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Invited Review

Aromaticity Index Can Predict and Explain the Stability of Polycyclic Conjugated Hydrocarbons

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Summary. For deciphering the secret of the conventional *Hückel*'s $(4n+2)$-rule and also for extending it to polycyclic systems the aromaticity index, ΔZ, is introduced based on the graph-theoretical molecular orbital method, which has been developed by the present author. All the information either stabilizing or destabilizing the π-electronic system of a given graph **G** is contained in the characteristic polynomial, $P_G(x)$, obtained by expanding the secular determinant of *H*MO theory. Instead of this conventional procedure the present author succeeded in obtaining the general expression of $P_G(x)$ in terms of the non-adjacent number, $p(G, k)$, for G, defined for the topological index, Z_G. By extending this idea ΔZ is defined by taking into account all the contributions not only from the constituting rings but also from the possible combinations of disjoint rings in **G**. By using ΔZ mathematical origin of the *Hückel*'s rule was clarified and expanded to the "extended *Hückel*'s rule" for polycyclic conjugated systems. Applications to bicyclic and polycyclic networks are demonstrated. Discussion on the aromaticity of fullerenes and nanotubes is presented.

Keywords. Aromaticity index; Graph theory; *Hückel* molecular orbital; Nonbenzenoid aromatic hydrocarbon; Topological index.

Introduction

How do chemists understand the nature of the chemical bond? Chemists who are engaged not only in research but also in education always seek several working hypotheses for understanding and explaining the plausibility of the structures and stability of specific molecules. Examples of those working hypotheses and theories are pairing of odd electrons to form a covalent bond, octet theory by *Lewis* and *Langmuir* [1, 2], diagrammatic method of molecular orbital theory [3–5], *Hückel*'s

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rule [3], *etc*. Several of those working hypotheses are grounded on firm theoretical and experimental studies of atoms and molecules, while many of them may have been called just empirically derived formalisms such as the old "organic electron theory" proposed by *Robinson* and *Ingold* [6, 7], the rigorous proof of which has never been publicized until recently [8]. Admitting that they are just expedient tools or tips among the closed society of chemists, nowadays it is impossible to draw a borderline within which chemical thinking and jargons are meaningful.

With quite a formal manipulation of structural formulas involving electron dots chemists can realize, not theoretically but sensuously, the meaning of the following reaction formula.

$$\mathrm{H}\cdot \;+\; \cdot\mathrm{H} \;=\; \mathrm{H}-\mathrm{H}.$$

Originally this formalism has been proposed even without the proper understanding of the dual nature of electron unveiled by the theoretical and experimental progress of quantum mechanics in and after the 1920s. However, since *Heitler*, *London*, and *Sugiura* [9, 10] clarified the physical meaning of the covalent bond in a H_2 molecule formed by "a pair of unpaired electrons" of two H atoms, this diagrammatic recipe was deemed to be qualified also in other pair of atoms of the same species but only in a qualitative sense. It is to be noted here that since the electron spin does not appear explicitly in their formalism, physically important concept of the electron spin is skipped over from the resonance theory which the majority of chemists are using.

Then by the aid of the vague notion of "octet" one can understand why formal triple, double, single, and zero bonds are formed in N_2, O_2, F_2, and Ne_2, respectively. Failure of forming a quartet bond in C_2 may be ascribed to exceedingly high steric strain in the valence electrons of the C atoms. Actually this manipulation of chemical formulas with dots is a good conventional tool for realizing some characteristics of a series of homopolar diatomic molecules, as long as electron spin is not considered. However, from this formal valence bond method, or resonance theory, one cannot explain the triplet ground state of O_2 molecule. This deadlock can easily be resolved by the *Hund* rule [11] using the diagram of the molecular orbitals formed between a pair of atoms of the same kind. Regardless of the nature of electron spin this empirical rule has been playing an efficient pedagogical role for chemists to realize the importance of electron spin.

The instability of He_2 and Ne_2 can be ascribed to the "exchange repulsion" between a pair of closed shells. Further, this can be applied to the instability of Be_2 due to the exchange repulsion between a pair of "pseudo-closed shells" of 2s electrons. Of course, more quantitative information in terms of wavefunction and energy is needed for settling this argument at the level of quantum theorists.

How about the situation in the case of unfamiliar Li_2, whose spectroscopic data is actually available? Although MO theory had gained an advantage over VB method in explaining the electronic structure of homopolar diatomic molecules, without detailed knowledge of the wavefunctions one cannot predict or explain why lithium atoms tend to form metallic crystal rather than to form Li_2 molecules [12].

If one extends this line of reasoning how to understand the relative stability of very popular heteropolar diatomic molecules to a certain degree of accuracy, one again is forced to come to a much higher deadlock. It is hopeless to explain the electronic structure (*e.g.*, bond length, bond multiplicity, polarity, *etc.*) of the typical molecules as CO and NO without recourse to the results of *ab initio* molecular orbital calculations [13].

However, the interest of the majority of chemists is not focused on the detailed structure of these small molecules but on larger ones. From the view point of organic chemistry numerous challenging targets can be found in cyclic and acyclic conjugated hydrocarbon molecules, together with their derivatives. Among them benzenoid hydrocarbon molecules supplied a number of interesting problems both to organic and theoretical chemists [14–16]. Relative stabilities among their isomers were explained just by counting the number of *Kekulé* structures. However, this approach was beginning to break down when applied to heteroatomic systems, and with the rapid progress in computers and programming the VB approach was gradually overwhelmed by various versions of MO methods [17–19].

It should be noted here that good interplay between theoretical and experimental studies promoted a tremendous progress in the field of nonbenzenoid aromatic hydrocarbon chemistry [20, 21], where the most powerful guiding principle was the *Hückel*'s rule. Actually relative stabilities among typical nonbenzenoid hydrocarbon molecules with a few rings of different size can be roughly explained by this rule and also supported by *H*MO calculations. However, even for relatively small systems it is usually rather difficult to predict correctly the stability of a given nonbenzenoid hydrocarbon molecule without any MO calculation.

Until today no single naïve method has ever won the fame of the highest popularity for predicting the stability of these molecules.

