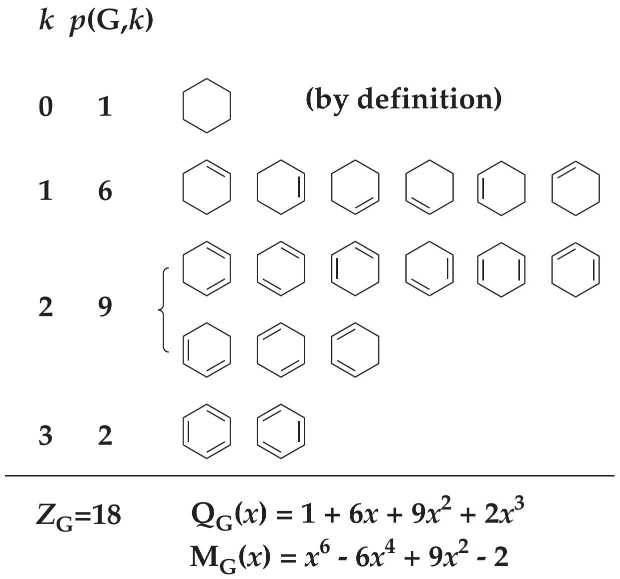


Fig. 3. Enumeration of the $p(\mathrm{G},k)$, $\mathrm{Q_G}(x)$, and Z_G of a hexagonal graph.

$$\mathrm{M_G}(x) = \sum_{k=0}^{m}(-1)^k p(\mathrm{G},k)x^{N-2k} = x^N \mathrm{Q_G}\left(-\frac{1}{x^2}\right). \tag{2.8}$$

Figure 3 illustrates how to obtain the $p(\mathrm{G},k)$, $\mathrm{Q_G}(x)$, and Z values with the hexagonal graph as an example. Note that $p(\mathrm{G},m)$ is the number of Kekulé structures, or perfect matching number for the cases with an even number of N.

The Z indices for several series of graphs are found to be related to important series of numbers. Namely, the Z values of alkanes (or alkenes), or path graphs, form the family of the famous Fibonacci numbers (1, 2, 3, 5, etc, see Table 1), while those of cyclic alkanes (or alkenes) or monocyclic graphs are Lucas numbers (1, 3, 4, 7, etc, see Table 2).[85,86] Although it is not contained in Table 1, $p(\mathrm{G},0)$ and Z_G of the vacant graph with no vertex and edge are both defined as unity. Both series of numbers in Tables 1 and 2 are characterized by the common recursion relation as

$$F_N = F_{N-1} + F_{N-2}. \tag{2.9}$$

Further similar recursion relations were found among the components of Z's. Namely, if the $\mathrm{Q_G}(x)$ of either linear or monocyclic graphs with N vertices is denoted by $\mathrm{Q}_N(x)$, then the following relation holds:

$$\mathrm{Q}_N(x) = \mathrm{Q}_{N-1}(x) + x\mathrm{Q}_{N-2}(x). \tag{2.10}$$

This recursion relation comes from that for the $p(\mathrm{G},k)$ numbers as illustrated in Fig. 4. Recall that the $p(\mathrm{G},k)$ number is the number of ways for choosing k disjoint edges from graph **G**. This number is the sum of the two sets of counting, the one including a given edge l and the other excluding l. The former number can be obtained by choosing $k-1$ edges from such a subgraph of **G** that is obtained by deleting edge l together with all the edges incident to l. Let us denote this subgraph as $\mathbf{G} \ominus l$. The latter number is the contribution from graph $\mathbf{G} - l$, which is obtained just by deleting edge l from **G** but leaving its terminal vertices. Then we have the following recursion formula for $p(\mathrm{G},k)$ as

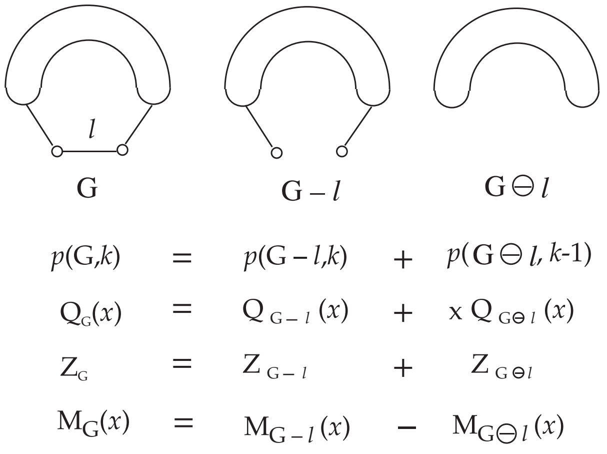


Fig. 4. Inclusion–exclusion principle and the recursion formulas for $p(\mathrm{G},k)$, $\mathrm{Q_G}(x)$, Z_G, and $\mathrm{M_G}(x)$.

$$p(\mathrm{G},k) = p(\mathrm{G}-l,k) + p(\mathrm{G}\ominus l,k-1). \tag{2.11}$$

By accumulating Eq. 2.11 for a given graph one obtains the recursion formula, 2.10, of $\mathrm{Q_G}(x)$. If one puts $x = 1$ in Eq. 2.10 the recursion formula of Z_G is obtained as

$$Z_\mathrm{G} = Z_{\mathrm{G}-l} + Z_{\mathrm{G}\ominus l}. \tag{2.12}$$

Similarly the recursion formula for the matching polynomial is obtained,

$$\mathrm{M_G}(x) = \mathrm{M}_{\mathrm{G}-l}(x) - \mathrm{M}_{\mathrm{G}\ominus l}(x). \tag{2.13}$$

This idea comes from the "inclusion–exclusion principle",[87] which is one of the main principles frequently used in the enumeration problems in discrete mathematics, such as graph theory and combinatorics.

By using these recursion formulas one can obtain quite easily these characteristic quantities for large graphs. Two examples for obtaining the Z values of slightly complicated graphs are illustrated in Fig. 5. Mastering this technique together with the Fibonacci numbers as given in Table 1 will be very helpful in following the discussion of this paper. Several groups of researchers developed efficient and fast algorithms for obtaining the $p(\mathrm{G},k)$.[88,89] It is to be noted here, however, that the recursion formula for $\mathrm{P_G}(x)$ is not so simple for polycyclic graphs where the decomposition of a graph is executed at an edge contained in a ring.[20,65]

Although the Z index does not uniquely determine the graph in general, for smaller graphs it can almost differentiate the isomeric difference. See Table 3, where the nine isomers of heptanes are nicely assigned by different Z values from 13 to 21 almost in parallel with the boiling points.[5,8] As has been stated before the Z index was originally proposed for analyzing the topological dependency of the thermodynamic properties of alkane isomers. However, since this paper is solely devoted to the quantum chemical relevance of the Z index in π-electronic systems, the interested readers are asked to refer to a series of papers on thermodynamic features and QSAR aspects of the Z index.[5,8,90–92]

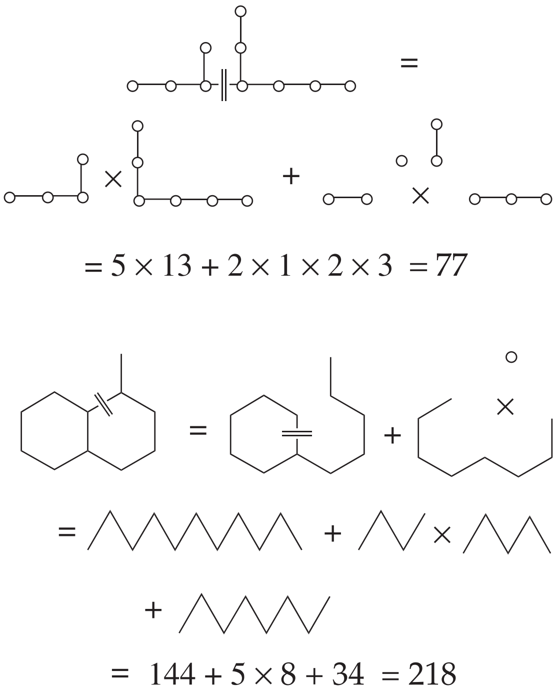


Fig. 5. Two examples of obtaining the Z values of large graphs.

Scrutinization of Table 3 would soon reveal the effect of branching on the p(G,2) and p(G,3).[5] That is,

(i) A mono-branching (bearing a Y-vertex) decreases $p(\mathrm{G},2)$ by 1, while a di-branching (bearing an X-vertex) decreases $p(\mathrm{G},2)$ by 3.

(ii) Both types of branchings surely decrease $p(\mathrm{G},3)$ but in a more complicated way.

As a result we have a theorem,

[Theorem 1] Among the isomer graphs, the value of Z_G of the branchless graph (path graph) is the largest, and branching always decreases the Z_G value.

Later, through the relation between E_π and $\log Z_\mathrm{G}$ (See Eq. 4.5) Rule A1 can be proved.

2.4. Relation between $\mathbf{Q}_N(x)$ and $\mathbf{P}_\mathrm{G}(x)$. This section will explain how the coefficients of $\mathrm{P}_\mathrm{G}(x)$ can be obtained from the manipulation of $p(\mathrm{G},k)$ numbers of **G** without expanding the secular determinant. For tree graphs, or for acyclic hydrocarbon molecules, a strikingly simple relation was found as follows.

[Theorem 2] The characteristic polynomial of a tree graph can be obtained from the counting of $p(\mathrm{G},k)$ numbers as

$$\mathrm{P}_\mathrm{G}(x) = \sum_{k=0}^{m} (-1)^k p(\mathrm{G},k) x^{N-2k} \quad (\mathrm{G} \in \text{tree}), \tag{2.14}$$

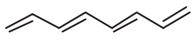
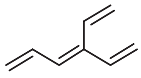
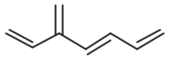
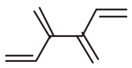
where m is the maximum number of k, or $[N/2]$.

