CHARACTERIZATION OF POLYHEX GRAPHS AS APPLIED TO CHEMISTRY

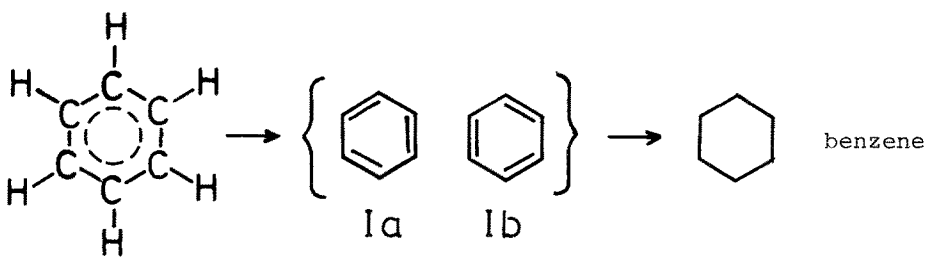
H. Hosoya
Department of Chemistry, Ochanomizu University,
Bunkyo-ku, Tokyo, Japan 112

Abstract. A polyhex graph represents the carbon atom skeleton of a condensed polycyclic aromatic hydrocarbon, a family of benzene-like molecules. Various methods for characterizing the polyhex graphs are described and discussed, including the topological index, characteristic polynomial, sextet polynomial, etc. Enumeration of the number of the maximum matching (or Kekulé patterns) is also discussed.

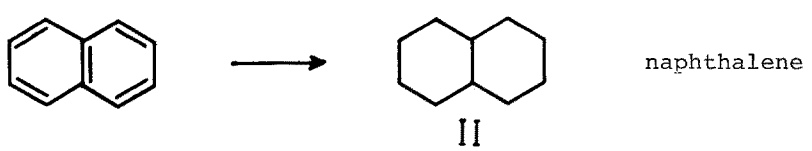
1. Introduction

There have been known among the chemists a number of "condensed polycyclic aromatic hydrocarbons (CPCAH)" whose skeletal structures are represented by what the graph-theoreticians like to call as polyhexes or hexagonal animals.

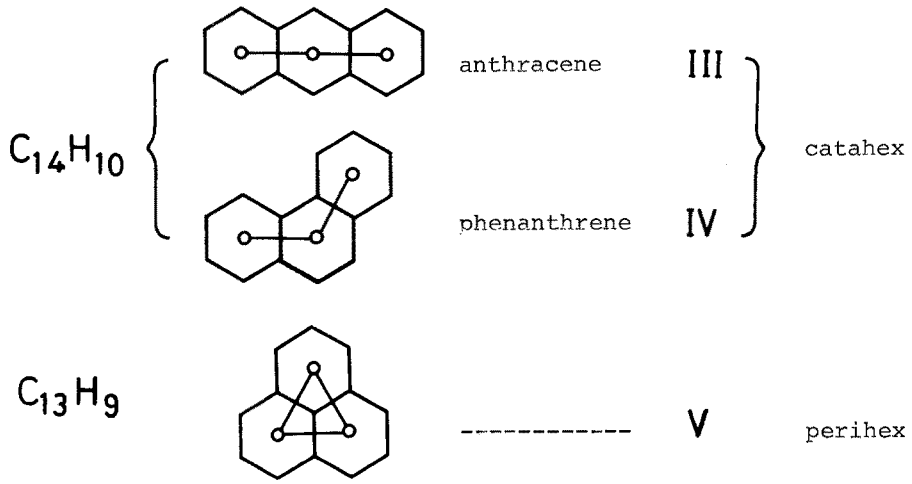
Benzene, C_6H_6, which is the most fundamental molecule among them, is a regular hexagonal molecule and plays as their unit structure.



Naphthanlene, $C_{10}H_8$, is known as a molecule in which two benzene rings are fused.



There are three possible structures for three regular hexagons to be fused into one connected graph as shown below:



Namely, there are three 3-hexagonal animals. However, no stable compound has ever been isolated or synthesized corresponding to the third entry (V), since it has an odd number of points (carbon atoms). Thus in chemical sense, only those polyhexes are called as isomers which have both the same numbers of hexagons and points. Anthracene (III) and phenanthrene (IV) are isomers each other, while compound (V) is not.