On the other hand, graph-theoretical molecular orbital theory which has been developed by the group of mathematical chemists succeeded in clarifying the mathematical structure between the solution of the secular determinant and the topology of a given hydrocarbon molecule. The present author defined the aromaticity index using his ''topological index'' and derived the ''Extended *Hückel*'s Rule'' which can predict and explain the π-electronic stability of small polycyclic hydrocarbon molecules. *Aihara* has proposed ''topological resonance energy'' and discussed the aromatic character of a number of conjugated systems including nonbenzenoids. Since he uses the solutions of the matching polynomial, $\mathrm{M}_{\mathrm{G}}(x)$, which is defined in terms of the non-adjacent number, $p(\mathrm{G}, k)$, whose sum gives the present author's *Z*-index.

The purpose of this paper is to demonstrate how aromatic stability or instability can be predicted by back-of-envelop calculation for a number of condensed polycyclic nonbenzenoid (including benzenoid) hydrocarbon molecules.

Kekulé Structure and Algebraic Structure Count

Resonance between the pair of two *Kekulé* structures (Fig. 1a) of benzene stabilizes to a large extent relative to any other acyclic 6-π-electron system. Actually this statement is supported by sophisticated quantum-chemical calculations. However, discussion using spin algebra tells us that a pair of two *Kekulé* structures for $4n$-π-electron systems cannot be mixed with each other to give resonance stabilization. Thus one cannot formally apply the resonance scheme of Fig. 1a to $4n$-π-electron systems, *e.g.*, cyclobutadiene and cyclooctatetraene, as in Figs. 1b and 1c.

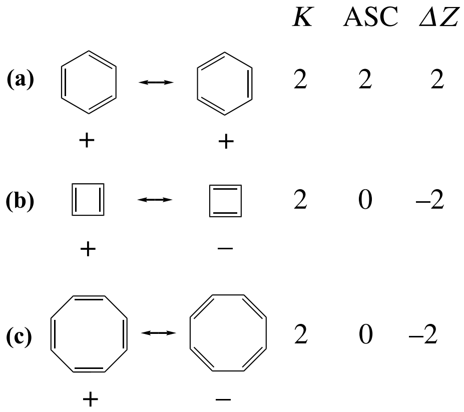


Fig. 1. Signed *Kekulé* structures and algebraic structure count of benzene, cyclobutadiene, and cyclooctatetraene

However, this difficulty has already been resolved by *Dewar* and *Longuet-Higgins* [22] who defined a parity to each *Kekulé* structure and showed that the algebraic sum of all the *Kekulé* structures can predict the stability of conjugated π-electronic systems. This algebraic sum is now called algebraic structure count (ASC) [23].

The relative signs of a pair of resonance structures are the same, when they are mutually interchanged by rotating an odd number of double bonds as in the case of benzene, while the signs become opposite for the interchange of an even number of double bonds as in the cases of cyclobutadiene and cyclooctatetraene (see the $+$ and $-$ signs in Fig. 1; see also Fig. 9). ASC is defined as the absolute value of the sum of the signs of all the *Kekulé* structures for a given conjugated hydrocarbon molecule. Thus ASC of benzene is 2 and those of the two antiaromatic $4n$-π-electron systems are zero.

By modifying in this way resonance theory can be formally used as a working hypothesis still compatible with the *H*MO theory proposed by *Hückel* [3]. It is strange to consider the fact that this useful concept of ASC is almost ignored by modern organic chemists, although quite an empirical formalism of the organic electron theory by *Robinson* [6] and *Ingold* [7] proposed before the birth of quantum mechanics is still used as a powerful guiding principle.

Since the essence of the *Hückel* theory is well known, only a few remarks related to it will be mentioned here. He showed that $(4n+2)$-membered cyclic hydrocarbon molecules get extraordinary high π-electronic stability relative to the acyclic counterparts, while the reverse is true for cyclic $4n$-membered systems. He has treated mainly monocyclic conjugated systems, and the conclusion he has drawn is based on the numerical solutions, though a little analytically, of the secular determinant automatically derived from the π-electronic systems according to his recipe. Thus the *Hückel*'s rule is not guaranteed to be applied to any polycyclic system and the origin of the difference in stability between $4n$- and $(4n+2)$-π-systems has not been clarified by him.

If we are concerned only with benzenoid aromatic hydrocarbons, all the *Kekulé* structures are shown to have the same sign and the number, *K*, of the *Kekulé* structures, which is equal to ASC, has been shown to be a good index for the stability of molecules. Further, *Clar* [24] introduced the concept of aromatic sextet represented by a circle in a hexagon for predicting the stability of polycyclic aromatic hydrocarbon molecules. Later mathematical foundation of his theory was given by the group of the present author [25].

Topological Index and Characteristic Quantities of a Graph

Consider the carbon atom skeleton of a given hydrocarbon molecule and represent it as a graph **G** composed of vertices (C atoms) and edges (CC bonds). Benzene is represented by a hexagon, whose algebraic expression is the adjacency matrix, **A**, with such element a_{ij} that is unity if vertices i and j are adjacent (or forming a CC bond) and zero otherwise. By using **A** and the unit matrix **E** (e_{ii} is 1 and 0 otherwise) the characteristic polynomial, $\mathrm{P_G}(x)$, of graph **G** with N vertices is defined by Eq. (1) which is also derived by expanding the secular determinant, $\Delta(x)$, of *Hückel* molecular orbitals (Eq. (2)) by putting $\varepsilon = \alpha + x\beta$.

$$\mathrm{P_G}(x) = (-1)^N \det(\boldsymbol{A} - x\mathbf{E}), \tag{1}$$

$$\Delta(x) = \begin{vmatrix} \alpha-\varepsilon & \beta & 0 & \cdots \\ \beta & \alpha-\varepsilon & \beta & \cdots \\ 0 & \beta & \alpha-\varepsilon & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{vmatrix} \tag{2}$$

For example, $\mathrm{P_G}(x)$ of benzene is obtained to be $x^6 - 6x^4 + 9x^2 - 4$.