In other words, the absolute values of all the corresponding coefficients of $\mathrm{Q}_N(x)$ and $\mathrm{P}_\mathrm{G}(x)$ of a tree graph are equal, or the characteristic and matching polynomials 2.8 of a tree graph are identical:

$$\mathrm{P}_\mathrm{G}(x) = \mathrm{M}_\mathrm{G}(x) \quad (\mathrm{G} \in \text{tree}). \tag{2.15}$$

It is rather difficult to prove this relation in a purely mathematical manner. However, if one decomposes the determinant into a polynomial iteratively term-by-term one can realize that Eq. 2.14 is equal to Eq. 2.3 for any tree graph.

Table 4. $p(\mathrm{G},k)$, Z_G, and E_π for the Four Isomers of Octatetraene

G	$p(\mathrm{G},k)$					Z_G	E_π
	$k=0$	1	2	3	4		
	1	7	15	10	1	34	9.5175
	1	7	14	9	1	32	9.4459
	1	7	14	8	1	31	9.4093
	1	7	13	7	1	29	9.3317

Recall that the path graphs in Table 1 represent the carbon atom skeletons of linear polyenes beginning from methyl radical ($N = 1$) and extending to infinitely large polyacetylenes. As stated before, the Z indices of this series of graphs form the Fibonacci numbers, $\{F_n\}$, and a number of mathematically interesting relations have been found for them.

For example, the characteristic polynomial of a path graph with N vertices can be expressed as[5]

$$\mathrm{P}_\mathrm{G}(x) = \sum_{k=0}^{m} (-1)^k \binom{N-k}{k} x^{N-2k}, \tag{2.16}$$

$$\binom{N-k}{k} = \frac{(N-k)!}{k!(N-2k)!}. \tag{2.17}$$

We have already seen in Table 3 ($N = 7$) that each of the coefficients 2.17 of the path graph for $k \geq 2$ decreases with branching. Another example is shown in Table 4 for the four isomers of octatetraene, where $\mathrm{P}_\mathrm{G}(x)$ (or set of $p(\mathrm{G},k)$), Z_G, and E_π are given. E_π is the total π-electron energy, to be explained later in this paper (See Eq. 3.11). Again a systematic change of the values of $p(\mathrm{G},2)$ and $p(\mathrm{G},3)$ are observed. Moreover, in this case a good linear correlation between E_π and Z_G is found. Later, through a more analytical relation between E_π and Z_G, 4.5, Rule A1 can be proved.

The monocyclic graphs given in Table 2 are the most simple cyclic graphs, corresponding to cyclopropenyl radical, cyclobutadiene, cyclopentadienyl radical, benzene, etc., for which Hückel calculated the "HMO" by solving their $\mathrm{P}_\mathrm{G}(x)$ and derived the famous $(4n+2)$-rule.

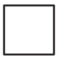
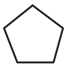
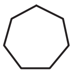
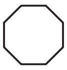
If one formally applies Eq. 2.14 to them and compares the result with the correct $\mathrm{P}_\mathrm{G}(x)$, an interesting relation can be observed. Namely, as in Table 5 the $\mathrm{P}_\mathrm{G}(x)$'s of monocyclic graphs can be expressed as the sum of the contribution from Eq. 2.14 and a small but *common* correction term of -2.

This result can be expressed in the following formula:

$$\mathrm{P}_\mathrm{G}(x) = \sum_{k=0}^{m} (-1)^k p(\mathrm{G},k) x^{N-2k} - 2 \quad (\mathrm{G} \in \text{monocyclic graph}), \tag{2.18}$$

or

Table 5. Decomposition of the Characteristic Polynomial ($P_G(x)$) of Monocyclic Graphs into the Matching Polynomial (M) and the Correction Term (C) $P_G(x) = M + C$

N	G	M	C
3		$x^3 - 3x$	-2
4		$x^4 - 4x^2 + 2$	-2
5		$x^5 - 5x^3 + 5x$	-2
6		$x^6 - 6x^4 + 9x^2 - 2$	-2
7		$x^7 - 7x^5 + 14x^3 - 7x$	-2
8		$x^8 - 8x^6 + 20x^4 - 16x^2 + 2$	-2

$$P_G(x) = M_G(x) - 2 \qquad (G \in \text{monocyclic graph}). \tag{2.19}$$

This is the secret of the Hückel rule. Namely, by extending Tables 2 and 5 down to higher members one may easily deduce that for $4n$-membered rings the constant term of the $P_G(x)$ is always zero ($= 2 - 2$), while for $(4n + 2)$-membered rings the last term comes to be -4 ($= -2 - 2$). Then the former group would have doubly degenerate NBMOs, while the HOMO–LUMO gap of the latter group would become large.

It is to be noted here that this discussion, as Hückel did, is limited solely to the monocyclic graphs; he derived his $(4n + 2)$-rule just from the calculated results of the distribution of the eigenvalues of these graphs but gave no indication of the cause of the results.

[Theorem 3] The π-electronic stabilization and destabilization caused by $(4n + 2)$- and $(4n)$-membered rings, respectively, can be attributed to the opposite trends of the ring contributions to the constant term of $P_G(x)$ of monocyclic graphs (Rule A2).

For discussing the effect of more than two rings in a conjugated system, one needs to have the full expression of $P_G(x)$ in terms of the $p(G, k)$ numbers, which was obtained by the present author in 1972.[61]

[Theorem 4] The characteristic polynomial of a polycyclic graph **G** is expressed in terms of the $p(G, k)$ numbers of **G** and its subgraphs as

$$\begin{aligned} P_G(x) = {} & \sum_{k=0}^{m} (-1)^k p(G, k) x^{N-2k} \\ & + (-2) \sum_{r}^{\text{Ring}} \sum_{k=0}^{m_r} (-1)^{k+n_r} p(G \ominus R_r, k) x^{N-n_r-2k} \\ & + (-2)^2 \sum_{r>s}^{\text{Ring}} \sum_{k=0}^{m_{rs}} (-1)^{k+n_r+n_s} \\ & \times p(G \ominus R_r \ominus R_s, k) x^{N-n_r-n_s-2k} \\ & + \ldots \end{aligned} \tag{2.20}$$

The first line is the matching polynomial $M_G(x)$ with no ring contribution, and the second line counts the contribution from the isolated rings, R_r's, where $\mathbf{G} \ominus R_r$ is the subgraph of **G** obtained by deleting ring R_r together with all the edges incident to R_r. The third line is the contribution from the pairs of disjoint rings, R_r and R_s, composed, respectively, of n_r and n_s vertices, and so on. Note that these additional terms have essentially the same mathematical form as the matching polynomial, or Eq. 2.8. It is easily seen that the relations 2.14 and 2.18 are contained in Eq. 2.20. In the latter case, since there is only one N-membered ring, the graph $\mathbf{G} \ominus R$ becomes vacant, making the contribution from the double summation in the second line unity.

The reason why the present author succeeded in getting this general expression might be the lucky start from the simplest tree graphs and their isomers as in Table 3. In the later discussion, expression (2.20) will be the basis for the extended Hückel rule of aromaticity applied to polycyclic conjugated systems.

2.5. Modified *Z* Index for Non-Tree Graphs. The discussion on $P_G(x)$ can be converted into the simpler index Z_G. First consider non-tree bipartite graphs, whose π-electronic energy is determined by $P_G(x)$ but not by $M_G(x)$. Then define the modified Z index, $\tilde{Z}_G$, as

$$\tilde{Z}_G = \sum_{k=0}^{m} (-1)^k a_{2k}, \tag{2.21}$$

and the aromaticity index ΔZ_G as the difference between Z_G and $\tilde{Z}_G$:[12]

$$\Delta Z_G = \tilde{Z}_G - Z_G, \tag{2.22}$$

corresponding to the contribution from the second and following lines in Eq. 2.20. Positive and negative values of ΔZ_G, respectively, indicate aromatic and anti-aromatic character of the π-electronic conjugated system **G**.

We have seen in the above discussion that the value of ΔZ_G (i) for tree graphs is always zero, while (ii) for $(4n + 2)$-membered monocyclic graph it is $+2$, and (iii) for $(4n)$-membered monocyclic graph it is -2. The definition of Eq. 2.21 was deliberately chosen, because for polycyclic graphs with more than two $(4n)$-membered rings there often arises a case in which the sign of $P_G(x)$ does not alternate.

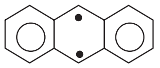
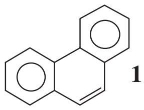
Aihara defines his topological resonance energy as the difference between the eigenvalue sums of $P_G(x)$ and $M_G(x)$; he has performed extensive studies on the aromaticity of a variety of conjugated hydrocarbon molecules and ions.[84] The numerical values of his analysis are naturally in parallel with what one can obtain by the aromaticity index.

