

SEXTET POLYNOMIAL. A NEW ENUMERATION AND PROOF TECHNIQUE FOR
THE RESONANCE THEORY APPLIED TO THE AROMATIC HYDROCARBONS.

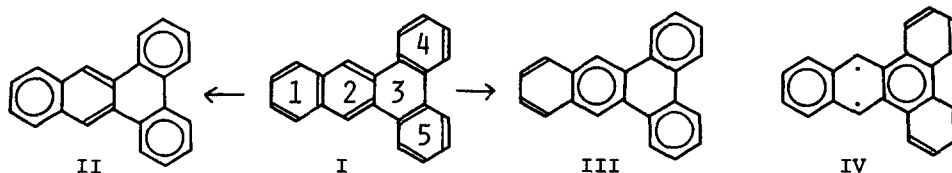
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Recently a naive picture of the resonance theory has been reevaluated from the graph and combinatorial theoretical points of view.¹⁻⁷ For example, for a group of aromatic hydrocarbon isomers the number of the Kekulé structures, or the structure count, is known to be a good index for representing the resonance energy. A number of methods for enumerating the number of the Kekulé structures have been proposed.^{5,8-13} There have also been proposed various quantities^{3,7,14} characterising the local and overall resonance stabilisation in an aromatic hydrocarbon molecule in order to explain the empirical rules such as that proposed by Clar¹⁵ on the structure and stability relationship. In this preliminary report a new technique "sextet polynomial" is introduced for a systematic enumeration of the Kekulé structures of aromatic hydrocarbons and it is shown that by the use of this polynomial various resonance theories independently proposed are found to be related to each other.

Let us confine ourselves to the Kekulé structures of aromatic hydrocarbons with an even number of carbon atoms, each of which supplies one π -electron to the network or graph G. In a given Kekulé structure an aromatic sextet (abbreviated as a sextet) is defined as a set of three double bonds circularly conjugated as in either of the two Kekulé structures of benzene and is represented by a circle.¹⁵ According to the Clar's definition no two sextets can have a common bond. Namely, if ring 1 in structure I is chosen as a sextet and represented as in II, ring 2 is not allowed to have a circle even though it can form a sextet at the sacrifice of ring 1 as in III.



From II and III it is shown that rings 1, 4, and 5 and rings 2, 4, and 5 are, respectively, mutually resonant with each other. On the other hand, ring 3 can

be chosen as a sextet by itself but can not be resonant with ring 1 (See IV).

Define the resonant sextet number $r(G,k)$ for graph G as the number of ways in which k disconnected but resonant sextets are chosen from G , $r(G,0)$ being defined as unity for all the cases. Except for very few cases as the central ring in perylene, any ring in an aromatic hydrocarbon can be chosen as a sextet in one or more Kekulé structures. Then $r(G,1)$ is equal to the number of hexagons for almost all the cases. For dibenz[a,c]anthracene the $r(G,2)$ value is obtained as five, i.e., there are five pairs of resonant sextets as (1,4), (1,5), (2,4), (2,5), and (4,5). The two structures II and III give $r(G,3)=2$.

The sextet polynomial $B_G(X)$ is defined as

$$B_G(X) = \sum_{k=0}^m r(G,k) X^k . \quad (1)$$

For dibenz[a,c]anthracene we get $B_G(X)=1+5X+5X^2+2X^3$. Note that the sum of the coefficients of the sextet polynomial, 13, is equal to the number of the Kekulé structures of this hydrocarbon. This is always the case for smaller members of the aromatic hydrocarbons as shown in Table. It can be proved that for a catafusene, i.e., a polycyclic aromatic hydrocarbon in which no three hexagons have a common carbon atom, the value $B_G(1)$ is exactly equal to the number of the Kekulé structures, $K(G)$, or the structure count, $SC(G)$,






















$$B_G(1) = K(G) = SC(G) . \quad (2)$$

Also for such a perifusene so slender as not to contain the coronene skeleton the relation (2) is exactly obeyed. For coronene we have $B_G(X)=1+7X+9X^2+2X^3$ and $B_G(1)=19$, whereas $K(G)=20$. The discrepancy can be explained and corrected by introducing the idea of super-ring, a ring composed of six hexagons forming the peripheral structure of coronene, which gives an additional term, X , to $B_G(X)$ (See Table). Useful recursion formulae and mathematical relations are found for obtaining the sextet polynomial of larger graphs but will not be explained here. Note, however, that a set of quantities, $r(G,k)$, $B_G(X)$, and $K(G)$, are in parallel with our previously proposed quantities, i.e., non-adjacent number, $p(G,k)$, Z-counting polynomial, $Q_G(X)$, and topological index, Z_G .¹⁶