The number of isomeric polyhexes (either graph-theoretical or chemical) rapidly increases with the number of hexagons, whose enumeration has been partly accomplished by Harary and Read [1]. Polyhexes are classified into two groups, i.e., catahexes and perihexes, depending that the dual graph is a tree or a non-tree. Graphs I to IV are catahexes, while V is a perihex. Enumeration of the number of perihexes seems to be almost impossible [2].

Generally isomeric compounds have different properties and stabilities. For example, compound III is less stable than IV. The reason for the difference in the stabilities is attributed to the difference in their mathematical properties, mainly in the following two respects. i) The number of the maximum matching or the Kekulé numbers K(G)'s for III and IV are, respectively, 4 and 5 as shown in Fig. 1. ii) The sum of the positive roots of the characteristic polynomial

$$P_G(x) = (-1)^N \det(A - XE)$$

$$= \sum_{k=0}^{N} a_k \, x^{N-k} \qquad (1)$$

is larger for IV than for III, which can be presumed from the absolute values of the determinant of the adjacency matrix A, or of the last term a_N of $P_G(x)$ as

$$P_{III}(x) = x^{14}-16x^{12}+98x^{10}-296x^8+473x^6-392x^4+148x^2-16$$

$$P_{IV}(x) = x^{14}-16x^{12}+98x^{10}-297x^8+479x^6-407x^4+166x^2-25.$$

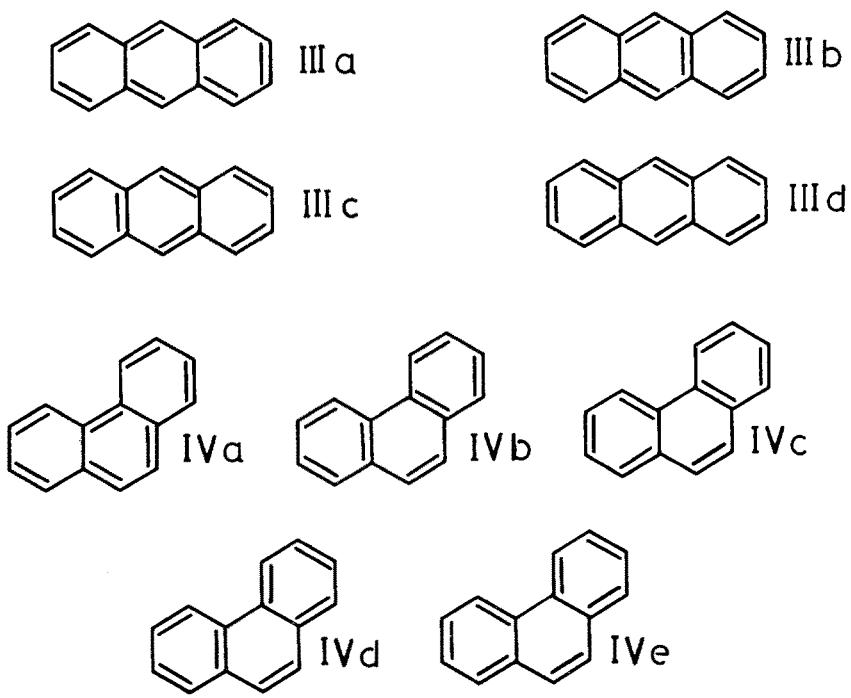


Fig. 1 Kekulé patterns.

Both of the above two facts are interrelated to each other through the following relation. Namely, for a polyhex with an even number (N=2m) of points we have [3]

$$a_N = (-1)^m \{K(G)\}^2. \qquad (2)$$

Besides this relation there have been proposed a number of interesting methods for enumerating the value of K(G) for a given polyhex graph, on which we are going to discuss.