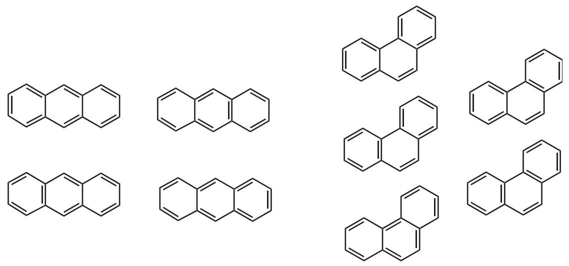
Table 6 compares $Q_G(x)$, $P_G(x)$, Z_G, $\tilde{Z}_G$, and ΔZ_G of anthracene, **3**, and phenanthrene, **1**.[49] In both the polynomials, all the coefficients of **1** below the fourth term are larger than the corresponding values of **3**, causing rather big differences in both Z_G and $\tilde{Z}_G$. The difference in the number of the Kekulé structures (See Fig. 6) appears not only in the last term of $Q_G(x)$, but also in the constant term of $P_G(x)$. Further, note that the absolute value of the constant term of $P_G(x)$ for these two isomers is just the square of $K(G)$,[56,93] or

$$|P_G(0)| = \{K(G)\}^2. \tag{2.23}$$

Although it is not explained in detail here, very beautiful mathematical relations are found in the set of the Kekulé struc-

Table 6. $Q_G(x)$, $P_G(x)$, Z_G, $\tilde{Z}_G$, and ΔZ_G of Anthracene, **3**, and Phenanthrene, **1**

 **3**	 **1**
$Q_G(x) = 1 + 16x + 98x^2$	
$+290x^3$	$+291x^3$
$+429x^4$	$+435x^4$
$+294x^5$	$+305x^5$
$+76x^6$	$+82x^6$
$+4x^7$	$+5x^7$
$1208 \Leftarrow Z_G \Rightarrow 1233$	
$P_G(x) = x^{14} - 16x^{12} + 98x^{10}$	
$-296x^8$	$-297x^8$
$+473x^6$	$+479x^6$
$-392x^4$	$-407x^4$
$+148x^2$	$+166x^2$
-16	-25
$1440 \Leftarrow \tilde{Z}_G \Rightarrow 1489$	
$232 \Leftarrow \Delta Z_G \Rightarrow 256$	



$$4 \Leftarrow K(G) \Rightarrow 5$$

Fig. 6. Kekulé structures of **1** and **3**.

tures of PCAHs. By using them one can give the empirically derived Clars aromatic sextet theory a reasonable mathematical foundation.[94–98] This theory is not directly connected to the graph-theoretical MO theory, but is another important facet of the application of graph theory by extensive use of the sextet polynomial, one of the counting polynomials proposed by the author's group.[81]

Formal application of graph-theoretical MO method does not usually yield a good result for conjugated systems containing a four-membered ring. However, Table 7 suggests some implications for the correlation between the topology of a graph and its π-electronic stability, where three conjugated hydrocarbons **4**–**6** with six carbon atoms are compared.[12] In this case the Z index cannot tell any useful information on the relative stability of these compounds, while the $\tilde{Z}_G$ values of all these three compounds are the same. However, if one takes a closer look at the distribution of the relative values of the coefficients, their relative stability can be detected. Namely, since only **6** has NBMOs, it is the least stable. The reasons why the constant term of $P_G(x)$ vanishes can clearly be traced from the decomposition of $P_G(x)$ into $M_G(x)$ and the ring correction term.

Both the coefficient, $p(G, 1)$, of the term x in $Q_G(x)$ and the absolute value of the coefficient of the term x^{N-2} in $P_G(x)$ are the number of edges in G. Then, by comparing the coefficients of the term x^4 in $P_G(x)$ for **4** and **5**, both with the same $\tilde{Z}_G$, one can infer that **4** is more stable than **5**. Although the aromaticity index ΔZ_G of **4** is negative, the effect is not so large as to wipe out the constant term. The difference between the destabilization caused by the introduction of a tetragon can be attributed to the Z index of the subgraph $\mathbf{G} \ominus \mathrm{R}$ (See Eq. 2.20). The relative magnitudes of E_π of **4–6** given in Table 7 are just as expected from the above discussion.

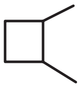
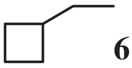
For non-alternant systems, extensive analyses have been performed; it was found that, although non-zero a_{2k+1} terms arise between a_{2k}'s, their effect on the eigenvalue distribution is usually small, giving subtle perturbations to the stability of the π-electronic system.[12]

3. Coulson's Perturbation Theory

3.1. Formalism of Hückel Molecular Orbital Method. Now let us recall several necessary formulas of HMO method for enhancing the discussion. Most of the important parts of the mathematical structure of HMO theory were constructed by Coulson's group by use of perturbation technique and contour integrals over the complex plane.[99]
(LCAOMO)

$$\varphi_n = \sum_r^{\mathrm{AO}} C_{nr} \chi_r \tag{3.1}$$

Table 7. $P_G(x)$, Z_G, $\tilde{Z}_G$, ΔZ_G, and E_π of Three Conjugated Systems with Six Carbon Atoms

G	$P_G(x)=$ $M_G(x)$ + cor. term	Z_G	$\tilde{Z}_G$	ΔZ_G	E_π
 **4**	$x^6 - 6x^4 + 5x^2 - 1$ $= x^6 - 6x^4 + 7x^2 - 1$ $-2x^2$	15	13	−2	7.2078
 **5**	$x^6 - 5x^4 + 6x^2 - 1$	13	13	0	6.9878
 **6**	$x^6 = 6x^4 + 6x^2$ $= x^6 - 6x^4 + 8x^2 - 2$ $-2(x^2 - 1)$	17	13	−4	6.6026

(Orbital energy)

$$\varepsilon_n = \langle \varphi_n | h | \varphi_n \rangle \tag{3.2}$$

(Total π-electron energy)

$$E_\pi = 2\sum_{n=1}^{\mathrm{OCC}} \varepsilon_n \tag{3.3}$$

$$= \sum_{r=1}^{\mathrm{AO}} q_r \alpha_r + 2 \sum_{r<s}^{\mathrm{BOND}} p_{rs} \beta_{rs} \tag{3.4}$$

(Coulson bond order)

$$p_{rs}^{\mathrm{C}} = 2\sum_{n=1}^{\mathrm{OCC}} C_{nr} C_{ns} \tag{3.5}$$

$$= \frac{1}{2} \frac{\partial E_\pi}{\partial \beta_{rs}} \tag{3.6}$$

(π-Electron density)

$$q_r = 2\sum_{n=1}^{\mathrm{OCC}} C_{nr}^2 \tag{3.7}$$

$$= \frac{\partial E_\pi}{\partial \alpha_r} \tag{3.8}$$

(Atom-atom polarizability)

$$\pi_{r,s} = \frac{\partial q_r}{\partial \alpha_s} = \frac{\partial q_s}{\partial \alpha_r} \tag{3.9}$$

(Bond-bond polarizability)

$$\pi_{rs,tu} = \frac{\partial p_{rs}}{\partial \beta_{tu}} = \frac{1}{2} \frac{\partial^2 E_\pi}{\partial \beta_{rs} \partial \beta_{tu}} \tag{3.10}$$

The summations over MOs are to be taken for the occupied orbitals (OCC). Among the set of these formulas the most important one is Eq. 3.4, which is obtained by using the definitions of bond order 3.5 and electron density 3.7 both obtained from the LCAOMO coefficients. Note that the total π-electron energy, which is a global information obtained from the molecular orbitals, can be expressed in terms of the local atomic and bond contributions.

By use of transformation 2.5 the energy expression of ε can be changed into that of dimensionless x. Since for hydrocarbons all the α_rs are set equal to α, the total π-electron energy is reduced to a simpler form as

$$E_\pi = 2\sum_{n=1}^{\mathrm{OCC}} \chi_n = 2 \sum_{r<s}^{\mathrm{BOND}} p_{rs}. \tag{3.11}$$

Partial differentiations of Eq. 3.4 with respect to β_{rs} and α_r, respectively, give Eqs. 3.6 and 3.8, whose physical meanings are as follows. Namely, the effect of forming a new bond between a pair of atoms on the π-electronic energy of a conjugated system can be estimated from the potential bond order between that pair of disjoint atoms, while the π-electron energy change upon substitution of a hetero atom can be estimated from the charge density on that atom.

Further, one can elaborate on this analysis by extending to the second order with respect to β_{rs} and α_r. Namely, two types of polarizabilities were defined as Eqs. 3.9 and 3.10, which are useful for analyzing the static and dynamic behavior of π-electrons in conjugated systems as in the following section.[99]

3.2. Coulson's Perturbation Theory. By using these quantities one can estimate quite accurately the change of π-electron densities and total π-electron energy caused by the perturbation of the atomic charge density $\delta\alpha_r$ on atom r and of the bond order $\delta\beta_{rs}$ on bond rs.

$$\delta q_s = \pi_{s,r} \delta\alpha_r \tag{3.12}$$

$$\delta E_\pi = q_r \delta\alpha_r + \frac{1}{2} \pi_{r,r} (\delta\alpha_r)^2 \tag{3.13}$$

$$\delta p_{tu} = \pi_{tu,rs} \delta\beta_{rs} \tag{3.14}$$

$$\delta E_\pi = 2 p_{rs} \delta\beta_{rs} + \pi_{rs,rs} (\delta\beta_{rs})^2 \tag{3.15}$$

The numerical values of various polarizabilities, $\pi_{r,s}$ and $\pi_{rs,tu}$, can be obtained by the standard method.[3,4] It is to be remembered here that the atom–atom polarizability $\pi_{r,s}$ measures the charge density change on atom r (or s) caused by the perturbation on atom s (or r), whereas the bond–bond polarizability $\pi_{rs,tu}$ measures the bond order change in bond rs (or tu) caused by the perturbation in bond tu (or rs). By using these quantities one can calculate rather accurate values of the π-electronic change caused by the formation of a new bond and hetero-atom substitution only from the coefficients of the molecular orbitals of the parent hydrocarbon molecule.[27]