Then with this x-expression the problem is reduced to get the sum of the upper half of the solution of $\mathrm{P_G}(x) = 0$, yielding the total π-electronic energy, E_π as shown by Eq. (3), for a graph with an even N.

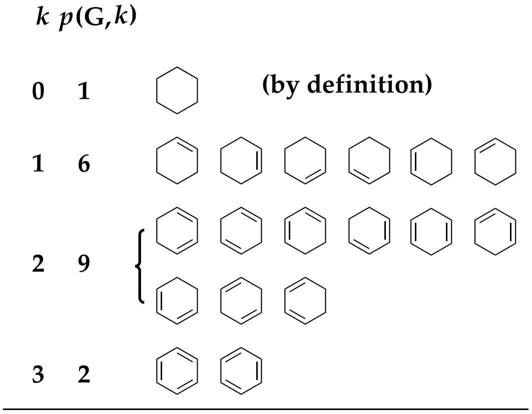
$$E_\pi = 2\sum_{k=1}^{[N/2]} x_k, \tag{3}$$

For benzene E_π is obtained to be $2(1+1+2) = 8$ as is well known. It has been shown that the conventional *H*MO method can be reduced to a great extent by using the graph-theoretical technique [8].

First define the non-adjacent number [26], $p(\mathrm{G}, k)$, as the number of ways for choosing k disjoint edges from **G**, with $p(\mathrm{G}, 0)$ being unity for any graph. Then the Z-index (originally coined as "topological index" by the present author [27]) is defined as the sum of all the $p(\mathrm{G}, k)$s for **G** (Eq. (4)) where m is the maximum number of $k = [N/2]$ for **G** with N vertices.

$$Z_\mathrm{G} = \sum_{k=0}^{m} p(\mathrm{G}, k). \tag{4}$$

Figure 2 illustrates how to obtain the $p(\mathrm{G}, k)$ and Z values by taking 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.



$Z_G = 18$ $\quad M_G(x) = x^6 - 6x^4 + 9x^2 - 2$

$\tilde{Z}_G = 20$ $\quad M_G(x) = x^6 - 6x^4 + 9x^2 - 4$

Fig. 2. Counting $p(G, k)$s and Z_G for hexagonal graph

By using $p(G, k)$s the matching polynomial [28], acyclic polynomial [29], or reference polynomial [30], $M_G(x)$, was proposed by several groups to be defined by Eq. (5).

$$M_G(x) = \sum_{k=0}^{m} (-1)^k p(G, k)\, x^{N-2k}. \tag{5}$$

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, $\{S_N\}$, form the family of the *Fibonacci* numbers ($F_N = 1, 1, 2, 3, 5$, *etc.*, see Table 1), while those of cyclic alkanes (or alkenes) or monocyclic graphs, $\{C_N\}$, are *Lucas* numbers ($L_N = 2, 1, 3, 4, 7$, *etc.*, see Table 2). Although it is not contained in Table 1, $p(G, 0)$ and Z_G of the vacant graph, denoted by ϕ, with no vertex and edge are both defined as unity.

Both series of the Z_G numbers in Tables 1 and 2 are characterized by a common recursion relation (Eq. (6)).

$$f_N = f_{N-1} + f_{N-2} \quad (f = F \text{ and } L). \tag{6}$$

Table 1. $p(G, k)$ numbers and Z-index of path graphs

N	$G = S_N$	p(G, k)				$Z_G = F_N$
		$k = 0$	1	2	3	
1	o	1				1
2	o–o	1	1			2
3	o–o–o	1	2			3
4	o–o–o–o	1	3	1		5
5	o–o–o–o–o	1	4	3		8
6	o–o–o–o–o–o	1	5	6	1	13

By rotating this table counter clockwise by 45° the Pascal's triangle appears

Table 2. $M_G(x)$, Z_G, and $P_G(x)$ of monocyclic graphs

N	$M_G(x)$[b]	$Z_G = L_N$[c]	$P_G(x)$
2[a]	$x^2 - 2$	3	$x^2 - 4$
3	$x^3 - 3x$	4	$x^3 - 3x - 2$
4	$x^4 - 4x^2 + 2$	7	$x^4 - 4x^2$
5	$x^5 - 5x^3 + 5x$	11	$x^5 - 5x^3 + 5x - 2$
6	$x^6 - 6x^4 + 9x^2 - 2$	18	$x^6 - 6x^4 + 9x^2 - 4$
7	$x^7 - 7x^5 + 14x^3 - 7x$	29	$x^7 - 7x^5 + 14x^3 - 7x - 2$
8	$x^8 - 8x^6 + 20x^4 - 16x^2 + 2$	47	$x^8 - 8x^6 + 20x^4 - 16x^2$

[a] This graph is composed of two vertices and two edges; the off-diagonal elements $a_{12} = a_{21} = 2$;
[b] the absolute values of the coefficients are the p(G, k)s; [c] *Lucas* number; $L_0 = 2$ and $L_1 = 1$

However, the relation between $P_G(x)$ and $M_G(x)$ is different in the cases of the two kinds of graphs, trees (Table 1) and non-trees (Table 2). Namely, for a tree graph $P_G(x)$ can easily be obtained just from the counting of $p(G, k)$ numbers without decomposing the determinant as has been shown by the present author (Eq. (7)) [26].

$$P_G(x) = \sum_{k=0}^{m} (-1)^k p(G, k)\, x^{N-2k} \quad (G \in \text{tree}). \tag{7}$$

Then from Eqs. (5) and (7) one gets Eq. (8).

$$P_G(x) = M_G(x) \quad (G \in \text{tree}) \tag{8}$$

It was also found that there is a one-to-one correspondence between the $p(G, k)$ numbers of $\{S_N\}$ and the elements of the *Pascal*'s triangle as symbolically expressed by Eq. (9), the lower members of which are already given in Table 1. For later discussion let us denote the $P_G(x)$ of a path graph S_N also as $S_N(x)$. Namely, we have Eq. (10).