2. Topological Index [4,5]

For graph G the non-adjacent number p(G,k) is defined as the number of ways for choosing k disconnected lines, p(G,0) being defined as unity. The number of the maximum matching for G is p(G,m),

$$p(G,m) = K(G) \qquad (m = [N/2]). \tag{3}$$

From now on we are concerned with even polyhexes (N=2m). The Z-counting polynomial $Q_G(x)$ is defined as

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

The topological index Z_G is the sum of the p(G,k)'s, or

$$Z_G = \sum_{k=0}^{m} p(G,k) = Q_G(1). \tag{5}$$

The graph G-ℓ is defined as the subgraph obtained from G by deleting line ℓ, and the graph $G \ominus \ell$ as the subgraph of G-ℓ obtained by deleting all the lines which were adjacent to ℓ in G (See Fig. 2).

Fig. 2 Subgraphs of G.

The inclusion-exclusion principle ensures the recursive relation for p(G,k) as

$$p(G,k) = p(G-\ell,k) + p(G \ominus \ell, k-1), \tag{6}$$

which gives

$$Q_G(x) = Q_{G-\ell}(x) + x \cdot Q_{G \ominus \ell}(x) \tag{7}$$

and

$$Z_G = Z_{G-\ell} + Z_{G \ominus \ell}(x). \tag{8}$$

A number of interesting methematical properties have been known for these quantities.

3. Characteristic Polynomial

Let the adjacency matrix A of graph G with N points be defined as the N×N square matrix with elements

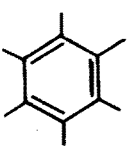
$$A_{ij} = \begin{cases} 1 & \text{i and j are neighbors} \\ 0 & \text{otherwise,} \end{cases} \qquad (9)$$

which gives the characteristic polynomial $P_G(x)$ as in Eq. (1).

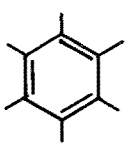
The p(G,k) numbers and the sets of the coefficients of $P_G(x)$ for smaller tree [6] and non-tree [7] graphs, and polyhex graphs [8] are extensively tabulated.

4. Sextet Polynomial

Consider a Kekulé pattern as shown in Fig. 1 for a given polyhex. If a set of three circularly arranged double bonds are located on a certain hexagon as Ia, one can get another Kekulé pattern as Ib just by rotating them by 60 degrees. For example, IIIa and IIIb are related to each other as in the relation between Ia and Ib, and we can find many other couplings among the group of Kekulé patterns IIIa-d. Let us call the sets of the three double bonds as shown below respectively as the proper and improper sextets. A couple of the proper and improper sextets in a given hexagon will be called as an aromatic sextet or simply as a sextet.



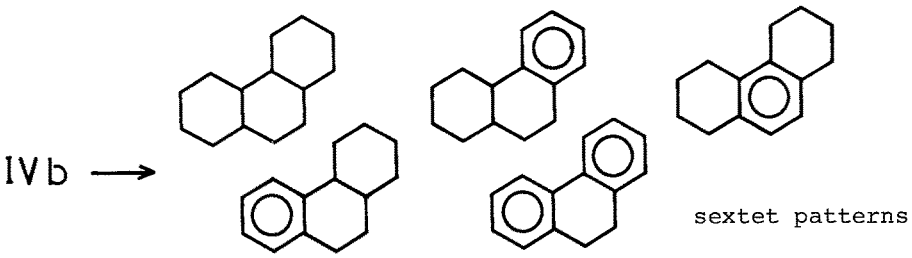
proper sextet



improper sextet

No two sextets are allowed to share a bond. However, it is possible for certain Kekulé patterns to have more than one sextet located on a set of disjoint hexagons. Such disjoint sextets are called to be resonant with each other. It is to be noted here that for certain kinds of Kekulé patterns there is no unique way for choosing a sextet or a set of resonant sextets.

According to Clar [9] let us denote a sextet by a circle and suppress the remaining double bonds to give a sextet pattern as shown below. The above arguments can be expressed in terms of the sextet patterns by taking IVb as an example.



Here the zero-sextet pattern is also defined that has no circle. It turned out that IVb generates all the posssble sextet patterns for IV.