Some mathematical background is necessary for the correct understanding of Coulson's perturbation theory, especially in its integral manipulation over the complex plane. Detailed discussions can be referred to the original papers by the present author.[12,13]

4. Graph-Theoretical Molecular Orbital Theory

4.1. Topological Bond Order. As mentioned before, the Z index was originally introduced for analyzing the topological features of thermodynamic properties of saturated hydrocarbons.[5] However, it was soon found that its formal application to Hückel molecular orbital theory yields unexpectedly excellent results.[11] The first finding was the topological bond order, p_l^{T}, which is defined for bond l in terms of the Z index as follows:

$$p_l^{\mathrm{T}} = \frac{Z_{\mathrm{G}\ominus l}}{Z_{\mathrm{G}}}, \tag{4.1}$$

where $Z_{\mathrm{G}\ominus l}$ is the Z index for the subgraph $\mathbf{G} \ominus l$ obtained from $\mathbf{G}$ by deleting bond l together with all the bonds incident to l. Although bond l is not included in $\mathbf{G} \ominus l$, $Z_{\mathrm{G}\ominus l}$ gives the contribution of bond l in counting the $p(\mathrm{G}, k)$ numbers and Z_{G} (See Fig. 4). When the topological bond order, p_l^{T}, for polyenes ($N \leq 10$, excluding radicals and ethylene) is plotted against the conventional bond order, or Coulson bond order,

$$p_{rs}^{\mathrm{C}} = 2\sum_{n=1}^{\mathrm{OCC}} C_{nr} C_{ns}, \tag{3.5}$$

a pair of parallel straight lines were obtained as shown in Fig. 7, corresponding to the single and double bonds in the Kekulé structures. Their correlation coefficients are as high as 0.998 for 43 single bonds and 0.997 for 58 double bonds. The bond order plots for radicals are found to lie in between the two straight lines.[11]

If the bond orders of the bonds in a given polyene molecule are to be compared, one only needs to enumerate the *Z* indices for the respective subgraphs, $\mathbf{G} \ominus l$'s as exemplified in Fig. 8 with a branched decapentaene treated in Fig. 5. In this case also, almost perfect linear correlation is attained within single and double bonds assigned by the conventional structural formula. It is to be noted that, if one masters the recursion formula exemplified in Figs. 4 and 5, these indices can be obtained even with mental arithmetic and one can estimate the relative magnitudes of their bond orders quite accurately!

This correlation study was extended to polycyclic hydrocarbon molecules including non-alternant hydrocarbons, and it was found that the relative magnitude of the Coulson bond order can well be approximated by the topological bond order p_l^{T} by adding a small contribution of the Pauling bond order, p_l^{P}, as

$$p_{rs}^{\mathrm{C}} = A(p_l^{\mathrm{T}} + c p_l^{\mathrm{P}}) \quad (0 < c \ll 1), \quad (l = \overline{rs}) \tag{4.2}$$

where p_l^{P} is defined as

$$p_l^{\mathrm{P}} = \frac{K(\mathrm{G} \ominus l)}{K(\mathrm{G})}. \tag{4.3}$$

This is not the original definition given by Pauling,[100] who used long sentences in defining p_l^{P}. However, by using the notation, $\mathbf{G} \ominus l$, proposed by the present author[13] the definition and its meaning become clearer, as seen in the mathematically analogical forms of Eqs. 4.1 and 4.3.

Suppose a molecule has $K(\mathrm{G})$ Kekulé structures, among which several have a double bond in the specific bond *l*. This number is equal to the Kekulé number for the graph $\mathbf{G} \ominus l$, as deduced from the discussion used in explaining Fig. 4. Then the Pauling bond order, a measure of the relative weight of the specific bond *l* with respect to the Kekulé structures, is given in the form of Eq. 4.3.

For polyenes the p_l^{P} is respectively one and zero for double and single bonds. Then the two-straight-line plot in Fig. 7 can be approximated by a single formula of Eq. 4.2 with *c* about 0.15. For polycyclic aromatic hydrocarbons the value of *c* was not so much different from the case of polyenes. The empirically derived relation 4.2 among the three bond orders, p_{rs}^{C}, p_l^{T}, and p_l^{P}, is thus very impressive, suggesting some deeply hidden mathematics. Remember that p_{rs}^{C} is derived from HMO, p_l^{P} is defined in the resonance theory, or valence bond method, and p_l^{T} comes from a new world. Before decipherment of this problem, another interesting bond order which is related to the three bond orders will be explained.

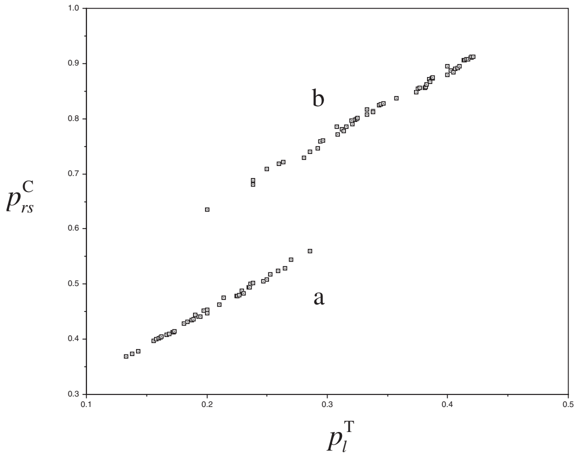


Fig. 7. Relation between the topological bond order P_l^{T} and the Coulson bond order P_{rs}^{C} for (a) single and (b) double bonds of lower members of conjugated acyclic polyenes up to decapentaene.

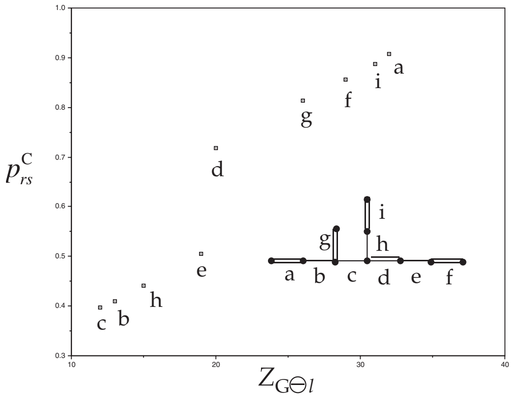


Fig. 8. Correlation between the Coulson bond order and the *Z* index of $\mathbf{G} \ominus l$ for a branched decapentaene (See Fig. 5).

Ham and Ruedenberg defined a bond order by using the LCAO coefficients and the eigenvalue, *x*, as[101]

$$p_{rs}^{\mathrm{HR}} = 2 \sum_{n=1}^{\mathrm{OCC}} \frac{C_{nr} C_{ns}}{x_n}. \tag{4.4}$$

They proved that for PCAHs this bond order is equal to the Pauling bond order.[102] This is quite an important mathematical relation, revealing that the HMO and resonance theory are closely connected with each other through some deep mathematical theory. We are not going into detailed discussions on this problem, but would like to point out that the *Z* index is related to the Kekulé number through the last entry of the $p(\mathrm{G}, k)$ numbers. Namely, for a graph with an even number of vertices, the $p(\mathrm{G}, m)$ is equal to the Kekulé number by definition, where *m* is the maximum number for *k*. Also recall the discussion in Fig. 6.

4.2. Topological π-Electron Energy.

Encouraged by the success of the topological bond order, we tried to correlate the total π-electron energy, E_π, with the logarithm of the *Z* index. As shown in Fig. 9 again almost perfect correlation was found for the 19 polyenes up to decapentaenes. In this case ethylene is included.[12]

If the relative stability of isomeric polyenes are to be compared it is not necessary to take the logarithm of the *Z* index. For example, Fig. 10 shows the almost perfect correlation between the *Z* index and E_π for the eleven isomers of decapentaene.

Again these *Z* indices can be obtained by mental arithmetic. These facts suggest that we define the topological π-electron energy as follows:

$$E_\pi^{\mathrm{T}} = \log Z_{\mathrm{G}} \quad \text{(for polyene)}. \tag{4.5}$$

Among isomers without taking the logarithm the *Z* index itself can be used as a measure of E_π.

These correlations were studied also for PCAHs and non-al-

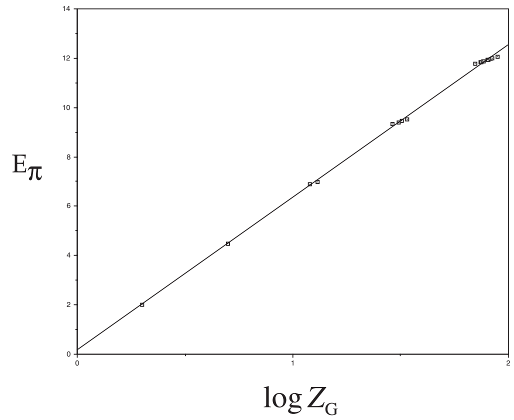


Fig. 9. Correlation between the Z_G and E_π of polyenes up to decapentaenes.

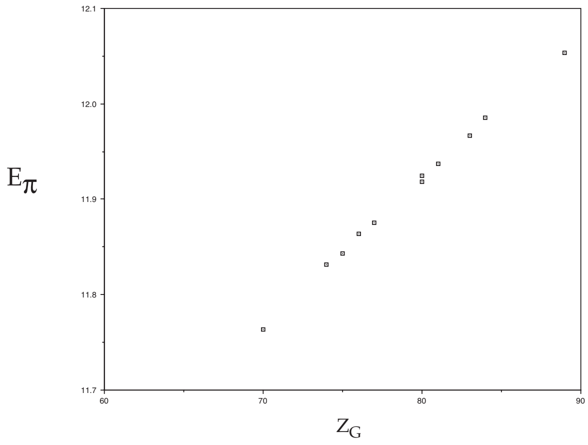


Fig. 10. Correlation between the Z_G and E_π of decapentaene isomers.

ternant hydrocarbons. For the former group of compounds, fairly good correlation was obtained as in Fig. 11, where the plots of the E_π values against the $\log Z_G$ for 77 PCAHs up to hexabenzenoids lie approximately on a straight line.[49]

In this class of compounds those with the same number of rings and carbon atoms are isomers with each other. Then the Z_G–E_π plots are much improved in the isomer plots.

