Resolution of Hosoya's Mystery?

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Synopsis. Three classes of polynomials for conjugated hydrocarbons are studied: characteristic polynomials (Hückel determinants) for cyclic polyenes, and combinatorial formulas for Kekulé structure counts of two classes of circulenes.

In the present communication three classes of polynomials are discussed, which all have relevance to molecular topology of conjugated hydrocarbons.

The characteristic polynomial of a conjugated system is very similar to the well-known Hückel determinant in the chemical context; see, e.g.[1] The simple Hückel molecular orbital theory is recognized as a part of molecular topology or graph theory.[2,3] In modern times these mathematical methods seem to penetrate into organic chemistry to a high degree.[4]

The two other classes of polynomials considered here describe the Kekulé structure counts (K) for classes of circulenes, which have counterparts in a new class of polycyclic aromatic hydrocarbons called cycloarenes.[5] Kekulene is a famous member of this class. The number K=200 for this molecule was probably given for the first time by Aihara.[6]

The present article is formulated as a comment on a remark by Hosoya,[7] who observed a coincidence between the forms of two polynomials, which are found in Table 1 under the designations $\phi_6(x)$ and $K_1(x, 6)$. In Hosoya's wording: "The reason for this mystic coincidence, however, is not known."[7] During the attempts to shed some light into this matter it was found that the coincidence is more far-reaching than the single example of Hosoya indicates.

The scope of the present work is, however, considerably broader than an attempt to resolve "Hosoya's mystery." It was aimed at a more general insight into the topological properties of circulene systems.

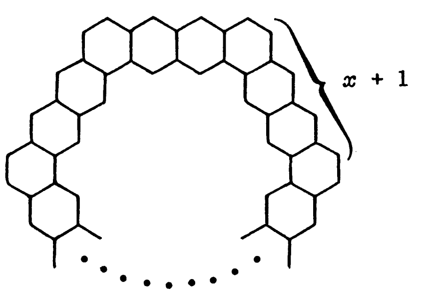

Fig. 1. Definition of a circulene. For N segments the number of hexagons is Nx.

Characteristic Polynomials. The class of characteristic polynomials for the cyclic polyacene systems (cyclopropenyl, cyclobutadiene, cyclopentadienyl, benzene,···) are considered and denoted $\phi_N(x)$ for N vertices (or N carbon atoms). An alternative to the well-known Hückel determinant is another standard formula, which reads

$$\phi_N(x)=\prod_k[x-2\cos(2k\pi/N)];$$
$$k=0, \pm1, \pm2, \cdots, \begin{cases} \pm(N-1)/2;\ N=3, 5, 7, \cdots \\ \pm(N-2)/2,\ N/2;\ N=4, 6, 8, \cdots. \end{cases} \quad (1)$$

Perhaps somewhat less known is the explicit formula

$$\phi_N(x)=2^{-N}[x+(x^2-4)^{1/2}]^N+2^{-N}[x-(x^2-4)^{1/2}]^N-2 \quad (2)$$

and the accompanying recurrence relation:

$$\phi_{N+3}=(x+1)(\phi_{N+2}-\phi_{N+1})+\phi_N \quad (3)$$

A special treatment of recurrence relations for characteristic (and other) polynomials is found in a paper of Hosoya and Ohkami,[8] which also may be consulted for some key references to this topic.

Cycloarenes with *N* Segments. Consider the class of circulenes consisting of N linear segments of x+1 hexagons each; see Fig. 1. The number of Kekulé structures is[9]

$$K_1(x, N)=2^{-N}[x+(x^2+4)^{1/2}]^N + 2^{-N}[x-(x^2+4)^{1/2}]^N+1+(-1)^N. \quad (4)$$

We find a striking similarity between Eqs. 2 and 4, which were derived from two apparently disconnected phenomena. The K formula for the class of circulenes considered by Hosoya,[7] and independently by others,[10,11] corresponds to N=6 in Eq. 4. The constant (x-independent) terms are somewhat elaborate. In the expanded polynomials (cf. Table 1) they manifest themselves in a repeating sequence (−2, 0, −2, −4) for $\phi_N(x)$ and (0, 4) for $K_1(x, N)$. Otherwise we find the same terms for a given N in the two polynomials, with the difference that they have alternating signs in ϕ, but