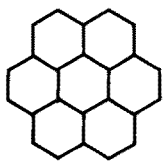
For a given polyhex, define the resonant sextet number $r(G,k)$ as the number of ways for choosing k disjoint but resonant sextets from G. Then the sextet polynomial $B_G(x)$ is defined as

$$B_G(x) = \sum_{k=0}^{m} r(G,k)\, x^k. \tag{10}$$

For graph IV we have

$$B_G(x) = 1 + 3x + x^2.$$

The present author has shown [10,11] that for catahexes and such "thin" perihexes that have no coronene skeleton as



coronene

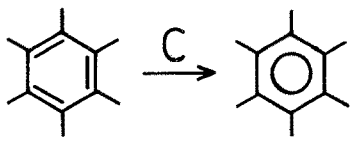
we have

$$B_G(1) = K(G). \tag{11}$$

5. Clar Transformation and Sextet Rotation

Since the both sides of Eq. (11) are derived from quite different enumeration problems, Eq. (11) is a very important relation. In order to analyze this problem the following two graphical operations are introduced.

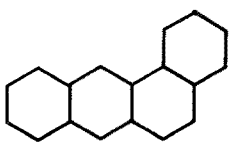
Define the Clar transformation C as a simultaneous substitution of all the proper sextets by circles in a given Kekulé pattern k_i followed by the transformation of the remaining double bonds into single bonds,



Clar transformation

as exemplified for graph VI in Fig. 3. It can symbolically be written as

$$C(k_i) = s_i. \tag{12}$$



VI

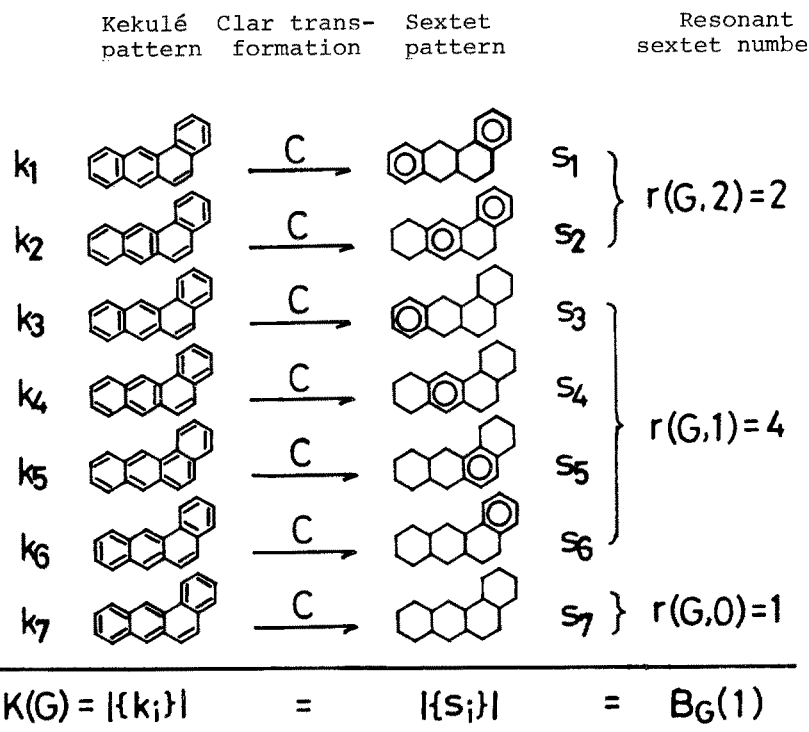
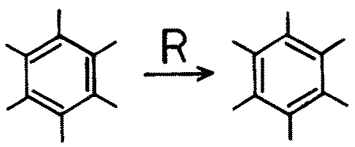


Fig. 3 Clar transformation and resonant sextet numbers.

Define the sextet rotation (R) as a simultaneous rotation of all the proper sextets in a given Kekulé pattern k_i into the improper sextets to give another Kekulé pattern k_j,



sextet rotation

or symbolically as

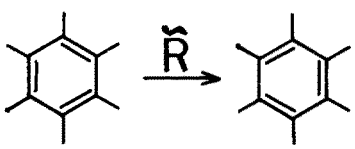
$$R(k_i) = k_j. \tag{13}$$

For example, we get $R(k_1)=k_7$ for graph VI. Note that for such k_i with no proper sextet, e.g., k_7 in Fig. 3, one cannot operate the sextet rotation. In this case let us put it down as

$$R(k_i) = \phi,$$

and call such k_i as the root Kekulé pattern.