However, these good correlations are fortuitous, because for PCAHs the E_π should be correlated to $\tilde{Z}_G$ rather than to Z_G which does not take into account the ring contribution. Actually the correlation as shown in Fig. 11 is a little improved if the abscissa is changed into $\tilde{Z}_G$. This fact is caused by the high correlation coefficient (~0.98) between Z_G and $\tilde{Z}_G$ of PCAH for each group of isomers.

There must thus exist some logical explanation for the excellent correlation obtained for the topological bond order, p_l^P, and the total π-electron energy, E_π both with the corresponding HMO quantities. The crucial key was found to be hidden in the Coulson perturbation theory.

4.3. Analysis of the Relations among the Three Bond Orders.[13] Here the main flow of the analysis will be introduced briefly. Consider the determinant $\Delta(x)$ giving the characteristic polynomial

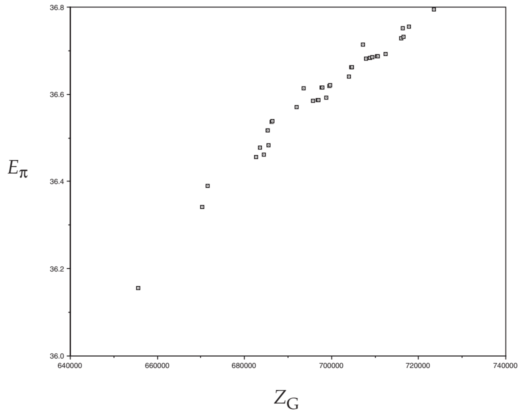


Fig. 11. Correlation between the Z_G and E_π of polycyclic aromatic hydrocarbons.

$$\Delta(x) = \begin{vmatrix} -x & 1 & 0 & \cdots & \cdots \\ 1 & -x & 1 & & \cdots \\ 0 & 1 & -x & & \cdots \\ \vdots & & & \ddots & \vdots \\ \cdots & \cdots & \cdots & \cdots & -x \end{vmatrix} = \mathrm{P}_G(x), \tag{4.6}$$

and its adjunct $\Delta_{r,s}(x)$ for a pair of atoms, r and s, obtained by deleting row r and column s as

$$\Delta_{r,s}(x) = (-1)^{r+s} \begin{array}{r|ccc|c|} & & & & s \\ & -x & 1 & \cdots & \cdots \\ & 1 & -x & \cdots & \cdots \\ & \cdots & \cdots & \ddots & \cdots \\ \hline r & \cdots & \cdots & \cdots & -x \end{array}\,. \tag{4.7}$$

By differentiating $\Delta(x)$ with respect to x one gets $\Delta'(x)$.

$$\Delta'(x) = \mathrm{P}'_G(x) = \partial \mathrm{P}_G(x)/\partial x \tag{4.8}$$

According to Coulson and Longuet-Higgins[99] the Coulson bond order can be expressed in terms of these determinants as

$$p_{rs}^C = -2 \sum_{n=1}^{\mathrm{OCC}} \frac{\Delta_{r,s}(x_n)}{\Delta'(x_n)}\,. \tag{4.9}$$

The adjunct 4.7 is expressed as the sum of the characteristic polynomials of a set of subgraphs of **G** as

$$\Delta_{r,s}(x) = -\mathrm{P}_{G\ominus l}(x) - \sum_{i}^{\mathrm{R}_i \supset l} \mathrm{P}_{G\ominus \mathrm{R}_i}(x) \quad (l = \overline{rs}), \tag{4.10}$$

where R_i runs over all the rings containing bond l. Since a tree graph has no ring, Eq. 4.10 is reduced to a simpler form as

$$\Delta_{r,s}(x) = -\mathrm{P}_{G\ominus l}(x) \quad (G \in \text{tree}). \tag{4.11}$$

By combining Eqs. 4.9 and 4.10, one can express the Coulson bond order in terms of the characteristic polynomial of **G** and the set of its subgraphs as

$$p_l^C = 2 \sum_{n=1}^{\mathrm{OCC}} \frac{\mathrm{P}_{G\ominus l}(x_n) + \sum_{i}^{\mathrm{R}_i \supset l} \mathrm{P}_{G\ominus \mathrm{R}_i}(x_n)}{\mathrm{P}'_G(x_n)}\,. \tag{4.12}$$

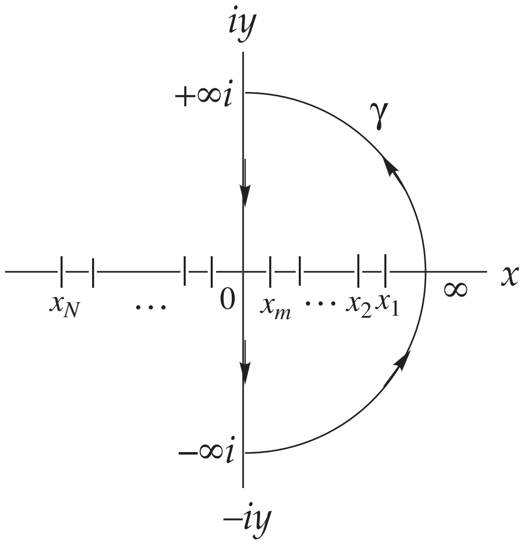


Fig. 12. The path γ of contour integration of the F function over the complex plane.

For a tree graph we have

$$p_l^{\mathrm{C}} = 2\sum_{n=1}^{\mathrm{OCC}} \frac{\mathrm{P}_{\mathrm{G}\ominus l}(x_n)}{\mathrm{P}'_{\mathrm{G}}(x_n)}. \quad (\mathrm{G} \in \text{tree}). \tag{4.13}$$

Following the procedure developed by Coulson and Longuet-Higgins to convert p_l^{C} into an expression of a complex integral, we have

$$\begin{aligned} p_l^{\mathrm{C}} &= -\frac{1}{\pi i}\oint_{\gamma} \frac{\Delta_{r,s}(z)}{\mathrm{P}_{\mathrm{G}}(z)}\mathrm{d}z \\ &= \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\Delta_{r,s}(iy)}{\mathrm{P}_{\mathrm{G}}(iy)}\mathrm{d}y, \end{aligned} \tag{4.14}$$

where the path of integration γ is the imaginary axis from ∞i to $-\infty i$ and the infinite semicircle to the right of the imaginary or y axis (See Fig. 12), and the integral over the latter part vanishes owing to the fact that the integrand is of the order z^{-2}.

Let us denote the integrand in the second line of Eq. 4.14 as

$$F_{\mathrm{G},l}(y) = \frac{\Delta_{r,s}(iy)}{\mathrm{P}_{\mathrm{G}}(iy)}, \tag{4.15}$$

which will play an important role in the following discussion. Now the Coulson bond order is expressed as

$$p_l^{\mathrm{C}} = \frac{1}{\pi}\int_{-\infty}^{\infty} F_{\mathrm{G},l}(y)\mathrm{d}y. \tag{4.16}$$

For an alternant hydrocarbon AH without any NBMO, p_l^{C} is reduced to

$$p_l^{\mathrm{C}} = \frac{2}{\pi}\int_{0}^{\infty} F_{\mathrm{G},l}(y)\mathrm{d}y \quad (\mathrm{G} \in \mathrm{AH}). \tag{4.17}$$

Then try to find the graphical meaning of the starting point of $F_{\mathrm{G},l}(y)$, or $F_{\mathrm{G},l}(0)$. For tree graphs the denominator and numerator, respectively, become $\mathrm{P}_{\mathrm{G}}(0) = p(\mathrm{G}, m) = K(\mathrm{G})$ and $\mathrm{P}_{\mathrm{G}\ominus l}(0) = p(\mathbf{G} \ominus l, m) = K(\mathbf{G} \ominus l)$. Then we have a novel relation:

$$F_{\mathrm{G},l}(0) = p_l^{\mathrm{P}}. \tag{4.18}$$

For polycyclic compounds, analysis is not so simple, but at least for those without a $(4n)$-membered ring Eq. 4.18 is also shown to hold. In this case it is easier to prove the following relation:

$$F_{\mathrm{G},l}(0) = p_l^{\mathrm{HR}}, \tag{4.19}$$

by the use of complex integrals. Now through the equality between p_l^{P} and p_l^{HR}, Eq. 4.18 is valid for almost all the networks except for "poly-$(4n)$-ring" systems.

The next problem is to find some connection between the $F_{\mathrm{G},l}(y)$ and p_l^{T}. Again for tree graphs the analysis is straightforward. Namely, from Eq. 2.14 the following two relations can be obtained:

$$\mathrm{P}_{\mathrm{G}}(i) = i^N Z_{\mathrm{G}}, \tag{4.20}$$

and

$$\mathrm{P}_{\mathrm{G}\ominus l}(i) = -i^N Z_{\mathrm{G}\ominus l}. \tag{4.21}$$

Then by putting them into Eq. 4.15 we have

$$F_{r,s}(1) = p_l^{\mathrm{T}}. \tag{4.22}$$

Although the ring contribution to $\mathrm{P}_{\mathrm{G}}(x)$ in Eq. 2.20 gives minor effect to the F function, extensive analysis ensures that the relation 4.22 approximately holds for most cyclic conjugated hydrocarbons without $(4n)$-membered ring or rings.