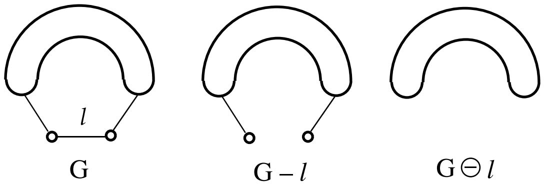
$$p(S_N, k) = \binom{N-k}{k} \tag{9}$$

$$S_N(x) = \sum_{k=0}^{[N/2]} (-1)^k \binom{N-k}{k} x^{N-2k}, \tag{10}$$

On the other hand, for non-tree graphs complicated correction terms should be added to $M_G(x)$ to get $P_G(x)$. However, for monocyclic graphs, $\{C_N\}$, $P_G(x)$ can be obtained just by subtracting 2 from $M_G(x)$ as deduced from Table 2 (Eq. (11)).

$$P_G(x) = M_G(x) - 2 \quad (G \in \text{monocyclic graph}) \tag{11}$$

This is the secret of the conventional *Hückel*'s rule. That is, by extending Table 2 down to higher members it is easily deduced 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 becomes to be -4 (=$-2 - 2$). Then the former group would



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

$$\mathrm{Z}_{\mathrm{G}} = \mathrm{Z}_{\mathrm{G}-l} + \mathrm{Z}_{\mathrm{G}\ominus l}$$

$$\mathrm{M}_{\mathrm{G}}(x) = \mathrm{M}_{\mathrm{G}-l}(x) - \mathrm{M}_{\mathrm{G}\ominus l}(x)$$

Fig. 3. Recursion relations for $p(\mathrm{G},k)$, Z_{G}, and $\mathrm{M}_{\mathrm{G}}(x)$

have doubly degenerate NBMOs, while the HOMO-LUMO gap of the latter group would become large.

Namely, aromaticity and antiaromaticity of monocyclic graphs is caused, respectively, by in-phase and out-of-phase combinations of the constant term of $\mathrm{M}_{\mathrm{G}}(x)$ and the ring-correction term in Eq. (11).

It is to be noted here that this discussion, as *Hückel* did, is solely limited to the monocyclic graphs, and 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.

In this paper we are going to show how these correction terms arise and work to the stability of π-electronic structure of hydrocarbon molecules containing a ring or rings, and how we arrive at the extended *Hückel*'s rule [31].

Before going into the main part of this theory the important recursion relations as Eq. (6) for other characteristic quantities will be explained here (see Fig. 3). 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 $\mathbf{G}\Theta l$. 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 given by Eq. (12).

$$p(\mathrm{G},k) = p(\mathrm{G}-l,k) + p(\mathbf{G}\Theta l,k-1). \tag{12}$$

By accumulating Eq. (12) for a given graph one can obtain the recursion formula of Z_{G} as shown by Eq. (13).

$$Z_{\mathrm{G}} = Z_{\mathrm{G}-l} + Z_{\mathrm{G}\Theta l}. \tag{13}$$

Similarly the recursion formula for the matching polynomial is obtained (Eq. (14)).

$$\mathrm{M}_{\mathrm{G}}(x) = \mathrm{M}_{\mathrm{G}-l}(x) - \mathrm{M}_{\mathrm{G}\Theta l}(x) \tag{14}$$

This idea comes from the "inclusion-exclusion principle" [32] which is one of the main principles frequently used in the enumeration problems in discrete mathematics, such as graph theory and combinatorics.

Direct application of Fig. 3 to a monocyclic graph, C_N, whose matching polynomial is expressed by $C_N(x)$, yields Eq. (15).

$$C_N(x) = S_N(x) - S_{N-2}(x). \tag{15}$$

Further, it is to be mentioned here that the recursion formula for $P_G(x)$ of polycylic graphs becomes rapidly complicated with increase of the number of rings [33, 34].

Characteristic Polynomial of Polycyclic Graphs

For discussing the effect of more than two rings in a conjugated system one needs to have the expression of $P_G(x)$ in terms of the $p(G,k)$ numbers, which was obtained by the present author in 1972 [35]. Namely, the characteristic polynomial of a polycyclic graph **G** is expressed in terms of the $p(G,k)$ numbers of **G** and its subgraphs as shown by Eq. (16).

$$\begin{aligned} P_G(x) &= \sum_{k=0}^{m} (-1)^k p(G,k)\, x^{N-2k} \\ &\quad + (-2) \sum_{r}^{\text{Ring}} \sum_{k=0}^{m_r} (-1)^{k+n_r} p(G\Theta R_r, k)\, x^{N-n_r-2k} \\ &\quad + (-2)^2 \sum_{r>s}^{\text{Ring}} \sum_{k=0}^{m_{rs}} (-1)^{k+n_r+n_s} p(G\Theta R_r \Theta R_s, k)\, x^{N-n_r-n_s-2k} \\ &\quad + \cdots \\ &= M_G(x) - 2 \sum_{r}^{\text{Ring}} M_{G\Theta R_r}(x) + 4 \sum_{r>s}^{\text{Ring}} M_{G\Theta R_r \Theta R_s}(x) - \cdots \end{aligned} \tag{16}$$

The first term is the matching polynomial $M_G(x)$ with no ring contribution, and the second summation term counts the contribution from the isolated rings, R_rs, where $G\Theta R_r$ is the subgraph of **G** obtained by deleting ring R_r together with all the edges incident to R_r. The third term 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 $P_G(x)$ of a polycyclic graph is expressed by the set of the matching polynomials of **G** and the subgraphs obtained by deleting a ring or set of disjoint rings from **G**. It is easily seen that the Eqs. (7), (8), and (11) are contained in Eq. (16), which is the basis for the extended *Hückel*'s rule of aromaticity applied to polycyclic conjugated systems.

Sachs has proposed an elegant formulation for generating the coefficients of $P_G(x)$ by using the "*Sachs* graph" [36, 37]. However, practically it is rather difficult to apply his theorem to a graph with at about ten vertices, because no recursive relation is available for handling many *Sachs* graphs.