Similarly the counter-sextet rotation ($\tilde{R}$) is defined as follows:



counter-sextet rotation

Note that the operation $\tilde{R}$ is not the inverse of R and vice versa.

Now try to operate the sextet and counter-sextet rotations to the set of the Kekulè patterns for graph VI. The resultant relationship among $\{k_i\}$ for VI is a hierarchical structure and can be expressed by directed rooted trees as shown in Fig. 4, where all the entries in $\{k_i\}$ can find the corresponding nodes including the root. It is to be noted that the two trees obtained by the sextet and counter-sextet rotations are not necessarily isomorphic as exemplified in Fig. 4.

The results obtained in Figs. 3 and 4 are valid for all the catahexes and "thin" perihexes. For "fat" perihexes one has to extend the concept of the sextet to the "super sextet", on which, however, we are not going to discuss here [11].

It has been shown [11] that the proof of Eq. (11) and of the results in Figs. 3 and 4 can be obtained straightforwardly if the following Lemma is proved:

[Lemma] For each polyhex graph, there exists one and only one root Kekulé pattern (a Kekulé pattern with no proper sextet).

6. Coefficients of NBMO

Herndon has proposed an interesting method for enumerating the K(G) value for a polyhex graph by using the coefficients of the non-bonding molecular orbital (NBMO) [12]. However, only the mathematical procedure for obtaining the K(G) value is introduced here.

Given a polyhex graph G with an even number of points. Of course G is bipartite. The component points are either starred (*) or unstarred. Delete from G a point p together with all the adjacent lines. The resultant graph $G \ominus p$ is also bipartite but with an odd number of points. Divide all the points into two groups, namely, the starred {s} and unstarred {r} so that the endpoints belong to {s}. Assign a set of integers ($n_s \gtrless 0$) to all the entries of {s} under the following conditions: (i) The point farthest to the endpoints is given 1 or -1. (ii) The "neighbor-sum" of these numbers for each unstarred point r becomes zero.

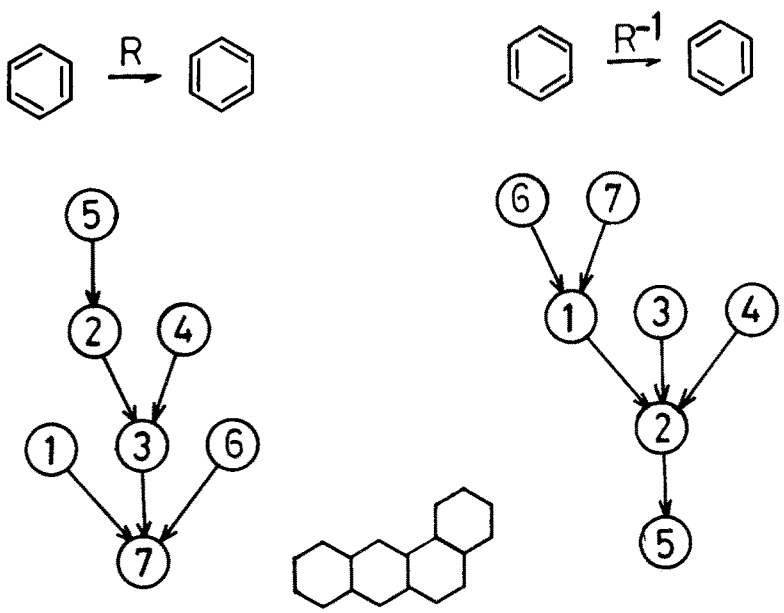


Fig. 4 Hierarchical trees of sextet rotations.

$$\sum_{s}^{\text{neighbors of } r} n_s = 0. \qquad (14)$$

Examples are given in Fig. 5 for several subgraphs derived from VI. Take the sum of these numbers for the starred points which were