Now for tree graphs, the starting point of the F function is p_l^{P} and it takes the value of p_l^{T} at $y = 1$, and the area under its whole curve from $y = 0$ to infinity gives p_l^{C}. These novel properties of the F function are shown in Fig. 13 with the three bonds in hexatriene as examples.

Although the starting point of the F function may differ from bond to bond, the shape of the curve F is found to be very smooth as in Fig. 13. Then the area under the curve F can be approximated as the sum of the two parts, the one between $y = 0$ and $y = 1$ and the other between $y = 1$ and $y = \infty$. The rough shape of the former is either a trapezoid or triangle, but in either case its area is a function of $(p_l^{\mathrm{P}} + p_l^{\mathrm{T}})/2$. On the other hand, the area of the latter part is expressed as p_l^{T} only. Then the whole area, proportional to p_l^{C}, is a linear function of both p_l^{P} and p_l^{T}, but the weight of the latter is much larger than that of the former, as in Eq. 4.2. Now we have

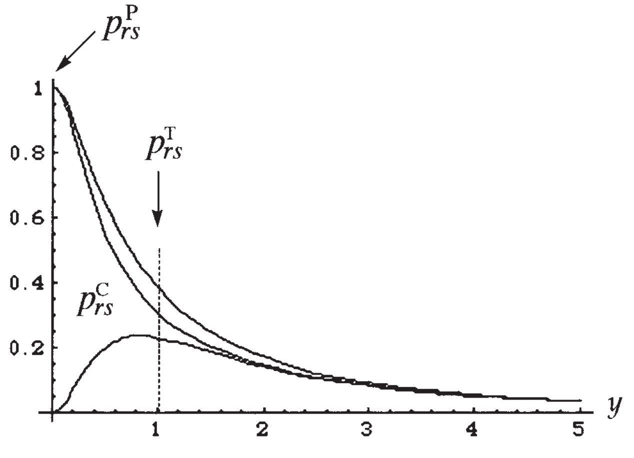


Fig. 13. The relation among the three bond orders with respect to the $F_{\mathrm{G},l}(y)$ curves for the three bonds of hexatriene.

[Theorem 4] The Coulson bond order of conjugated hydrocarbons can be estimated well by the topological bond order, p_l^{T}.

4.4. Analysis of the Topological π-Electron Energy.[12]

[Theorem 5] That the topological π-electron energy, either in the form of 4.5 or

$$E_\pi^{\mathrm{T}} = \log \tilde{Z}_{\mathrm{G}} \quad \text{(for PCAHs)}, \tag{4.23}$$

gives a rough estimate of E_π can also be proved mathematically by using the contour integral over the complex plane.

This time the key equation is as follows:

$$\begin{aligned} E_\pi &= \frac{1}{\pi i}\oint_\gamma \left\{\frac{z\mathrm{P}'_{\mathrm{G}}(z)}{\mathrm{P}_{\mathrm{G}}(z)} - N\right\}\mathrm{d}z \\ &= \frac{1}{\pi}\int_{-\infty}^{\infty}\left\{N - \frac{iy\mathrm{P}'_{\mathrm{G}}(iy)}{\mathrm{P}_{\mathrm{G}}(iy)}\right\}\mathrm{d}y, \end{aligned} \tag{4.24}$$

where the contour γ is the same as in Fig. 12. In this analysis we had better exclude the following three types of conjugated systems:

(i) molecule whose HOMO is anti-bonding,
(ii) molecule whose LUMO is bonding,
(iii) molecule with an NBMO or NBMOs,

as in the case of the analysis of the topological bond order. Those ill-behaved molecules usually have two or more $(4n)$-membered rings or belong to unstable non-alternant molecules like **7** and **8** (Chart 2).

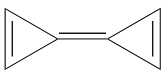
Actually **7** has never been synthesized and **8** is described as a very unstable compound,[103] while the following nonbenzenoid aromatic hydrocarbons have been synthesized as rather stable molecules[104,105] **9** and **10** (Chart 3).

Then let us solve this problem. Why are **7** and **8** unstable, whereas **9** and **10** are stable?

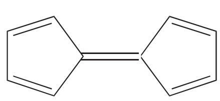
Equation 4.25 tells us that whether the total π-electronic energy of a conjugated system is large or small should be attributed to the set of the coefficients of the characteristic polynomial $\mathrm{P}_{\mathrm{G}}(x)$ and, accordingly through the set of the $p(\mathrm{G}, k)$ numbers of the system **G** together with those of the subgraphs $\mathbf{G} \ominus \mathrm{R}$'s obtained by deleting a ring and pair of disjoint rings, and so on, which is implied in Eq. 2.20.

The result of this analysis is obtained as the extended Hückel rule.[12]

[Theorem 6] The extended Hückel rule for the aromaticity of polycyclic aromatic hydrocarbons can be written down symbolically as follows:

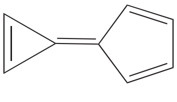


7



8

Chart 2.



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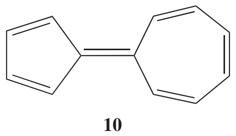
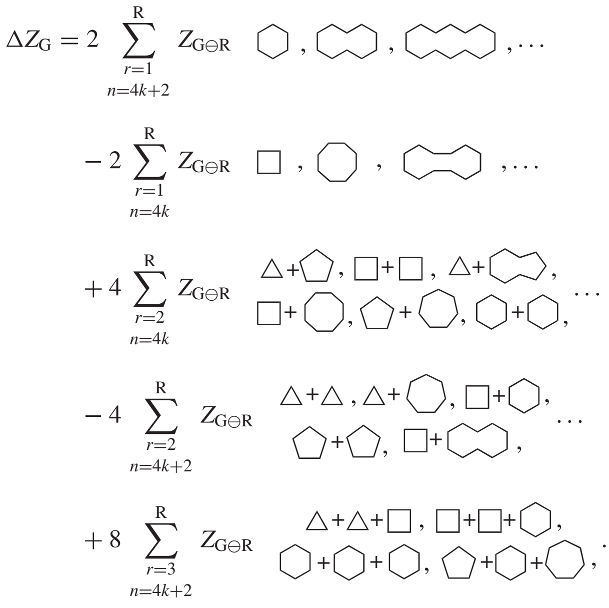


10

Chart 3.



$$+ \ldots. \tag{4.25}$$

The ΔZ_{G} is the aromaticity index 2.21, whose positive contribution gives extra stability caused by a ring or a set of disjoint rings. This equation shows two important factors governing the π-electron stability of a ring network, namely, the value of the Z index of subgraph $\mathbf{G} \ominus \mathrm{R}$ and the sign given to each term. The first two lines give the well-known Hückel rule. Namely, a $(4n+2)$-membered ring stabilizes and a $(4n)$-membered ring destabilizes the π-electronic conjugated system. The third line tells us that a pair of disjoint rings with a total of $4n$ vertices stabilizes, while the fourth line shows a destabilization contribution by a pair of two disjoint rings with a total of $4n+2$ vertices. Notice the stabilizing pairs of rings of the sizes, $3+5, 4+4, 5+7$, and $6+6$, among which the stable nonbenzenoids of **9** and **10** are included. On the other hand, one can find the unstable systems **7** $(= 3+3)$ and **8** $(= 5+5)$ in the fourth line. These are the most typical examples of the extended Hückel rule.

Similar arguments can be proposed for the fifth and the following lines of the contributions of more than three disjoint rings. It is important to notice that any number of disjoint hexagons always contribute toward stabilization of the system. Just the opposite trend can be inferred for the hypothetical polycubic network. Further, controversial discussions on the stability of novel polycyclic nonbenzenoid hydrocarbons can be settled by this extended Hückel rule.

4.5. Topological Factors Governing the Stability of PCAHs. The global trend of the stability of polycyclic conjugated systems was clarified in Eq. 4.25. In the end of discussion of this problem let us see from where the relative stability between anthracene, **3**, and phenanthrene, **1**, introduced in **2.5** comes. As mentioned before the relative stability of PCAHs can be quite easily and accurately predicted by the Kekulé number, $K(\mathrm{G})$. The reason why the isomer **1** with a kink structure has a larger $K(\mathrm{G})$ value can be explained as follows. According to Clar, the ground state of **1** can be represented as the Clar structure with a pair of aromatic sextets resonant with each other as depicted in Table 6.[28] Since each aromatic sextet repre-

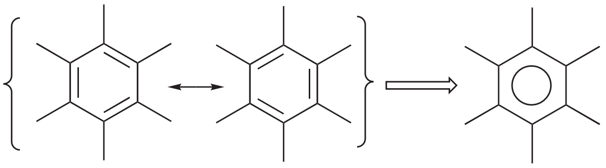


Chart 4.

sents a pair of Kekulé structures as shown in Chart 4, a pair of resonant sextets represent at least four Kekulé structures as in the case with **1**. On the other hand, for **3** if a pair of aromatic sextets are assigned on both the terminal hexagons, a Kekulé structure is not allowed to be drawn as shown as the incomplete Kekulé structure in Table 6.

Graph-theoretical analysis of the Clar's aromatic sextet was performed by introducing the sextet polynomial.[94–98] By the use of this counting polynomial, one can translate the enumeration of the Kekulé structures and the discussion on the resonance theory into problems of algebra and group theory, and the chemical logic which has long been used only by chemists can be interpreted by the terms and formulations of mathematics.