Table 1. Three Classes of Polynomials in Expanded Form for Some Values of N

N	$\phi_N(x)$	$K_1(x, N)$	$K_2(x, N)$
3	x^3-3x-2	x^3+3x	x^3-3x+2
4	x^4-4x^2	x^4+4x^2+4	x^4-4x^2+4
5	x^5-5x^3+5x-2	x^5+5x^3+5x	x^5-5x^3+5x+2
6	$x^6-6x^4+9x^2-4$	$x^6+6x^4+9x^2+4$	$x^6-6x^4+9x^2$
7	$x^7-7x^5+14x^3-7x-2$	$x^7+7x^5+14x^3+7x$	$x^7-7x^5+14x^3-7x+2$
8	$x^8-8x^6+20x^4-16x^2$	$x^8+8x^6+20x^4+16x^2+4$	$x^8-8x^6+20x^4-16x^2+4$

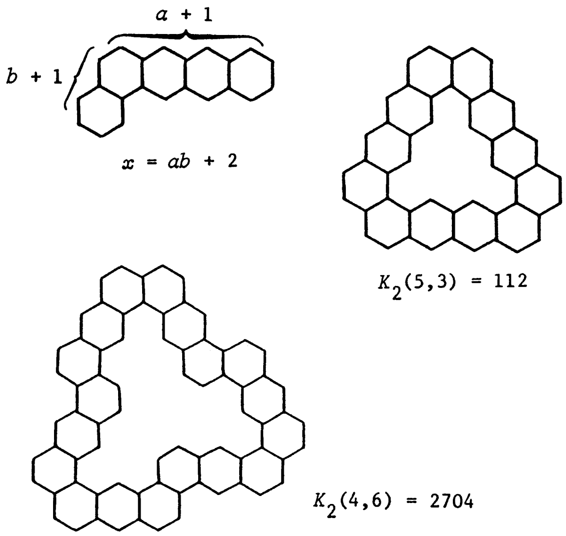

Fig. 2. Another class of circulenes. For N units the number of hexagons is $N(a+b)$. Two examples of complete systems are shown, and their K numbers are indicated.

are all positive in K_1. This feature is a consequence of the different signs in the square roots of Eqs. 2 and 4.

The function $K_1(x, N)$ may, as an alternative to Eq. 4, be expressed in terms of an $N\times N$ determinant as:

$$K_1(x, N)=(-1)^N \begin{vmatrix} -x & 1 & 0 & \cdots & 0 & 1 \\ -1 & -x & 1 & \cdots & 0 & 0 \\ 0 & -1 & -x & \cdots & 0 & 0 \\ \cdot & \cdot & \cdot & \cdots & \cdot & \cdot \\ 0 & 0 & 0 & \cdots & -x & 1 \\ -1 & 0 & 0 & \cdots & -1 & -x \end{vmatrix} \quad (5)$$

Cycloarenes with 2N Segments. We wish to show a modification of the system in Fig. 2 so that the K formula becomes a polynomial with alternating signs as in Eq. 2; it will in fact be identical with Eq. 2 apart from the constant term.

Consider a circulene with N units, each of them being a chain with two linear segments as shown in Fig. 2. The variable x, as determined by the two segments of one unit, is specified in the figure. An explicit equation for the K numbers was derived and reads

$$K_2(x, N)=2^{-N}[x+(x^2-4)^{1/2}]^N + 2^{-N}[x-(x^2-4)^{1/2}]^N+2. \quad (6)$$

It should be compared with Eq. 2. The sequence for constant terms of the polynomial $K_2(x, N)$ is (2, 4, 2, 0); cf. Table 1.

We give also a determinant formula for $K_2(x, N)$, which may be related to the characteristic polynomial of a Möbius ring.[12)]

$$K_2(x, N)=(-1)^N \begin{vmatrix} -x & 1 & 0 & \cdots & 0 & -1 \\ 1 & -x & 1 & \cdots & 0 & 0 \\ 0 & 1 & -x & \cdots & 0 & 0 \\ \cdot & \cdot & \cdot & \cdots & \cdot & \cdot \\ 0 & 0 & 0 & \cdots & -x & 1 \\ -1 & 0 & 0 & \cdots & 1 & -x \end{vmatrix} \quad (7)$$

Conclusion

In the present note some similarities are pointed out for a class of characteristic polynomials and formulas for Kekulé structure counts of certain classes of circulenes. The results have bearings on a coincidence between the forms of two polynomials, viz. $\phi_6(x)$ and $K_1(x, 6)$, which Hosoya[7)] observed and characterized as a mystery. The present work does not pretend to give a complete resolution, since it is still unknown, in a deeper sense, why these coincidences should appear.

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