Modified *Z* Index and Extended *Hückel*'s Rule

Coulson and *Longuet-Higgins* have developed beautiful perturbation theory in *H*MO without solving $P_G(x)$ but by taking the contour integrals of the functions derived from $P_G(x)$ over the complex plane around the poles at the eigenvalues [38]. However, they did not scrutinize the contribution of each component of a graph. The essence of our graph-theoretical molecular orbital theory (GTMO)

[8, 31] has filled this gap by defining the topological bond order [39, 40] and modified Z-index [31] supported by Eq. (16). In these studies it was clarified that the contribution from the terms of odd powers in $P_G(x)$ is almost wiped out by taking the integral along the imaginary axis [31].

Then the modified Z index, $\tilde{Z}_G$, was proposed to be defined by Eq. (17) and the aromaticity index, ΔZ_G, was defined as the difference between $\tilde{Z}_G$ and Z_G (Eq. (18)).

$$\tilde{Z}_G = \sum_{k=0}^{m} (-1)^k a_{2k}, \tag{17}$$

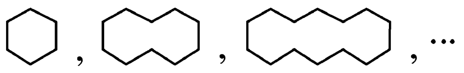
$$\Delta Z_G = \tilde{Z}_G - Z_G \tag{18}$$

The index $\tilde{Z}_G$ extracts the essential contribution to the π-electronic energy from $P_G(x)$, while Z_G sums up the topological contribution other than ring formation from $M_G(x)$. Then positive and negative values of ΔZ_G, respectively, indicate aromatic and anti-aromatic character of the π-electronic conjugated system **G**.

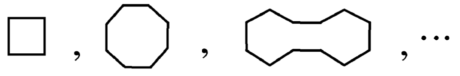
Aihara defines his topological resonance energy as the difference between the eigenvalue sums of $P_G(x)$ and $M_G(x)$, and has performed extensive study on the aromaticity of a variety of conjugated hydrocarbon molecules and ions [30]. The numerical values of his analysis is naturally in parallel with what is obtained by the aromaticity index, as his theory is also based on the $p(G, k)$ numbers.

By taking into account the meaning of Eq. (16) the contributions from the component rings of graph **G** can be divided into several categories as follows (Eq. (19)).

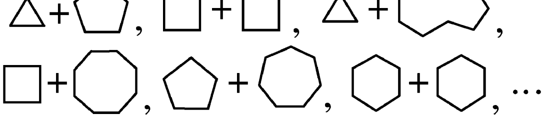
$$\Delta Z_G = 2 \sum_{\substack{r=1 \\ n=4k+2}}^{R} Z_{G\ominus R}$$



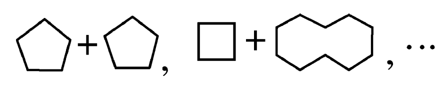
$$-2 \sum_{\substack{r=1 \\ n=4k}}^{R} Z_{G\ominus R}$$



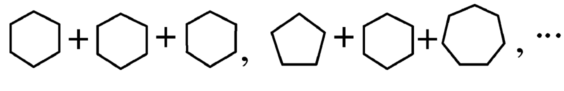
$$+4 \sum_{\substack{r=2 \\ n=4k}}^{R} Z_{G\ominus R}$$



$$-4 \sum_{\substack{r=2 \\ n=4k+2}}^{R} Z_{G\ominus R}$$



$$+8 \sum_{\substack{r=3 \\ n=4k+2}}^{R} Z_{G\ominus R}$$



$$+ \cdots \tag{19}$$

This equation shows two important factors governing the π-electron stability of a ring network, namely, the value of the Z-index of subgraph GΘR and the sign given to each term. The first two lines give the well-known *Hückel*'s rule. Namely, a $(4n+2)$-membered ring stabilizes, while 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.

The selection rule for the combined contribution from odd number of rings goes back to the case of a single ring, while for the case with even number of disjoint rings the selection rule is the same as the case with a pair of disjoint rings.

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 graphs $+2$, and (iii) for $(4n)$-membered monocyclic graphs -2. The definition of Eq. (17) was deliberately chosen so, 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.

Bicyclic Networks

Consider the relative energies of naphthalene and two other bicyclic 10-π isomers as shown in Fig. 4, whose calculated π-electronic properties are also given. Although the hydrocarbon **48** composed of a tetragon and an octagon is the least stable, it has the largest Z-index and *Kekulé* number. However, $\tilde{Z}_G$ index and ΔZ show good correlation with E_π. Further, algebraic structure count (ASC) reflects

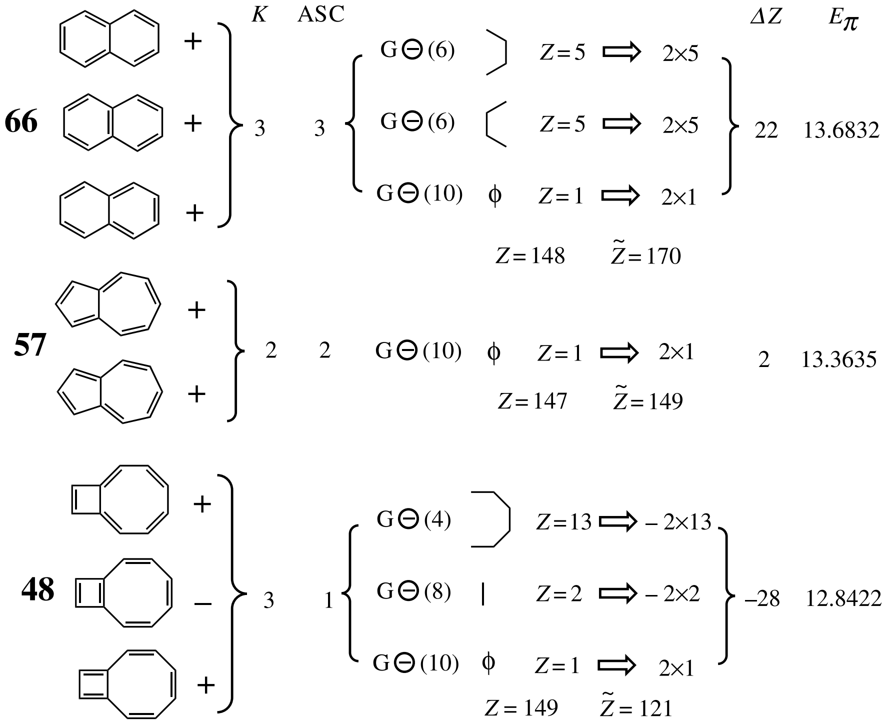


Fig. 4. Calculation of ΔZ values for three isomers of naphthalene

correctly the order of stability. Note that even if nonbenzenoid hydrocarbons are treated in this study, the absolute values of the constant term of $P_G(x)$, which are not shown here, were found to be equal to the square of ASC in parallel with the π-electronic stability.