For analyzing the aromatic character of the component benzene rings in PCAHs, Polansky's group introduced the benzene character using the HMO coefficients.[106–108] For enumerating the number of Kekulé structures of PCAHs a number of interesting papers and monographs have been published.[109–115] Based on these studies the following fact has been approved as a well-established theorem:

[Theorem 7] Introduction of a kink in a linear polyacene network increases the number of Kekulé structures and stabilizes the π-electron system (A3).

By using the HOMO–LUMO interaction scheme given by Fukui's frontier orbital theory it is also easy to explain the stabilizing effect of a kink in a polyacene network.[116]

By extending similar arguments of graph-theoretical analysis one can explain the extra stability of hexagonal branching in the catacondensed aromatic hydrocarbons as depicted in (A4) of Fig. 1. Graph-theoretical analysis of the aromaticity of polycyclic aromatic hydrocarbons can also be pursued by using the concept of the conjugated circuit. The readers are advised to read the extensive review by Randić.[117] Now let us go into the problem of hetero-atom substitution in conjugated systems.

5. Classical Organic Electron Theory

5.1. Diagrammatic Recipe by Robinson and Ingold.

A) Electron flow from the lone pair to conjugated system

The most famous and simplest example of organic electron theory is the *ortho–para* orientation effect in the ionic substitution reaction of substituted benzenes, such as aniline and phenol. Dewar,[118,119] Fukui,[116,120,121] Woodward and Hoffmann,[122,123] and others have succeeded in elaborating the classical organic electron theory up to the stereo-selective reactions of homo-conjugated systems even with the simple HMO method. However, there has never been given any general proof of the correctness of the diagrammatic recipe of the π-electron movement in conjugated systems proposed more than three quarters of a century.[23–26]

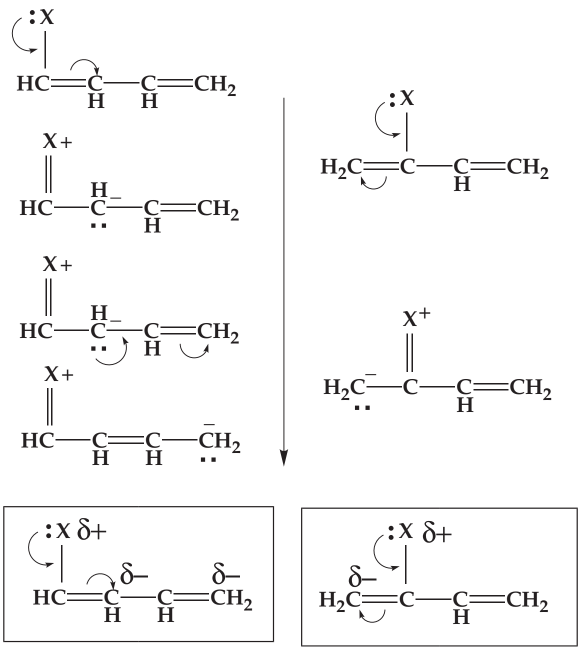


Fig. 14. Electron flow diagrams caused by the substitution of an electron-repelling atom to sites 1 and 2 of butadiene.

As seen in Fig. 14, there are two different modes for subsituting an electron-donation atom or group, X, such as NH_2, OH, and Cl, to butadiene at the sites 1 and 2. In both cases, X pushes some portion of an electron from the lone pair toward the π-electronic system of the butadiene moiety. This electron flow, depicted by a curved arrow, repels the pair of π-electrons in the adjacent C=C bond onto the carbon atom situated at the remote end to give a negative charge on it (Look down from the top to bottom of Fig. 14).

In the case of site-1 substitution the new lone pair electrons tend to flow into the next double bond to create another lone pair on the remote carbon atom in that bond, and this process continues up to the end of the conjugated system. On the other hand, the electron flow in the site-2 substitution terminates at site 1. Namely, in these two cases the π-electron flow from X to the conjugated system is, respectively, global and local, as depicted in the boxes of Fig. 14, where the symbols, $\delta+$ and $\delta-$, are supposed to express some indefinite but small fraction of a unit charge. The flow of π-electrons in these cases can be expressed as in the following scheme:

$$\text{lone pair—(single—double)}_n. \tag{A}$$

B) Electron withdrawal by electronegative atom

When a carbon atom in butadiene is substituted by a more electronegative atom X, such as N and O, some portion of the π-electrons in the conjugated system is attracted toward X. There are two possible modes of substitution also in this case (See Fig. 15). By the movement of π-electrons from the double bond a lone pair is diagrammatically created on atom X with a unit minus charge. Quite similarly to the former case, organic electron theory predicts the direction and extent of the π-electron flow as in the boxes of Fig. 15.

Then the mode of π-electron flow can be expressed as in the following scheme,

$$\text{hetero atom—double—(single—double)}_n. \tag{B}$$

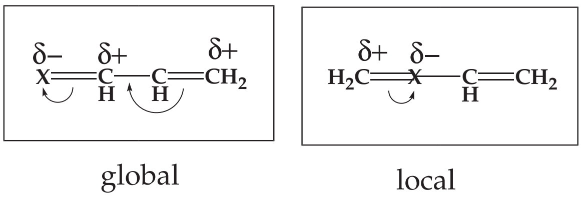


Fig. 15. Electron flow diagrams caused by the substitution of an electron-withdrawing atom to sites 1 and 2 of butadiene.

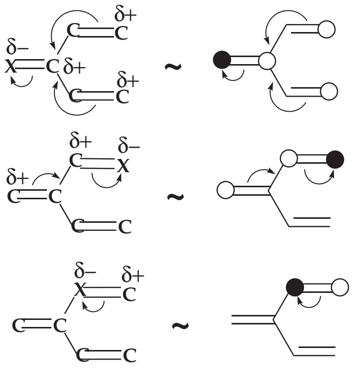


Fig. 16. Electron flow diagrams showing different modes in a cross-conjugated system.

Note that in both cases, (A) and (B), the range of effect is global and local, respectively, by substitution at sites 1 and 2. Robinson already pointed out that this "electrometry" effect is expected to decrease rather rapidly with the distance from the site of substitution.[23,24] The rate of damping cannot a priori be estimated from these diagrams. However, both the direction and range of effect are in accordance with the experiments.

As seen in these two cases, (A) and (B), the directions of the π-electron flow are quite the reverse with each other. However, the direction is not an important issue in this theory. Namely, although the sign of the induced charges on C and X atoms is just the reverse in Figs. 14 and 15, the perturbed sites and range are the same in both the cases. The important points to be discussed here are the perturbed sites and range caused by a hetero-atom substitution.

C) Acyclic cross conjugation

For a typical example of cross-conjugation in acyclic systems, see Fig. 16, where the substituted and perturbed sites are respectively marked with black and white circles. In all the three cases of substitution of a hetero-atom, the sites and range of "conjugated electrometry" effects[23–26] are quite easily predicted according to the recipe of organic electron theory used in Scheme (B).

5.2. Simplest Explanation with NBMO.[27] By using the Hückel NBMO almost the same tendency of π-electron flow in Scheme (A) (Fig. 14) can be obtained. See Fig. 17, where the wavefunctions of NBMOs[119] of pentadienyl radical and its isomer are compared with the corresponding diagrams of organic electron theory. With an extension of any number of ethylene units to the right end of the π-electronic system in Fig. 17a its NBMO can automatically grow in analogy with the π-electron flow in Scheme (A) in Fig. 14a. Thus in this case the diagrammatic method of organic electron theory is shown to yield the same result as the HMO method, which also does not give the damping effect.

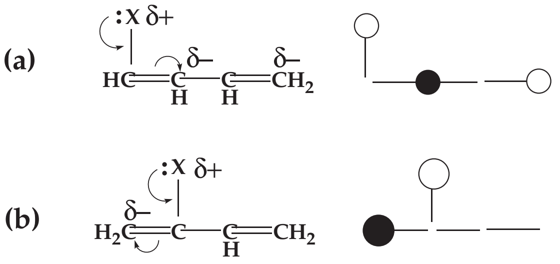


Fig. 17. Correspondence between the electron flow diagram and NBMO of the corresponding hydrocarbon radical: (a) global and (b) local.

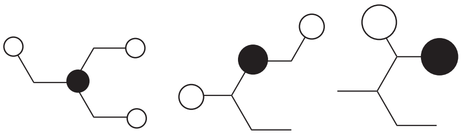


Chart 5.

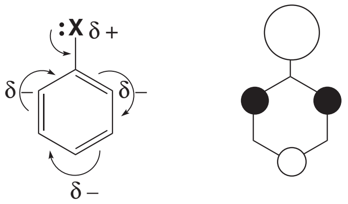


Chart 6.

For the cross conjugated system shown in Fig. 16 the non-zero coefficients of the NBMOs of the three alkene radicals corresponding to the different modes of hetero-atom substitution appear just at the white circles as shown in Chart 5.

Quite similarly the *ortho–para* orientation of aniline and phenol can be explained by the NBMO wavefunction of benzyl radical as shown in Chart 6. In the cases where more than one benzene ring are condensed and conjugated, as in naphthalene derivatives, the parallelism between organic electron theory and Hückel NBMO wavefunctions is usually observed. Although in this case some damping tendency can be seen, its rate is too slow to be compared with experiments.

The NBMO coefficients of a given alternant hydrocarbon radical can be obtained quite easily with a back-of-envelope calculation by using the well-known recipe,[124] and one can trace how non-zero coefficients appear only on the starred atoms. However, this is not a plausible explanation why NBMO coefficients are non-zero on such and such carbon atoms. By using graph-theoretical MO theory one can answer this question.