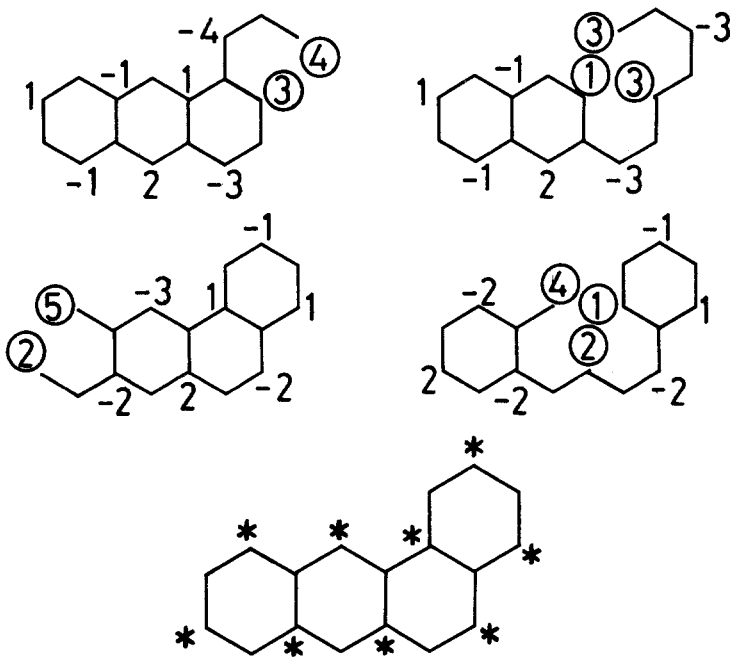
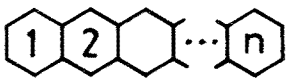
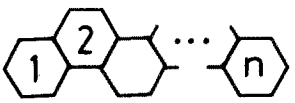
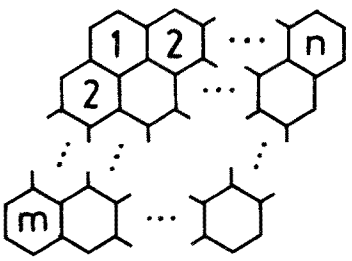


Fig. 5 NBMO and Kekulé numbers.

adjacent to p in the original graph G. As evident from Fig. 5 the (absolute) value of this sum is independent of the choice of p and is equal to the number K(G) of the maximum matching for G. Although this relation is known to be related to Eqs. (2) and (3), a rigorous proof has not yet been obtained. Further study is expected.

7. Several Series of K(G) Numbers

The numbers of the maximum matching K(G) for certain series of graphs are known to form interesting series of numbers. A few examples are shown:

Gn	K(Gn)
	$n + 1$
	$\frac{\left(\frac{1 + \sqrt{5}}{2}\right)^{n+2} - \left(\frac{1 - \sqrt{5}}{2}\right)^{n+2}}{\sqrt{5}}$
	$\binom{m + n}{n}$

References

[1] F. Harary and R. C. Read, Proc. Edinburgh Math. Soc., Ser. II, 17, 1 (1970).

[2] F. Harary, private communication.

[3] H. C. Longuet-Higgins, J. Chem. Phys., 18, 265 (1950).

[4] H. Hosoya, Bull. Chem. Soc. Jpn., 44, 2332 (1971).

[5] H. Hosoya, Fibonacci Quarterly, 11, 255 (1973).

[6] K. Mizutani, K. Kawasaki, and H. Hosoya, Natural Science Report, Ochanomizu Univ., 22, 39 (1971).

[7] K. Kawasaki, K. Mizutani, and H. Hosoya, Natural Science Report, Ochanomizu Univ., 22, 181 (1971).

[8] T. Yamaguchi, M. Suzuki, and H. Hosoya, Natural Science Report, Ochanomizu Univ., 26, 39 (1975).

[9] E. Clar, "The Aromatic Sextet", Wiley Interscience, London (1972).

[10] H. Hosoya and T. Yamaguchi, Tetrahedron Lett., 1975, 4659.

[11] N. Ohkami, A. Motoyama, T. Yamaguchi, H. Hosoya, and I. Gutman, Tetrahedron, in press.

[12] W. C. Herndon, Tetrahedron, 29, 3 (1973).