In this case the ΔZ value is contributed either from the first or second line of Eq. (19) as depicted in Fig. 4. For example, delete a hexagon together with the two incident edges from naphthalene **66**, and a butadiene skeleton S_4 is left, whose Z-index is 5. Then according to the first line in Eq. (19) one gets $+10$ for each hexagon. By deleting the peripheral 10-membered ring, which is to be counted as a component ring, a vacant graph S_0 is left, whose Z-index is unity, and one gets $+2$. The ΔZ value of **66** is thus 22. As the azulene skeleton **57** receives only $+2$ for ΔZ from the peripheral ring, its π-electronic character is slightly aromatic. On the other hand, the network **48** becomes highly anti-aromatic by receiving negative contributions from the component tetragon and octagon.

Next consider a group of bicyclic graphs with an even N constructed by joining a pair of rings with an edge of a unit length as the biphenyl network **6**–**6** (See Fig. 5). In this case the third and fourth lines of Eq. (19) need to be considered.

Comparison of ΔZ values should be made among the isomers with the same number of vertices. However, the aromaticity of biphenyl **6**–**6** is prominent by receiving positive contributions both from the component hexagons and the pair of disjoined hexagons as implied in the first and third lines of Eq. (19). It is important to notice that in larger polycyclic aromatic hydrocarbons toward graphite each hexagon contributes toward stabilization of the system not only by itself but also by forming sets with as many disjoint hexagons as possible.

It is instructive to see how the 10-π **4**–**6** network becomes anti-aromatic. For compounds in which $4n$- and $(4n+2)$-rings are competing, the contribution from the smaller ring exceeds that from the larger ring, because of the difference in the size of **G**ΘR.

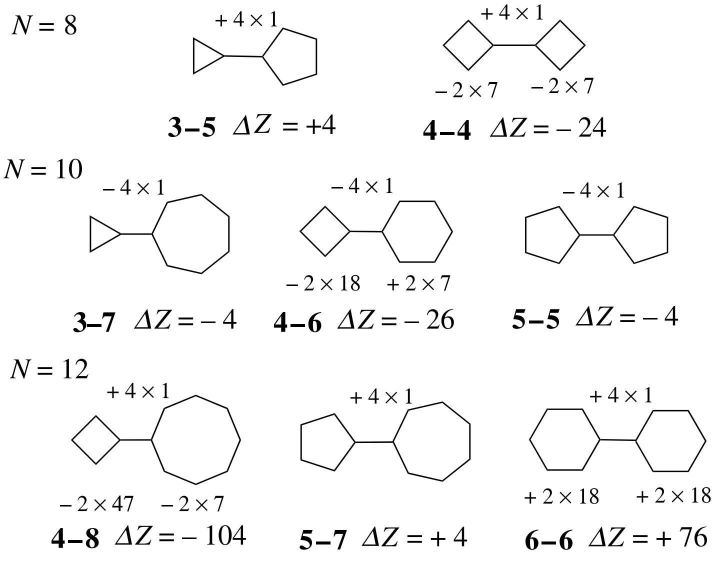


Fig. 5. Aromaticity indices of analogues of biphenyl

In Fig. 5 there are four networks composed of only odd-membered rings, among which **3**–**5** and **5**–**7** are predicted to be a little aromatic and actually have been synthesized, while **3**–**7** and **5**–**5** are a little anti-aromatic and have not been synthesized yet. This difference comes from the "reverse-$(4n+2)$-rule" in the third and fourth lines of Eq. (19) for the pair of disjoint rings.

Tricyclic Networks

Let us consider the relative energies of twenty-one isomers of anthracene **6662** with three catacondensed rings and 14-π-electrons as shown in Fig. 6, where the dashed lines divide the isomers into five subgroups, **A** to **E**, within each of which the set of the constituting ring components are common. The first three digits denote the size and ordering of the constituting rings, while the last digit distinguishes the positional isomers of the systems with the same order and same size of the constituting rings. In Table 3 the ΔZ values and all the contributions from the component rings of the isomers are shown and compared with E_π, K, and ASC. They are arranged in the descending order of ΔZ, and are rather well correlated with E_π as seen in Fig. 7. It can be deduced from these results that the relative π-electronic stability of these hydrocarbons are roughly determined by the constituent rings in the order of the groups, $\mathbf{A} > \mathbf{B} > \mathbf{C} > (\mathbf{D}, \mathbf{E})$. Among all the isomers only **8642** is triplet in the ground state and behaves as an outlyer from the group of plots of all other isomers in Fig. 7.

Although the ring contributions to the ΔZ values for each isomer can be traced from Table 3, a detailed breakdown is illustrated in Fig. 8 with **6842** chosen as an example, where the dashed rings and bold-lined graphs, respectively, represent the Rs to be deleted and resultant **G**ΘRs contributing to stabilization or destabilization of the π-electronic system. By following this figure one can realize why **6842** is