5.3. Analysis by Perturbed HMO Theory.[27] First, let us see how the perturbation theory can accurately reproduce the π-electron distribution which is obtained by the direct calcula-

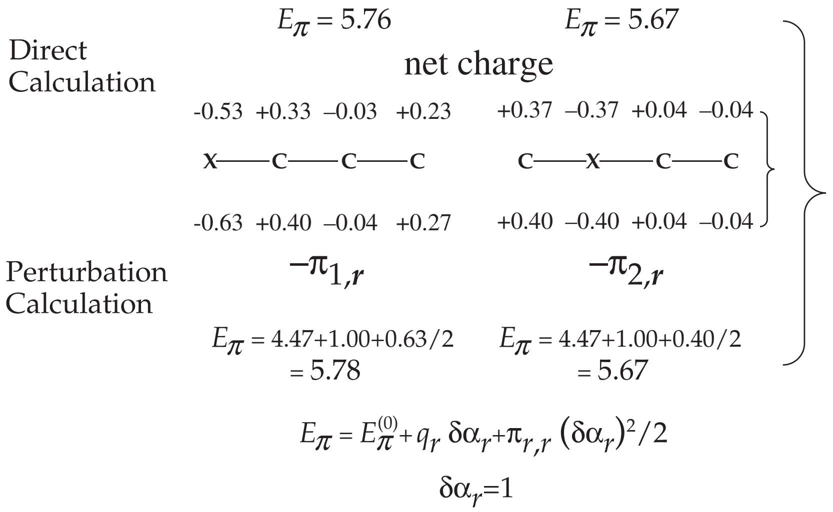


Fig. 18. Comparison of the charge density of substituted butadienes obtained from the direct and perturbation calculations. π-Electron energy E_π and Coulomb integral β are in units of α. Due caution is necessary for the sign of π in numerical calculation.

tion in which the hetero-atom substitution is explicitly taken into account. In Fig. 18 the results of the perturbation calculation prescribed by Coulson and Longuet-Higgins are compared with the results of direct calculation, in which the Coulomb parameter on X is chosen as $\alpha + \beta$. Agreement between the two methods is fairly good, and both the methods predict that π-electron transfer occurs globally and locally, respectively, by the hetero-atom substitutions at sites 1 and 2 (See also Fig. 15).

Eq. 4.16 is the integral form of the bond order for bond l in graph G, but it can be generalized to any pair of atoms r and s irrespective of forming a bond as in

$$p_{r,s}^{\mathrm{C}} = \frac{1}{\pi}\int_{-\infty}^{\infty} F_{\mathrm{G},rs}(y)\mathrm{d}y. \tag{5.1}$$

Similarly the integral form for the atom–atom polarizability $\pi_{r,s}$ can be given as

$$\pi_{r,s} = -\frac{1}{\pi}\int_{-\infty}^{\infty} \{F_{\mathrm{G},rs}(y)\}^2\mathrm{d}y. \tag{5.2}$$

It is remarkable that the same function $F_{\mathrm{G},rs}(y)$ is responsible for both p_l^{C} and $\pi_{r,s}$. Since $F_{\mathrm{G},rs}(y)$ is defined in a complex plane, the value of $\pi_{r,s}$ can be positive and negative. Further, because of the square form of the integrand almost all the pairs of atoms give non-zero values for $\pi_{r,s}$ contrary to the case of p_l^{C}. Therefore the integration of F^2 in Eq. 5.2 is not so simple as that of Eq. 5.1. However, one can perform detailed analysis for this integration and obtain the following results:

[Theorem 8]

i) The value of $\pi_{r,r}$ is always positive and is the largest among the set of $\pi_{r,s}$.

ii) The $\pi_{r,s}$ is positive for the pair of atoms belonging to the same group (starred or unstarred), and negative otherwise.

iii) Positive $\pi_{r,s}$ rapidly decreases with the distance between r and s.

iv) The absolute value of negative $\pi_{r,s}$ slowly decreases along the path rs determined by Scheme (B), or a large but negative $\pi_{r,s}$ is expected for rs with non-zero $K(\mathbf{G} \ominus rs)$.

v) The relative magnitudes of $\pi_{r,s}$ in each group can be predicted from the value of $Z_{\mathrm{G}\ominus rs}$.

Due caution is necessary for discussing the sign of the polarizabilities as given in detail in Ref. 27. Among the above five rules iv) is the most important. Namely, a fair amount of π-electrons in the conjugated hydrocarbon can flow along a path rs composed of alternately arranged double and single bonds, as in Scheme (B), so that the integral 5.2 becomes large. On the other hand, the working hypothesis used in the organic electron theory was found to be paraphrased to finding the route as in Scheme (B), which is now given a strong mathematical foundation.

Actually, in the case of cross-conjugation (Fig. 16), all the directions and regions of the electron flow caused by the hetero-atom substitution can be explained rather quantitatively in terms of the values of the Z index and Kekulé numbers through the characteristic polynomial for the relevant graph $\mathbf{G} \ominus rs$. Then Rule B2 could be explained by the graph-theoretical MO method.

For cyclic conjugated hydrocarbons, similar discussions can be followed and the conclusion obtained for acyclic systems can be applied to the general π-conjugated systems.

Recently the author extended this theory to exceedingly large PCAH networks with tens and hundreds of benzene rings, and found abnormal "tunneling electron transfer".[125] Namely if a single hetero-atom is substituted at one of the terminal carbon atoms of a large parallelogram-shaped PCAH, the interior π-electrons are unaffected and only those on the peripheral carbon atoms are perturbed. A big tide of electron waves comes from the opposite but not from the farthest end of the network. This phenomenon is not expected either from the classical organic electron theory or from the modern common understanding based on quantum chemistry. However, the cause of this interesting behavior could be explained by the same argument of the graph-theoretical MO method described here. The essence of this anomaly, though observed only in hypothetical systems, lies in intrinsic instability of parallelogram-shaped PCAH networks as shown in Chart 7.

Works along this line are in progress in the author's group.

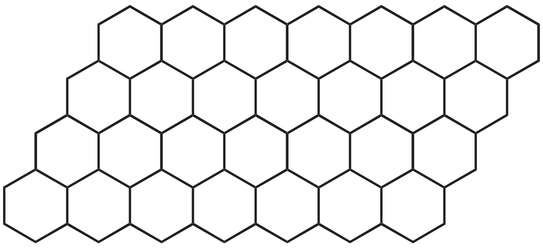


Chart 7.

The author expresses his sincere thanks to all the former (lady) students who have worked in his laboratory during his professorship in Ochanomizu University for 33 years. Although many names are documented as coauthors in the references cited above, all the results and discussions are supported also by the calculations and trials by other people. Special thanks are given to Professor Keiko Takano and Dr. Umpei Nagashima, without whose assistance the computer environment and guidance to the students would not have been established in his laboratory. The author has been encouraged by the colleagues in the fields of mathematical chemistry, chemistry, and mathematics in many countries, whose names are given below without their titles and affiliations: J.-I. Aihara, S. Aono, A. T. Balaban, K. Balasubramanian, S. Basak, D. Bonchev, R. Carbó-Dorca, S. Cyvin, J. R. Dias, M. Fujita, S. Fujiwara, K. Fukui, R. L. Graham, A. Graovac, I. Gutman, F. Harary, W. C. Herndon, K. Hirao, S. Hitotsumatsu, V. E. Hoggatt, Jr., S. Iwata, Y.-S. Jiang, R. B. King, E. C. Kirby, D. J. Klein, T. L. Kunii, R. B. Mallion, P. G. Mezey, N. Mizoguchi, H. Narumi, K. Nishimoto, E. Ōsawa, J. R. Platt, M. Randić, D. H. Rouvray, S. Sasaki, S. Tokita, and N. Trinajstić. Finally the author thanks to Professor H. Nohira who kindly offers him the opportunity to use the facilities of Saitama University for writing this paper.

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Haruo Hosoya , Emeritus Professor of Ochanomizu University received his Ph.D. degree in chemistry from University of Tokyo in 1964 under the supervision of Professor Saburo Nagakura, who also had a research group at The Institute of Physical and Chemical Research (RIKEN). Right after taking Ph.D. Hosoya joined this group as a researcher and worked for five years, during which he was a postdoctoral fellow at John Platt's group in University of Michigan for one year (1967–1968). In 1969 he became Associate Professor of Chemistry in Ochanomizu University. His appointments there for 33 years till his retirement are as follows: Associate Professor, 1969–1984; Professor, 1984–2002; Dean of Student Affairs, 1986–1987, Dean of Faculty of Science, 1990–1992. During this period he moved from Department of Chemistry to Department of Information Sciences in the same Faculty of Science in 1992. In 1988 he was a Visiting Professor at Arizona State University. He has also served in other scientific activities: In The Chemical Society of Japan, Vice President, 1996–1998, Editor of "Chemistry and Education", 1992–1994, Vice Chairman of Council of Chemical Education, 1998–2001, Chairman of Council of Chemical Education, 2001–present, Chairman of Division of Chemical Information, 1994–1996, 2002–present. He has been Chairman of CBI Association, 1993–2001, Chairman of Society of Chemical Software, 1996–2001, Chairman of Society of Computer Chemistry, Japan, 2002–present, Representative of Quantum Chemistry Data Base Group, 1990–present. He has been a member of more than five other societies. His research interests has included (1) Experimental and theoretical study on the reactive intermediate of organic reactions, (2) Molecular orbital calculations on the electronic structure of conjugated organic molecules, (3) Application of graph theory to chemistry and physics, (4) Chemistry in information sciences, (5) Construction of a new field, mathematical chemistry, in chemistry, (6) Chemical Education.