According to Clar¹⁵ the Kekulé structure with the largest number of sextets is representative of the electronic structure of the ground state of a polycyclic hydrocarbon, and the stability increases with the number of sextets, which is nothing else but the largest exponent m to X in $B_G(X)$ (See Table).

Next let us differentiate $B_G(X)$ with respect to X . The value $B'_G(1)$ is turned out to be equal to the value $\sum \gamma_i$ proposed by Herndon and Ellzey³ as the sum of the numbers of the Kekulé structures for the subgraph $G \ominus R_i$ ¹⁷ derived from G by deleting hexagon R_i together with all the bonds adjacent to R_i ,

$$B'_G(1) = \sum_i K(G \ominus R_i) = \sum \gamma_i . \quad (3)$$

Compound	$B_G(X)$	$B'_G(X)$	$B_G(1)$	$B'_G(1)$	m
	$1 + X$	1	2	1	1
	$1 + 2X$	2	3	2	1
	$1 + 3X$	3	4	3	1
	$1 + 3X + X^2$	$3 + 2X$	5	5	2
	$1 + 4X$	4	5	4	1
	$1 + 4X + 2X^2$	$4 + 4X$	7	8	2
	$1 + 4X + 3X^2$	$4 + 6X$	8	10	2
	$1 + 4X + 3X^2 + X^3$	$4 + 6X + 3X^2$	9	13	3
	$1 + 4X + X^2$	$4 + 2X$	6	6	2
	$1 + 5X$	5	6	5	1
	$1 + 5X + 3X^2$	$5 + 6X$	9	11	2
	$1 + 5X + 4X^2$	$5 + 8X$	10	13	2
	$1 + 5X + 5X^2$	$5 + 10X$	11	15	2
	$1 + 5X + 5X^2 + X^3$	$5 + 10X + 3X^2$	12	18	3
	$1 + 5X + 6X^2 + X^3$	$5 + 12X + 3X^2$	13	20	3
	$1 + 5X + 5X^2 + 2X^3$	$5 + 10X + 6X^2$	13	21	3
	$1 + 5X + 6X^2 + 2X^3$	$5 + 12X + 6X^2$	14	23	3
	$1 + 5X + 3X^2$	$5 + 6X$	9	11	2
	$1 + 4X + 4X^2$	$4 + 8X$	9	12	2
	$1 + 5X + 4X^2 + X^3$	$5 + 8X + 3X^2$	11	16	3
	$1 + 7X + 9X^2 + 2X^3$	$7 + 18X + 6X^2$	19	31	3
	{ * $1 + 8X + 9X^2 + 2X^3$	$8 + 18X + 6X^2$	20	32	3

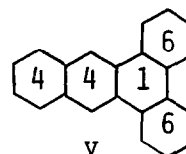
* Corrected with the super-ring. Note that the corrected $B'_G(1)=32$ also gives the correct $\sum \gamma_i$ value. Refer to Ref.18.

For dibenz[a,c]anthracene we have $B'_G(X) = 5 + 10X + 6X^2$ giving the value $B'_G(1) = 21$, which is also obtained from the $K(G\ominus R_i)$ values as in V. From the graph theoretical standpoint the values $K(G\ominus R_i)$'s for polyhexes are extensively tabulated.¹⁸

Randić⁷ and Aihara¹⁴ independently proposed an idea of the index of local aromaticity (ILA) and overall index of aromaticity (OIA) expressed by the use of our notations as

$$ILA_i = 2 K(G\ominus R_i) / K(G) \quad (4)$$

$$OIA = 2 \sum_i \{K(G\ominus R_i) / K(G)\} = 2 B'_G(1) / B_G(1). \quad (5)$$



Thus many of the resonance theories independently proposed are shown to be mathematically related to each other through the sextet polynomial. Proofs and details will be published elsewhere.

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