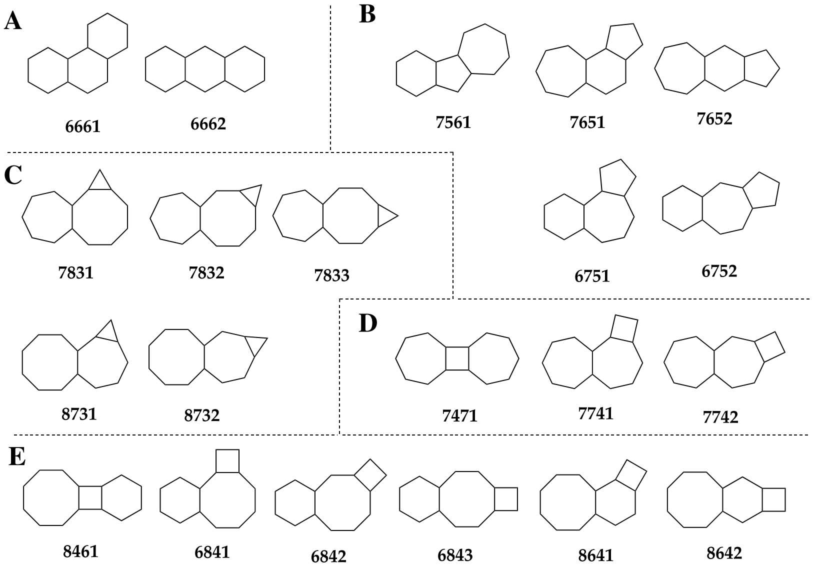


Fig. 6. Twentyone isomers of 3-ring and 14-π catacondensed hydrocarbons

Table 3. Ring contribution to the ΔZ value and other characteristic quantities of 3-ring 14-π catacondensed hydrocarbons

No.	E_π	ΔZ	Ring contribution	K	ASC	Note
6661	19.4483	256	+256 (6×3, 10×2, 14, 6 + 6)	5	5	
6662	19.3137	232	+232 (6×3, 10×2, 14, 6 + 6)	4	4	
6751	19.1086	98	+98 (6, 10, 14)	3	3	
7561	19.0949	96	+96 (6, 10, 14)	3	3	
6752	19.0837	92	+92 (6, 10, 14)	3	3	
7651	19.0377	58	+58 (6, 14, 6 + 6)	2	2	
7652	18.8942	54	+54 (6, 14, 6 + 6)	2	2	
7832	18.8317	−26	+2 (14) −28 (8, 3 + 7)	2	2	
7833	18.6831	−30	+2 (14) −28 (8, 3 + 7)	2	2	[a]
7831	18.6890	−34	+2 (14) −36 (8, 3 + 7)	2	2	[a]
8732	18.6258	−54	+2 (14) −56 (8×2)	3	1	
8731	18.6286	−56	+2 (14) −58 (8×2)	3	1	
8461	18.6061	−90	+106 (6, 10, 14) −196 (4, 8×2, 8 + 6)	5	1	
7471	18.5328	−130	+2 (14) −132 (4, 12)	2	2	[a]
6842	18.6791	−152	+92 (6, 10, 14) −244 (4, 8, 12, 4 + 6)	4	2	
6843	18.4940	−162	+96 (4, 10, 14) −258 (4, 8, 12, 4 + 6)	5	1	
6841	18.4858	−172	+100 (6, 10, 14) −272 (4, 8, 12, 4 + 6)	5	1	
8642	18.0924	−206	+58 (6, 14, 4 − 8) −264 (4, 8×2, 12)	4	0	[b,c]
7742	18.4128	−212	+2 (14) −214 (4, 12)	3	1	
7741	18.3950	−228	+2 (14) −230 (4, 12)	3	1	
8641	18.3443	−232	+62 (6, 14, 4 + 8) −294 (4, 8×2, 12)	5	1	

[a] With one NBMO; [b] With 2-NBMOs and expected to be triplet ground state; [c] outlyer

highly anti-aromatic as the result of competition between the $4n$- and $(4n+2)$-membered rings in the network. The first, second, and third columns in Fig. 8 correspond, respectively, to the first, second, and fourth lines of Eq. (16). The most crucial factor for determining the anti-aromatic character of this network is in the difference between the effects caused by the tetragon and hexagon. The destabilizing effect by the smaller tetragon (104×2) is much larger than the stabilizing effect by the hexagon (40×2). In this way one can predict and explain why and how a given polycyclic hydrocarbon network becomes aromatic or anti-aromatic

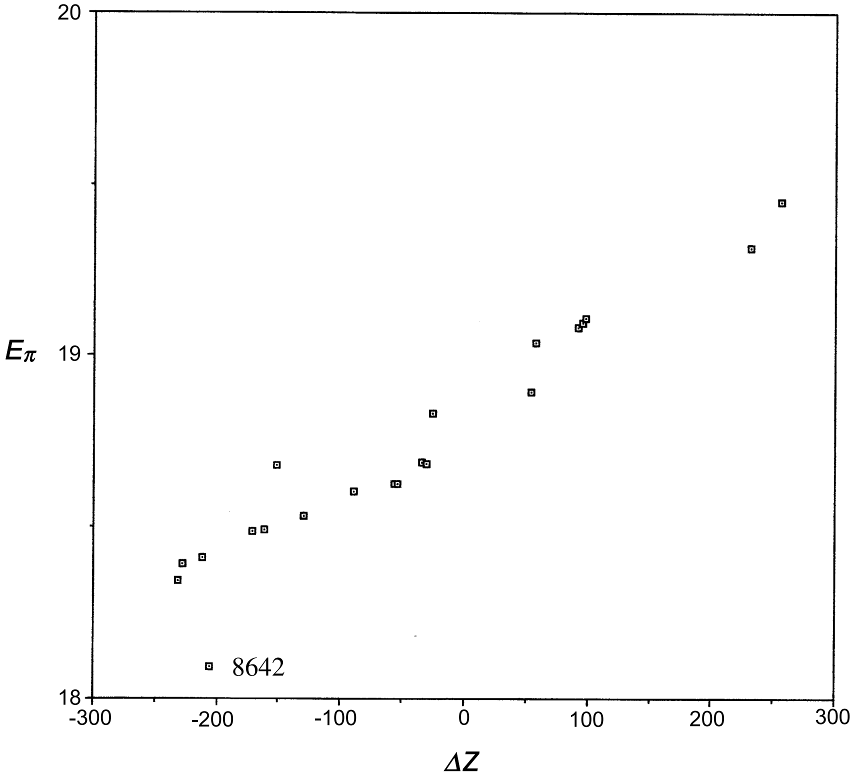


Fig. 7. Correlation between ΔZ and E_π of 3-ring and 14-π catacondensed hydrocarbon isomers

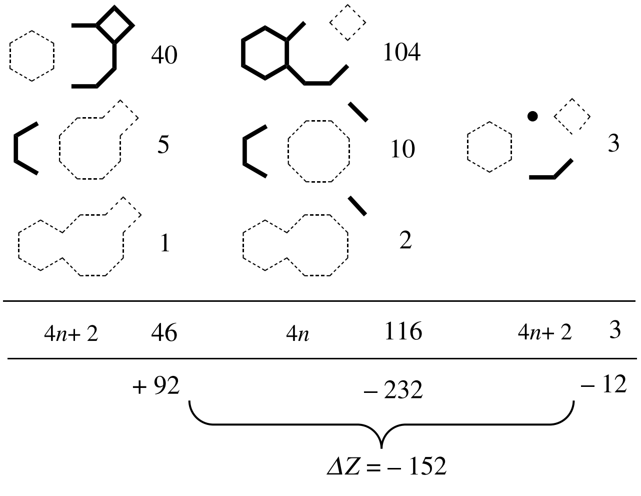


Fig. 8. Competition between the stabilizing and destabilizing effects by the component rings of **6842**

determined not only by the constituent rings but also by all the possible combinations of them. To the author's awareness there has been proposed no other simple index to be compatible with ΔZ for this purpose.

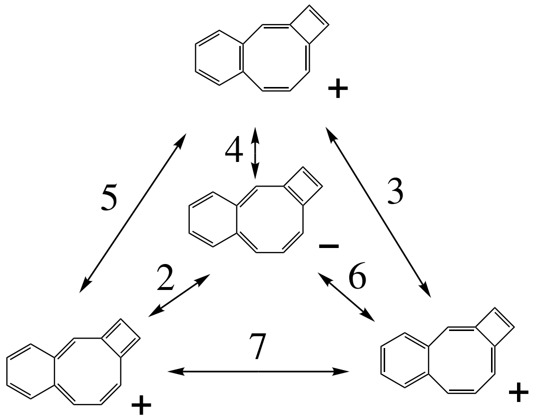


Fig. 9. Assignment of the parity (+, −) to each *Kekulé* structure of **6842** by enumerating the number of conjugated double bonds for cyclic interchange between the pair of *Kekulé* structures

It is to be remarked on the ASC of these isomeric systems. Just by looking at Table 3 correlation between ASC and E_π does not seem to be high. However, if one compares the results within each subgroup, correlation turns out not to be so bad.

Here assignment of the parity to each *Kekulé* structure to get ASC is illustrated in Fig. 9 with **6842** taken as an example, where the number attached to a double-headed arrow denotes the number of conjugated double bonds to be interchanged between the pair of *Kekulé* structures. In this case the central *Kekulé* structure is transformed to all other *Kekulé* structures with cyclic interchange of an even number of double bonds, while the outer three members are transformed into each other by interchanging an odd number of conjugated double bonds, and thus have the same sign.

However, it is known that for some special types of pericondensed ring systems a sign cannot uniquely be given to each *Kekulé* structure, and ASC does not work at all [37, 41]. On the contrary, the idea of the aromaticity index, ΔZ, can quite easily and successfully be applied to any polycyclic conjugated hydrocarbon network to predict and explain its aromatic or anti-aromatic character. Finally a brief discussion on the aromaticity of fullerene and nanotube networks will be given.

Fullerenes, Nanotubes, and Graphite

First consider the graphite network which is composed of only hexagons. As Eq. (19) implies, the sign of the ΔZ-contribution from the disjoint set of any number of hexagons is positive accelerating enhanced aromatic character to the whole network of graphite. However, there are also negative contributions arising from certain kinds of combinations of hexagonal rings. As shown in Fig. 10 a ring component circumscribing a group of condensed hexagons belongs either to $4n$- or $(4n+2)$-membered ring, respectively, giving negative or positive contribution to ΔZ according to the first two lines in Eq. (19). The former component is characterized by an odd number of inner vertices, while the latter by an even number or zero. Although it is difficult to perform rigorous analysis, enumeration for smaller ring components reveals that the number of possible $(4n+2)$-membered rings exceeds that of the $4n$-group. Further, a pair of rings fiom the same class gives

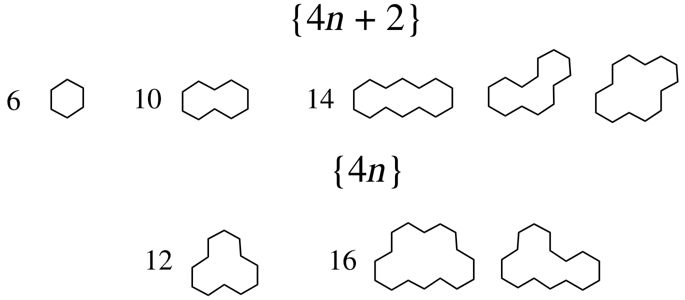


Fig. 10. Two classes of circumscribing condensed hexagons

positive contribution to ΔZ, while a pair of rings originating from different classes negative. Similar arguments follow for the group contribution of disjoint rings of more than two. Anyway the above analysis of the tricyclic isomers ensures that polybenzenoid networks toward graphite gain extraordinary higher aromatic character than nonbenzenoids.

A nanotube is constructed by rolling up a graphite sheet and capping at the both ends. According to the *Euler*'s theorem mathematically simplest capping at each end is performed by inserting six pentagons in the graphite network. Just consider a pair of pentagons in a nanotube network. Whether they are isolated from each other or condensed to form an octagon, their contribution to ΔZ is negative as deduced from the above discussion. Note that the degree of instability brought by an octagon is larger than a pair of isolated pentagons. As derived from the second and fourth lines in Eq. (19). Thus the set of twelve pentagons in any nanotube or fullerene network diminishes the aromatic character of the parent graphite sheet to some extent, which is strengthened as the degree of condensation of pentagons in the network. As a consequence the soccer-ball type C_{60}, in which all the twelve pentagons are isolated from other pentagons, is the most stable among the 1812 isomers. Actually the ΔZ values of all the isomers of C_{60} were found to be beautifully classified into several groups stepwise depending on the number of adjacent pairs of pentagons [42].

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