A New Method for the Calculation of the Sextet Polynomial of Unbranched Catacondensed Benzenoid Hydrocarbons

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A method for the calculation of the sextet polynomial of unbranched catacondensed benzenoid molecules is proposed. It requires the multiplication of a small number of 2×2 matrices and is therefore very simple.

The concept of the sextet polynomial was introduced by Hosoya and Yamaguchi[1] in 1975 and was thereafter subject of numerous investigations.[2-19] The theory based on the sextet polynomial and its various chemical applications can be found in the reviews[20,21] and books.[22,23]

The sextet polynomial is defined via the resonant sextet numbers $r(\mathrm{B}, k)$. Let B be a benzenoid system. Then $r(\mathrm{B}, k)$ is the number of distinct Clar-type formulas for B, in which exactly k hexagons contain a resonant sextet, $k=1,2,\cdots,s$. Here s is the maximal number of aromatic sextets which can be inserted in a Clar-type formula for B, i.e. $r(\mathrm{B}, s)\neq 0$, $r(\mathrm{B}, s+1)=0$. By definition, $r(\mathrm{B}, 0)=1$.

Then the sextet polynomial of B is

$$\sigma(\mathrm{B}, x)=\sum_{k=0}^{s} r(\mathrm{B}, k)\, x^k. \tag{1}$$

If B is an unbranched catacondensed benzenoid system, then an acyclic graph $\mathrm{G}=\mathrm{G}(\mathrm{B})$ can be constructed,[4] such that for all values of k,

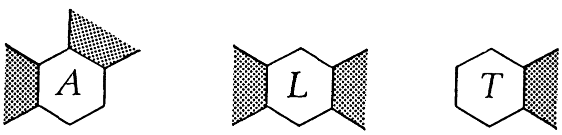
$$r(\mathrm{B}, k)=m(\mathrm{G}, k) \tag{2}$$

where $m(\mathrm{G}, k)$ is the number of k-matchings of the graph G. When Eq. 2 is substituted back into Eq. 1 we obtain

$$\sigma(\mathrm{B}, x)=\sum_{k=0}^{s} m(\mathrm{G}, k)\, x^k. \tag{3}$$

The right-hand side of Eq. 3 is exactly the so-called "Z-counting polynomial" (of the graph G), introduced in 1971 by Hosoya.[24] Therefore in the case of unbranched catacondensed benzenoids, the calculation of the sextet polynomial reduces to the finding of the Z-counting polynomial of the associated graph.

The graph G has the following structure. Suppose that the unbranched catacondensed molecule considered possesses n hexagons of type A (i.e. n kinks). The number of hexagons of type L between the i-th and the $(i+1)$-th A hexagon is t_i, $i=1, 2, \cdots, n-1$. Further, t_0 is the number of L hexagons lying between the terminal (T) hexagon and the first A hexagon.



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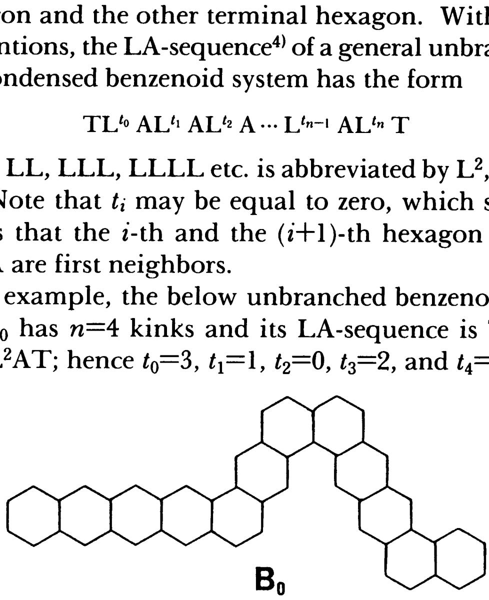
Similarly, t_n counts the L hexagons between the n-th A hexagon and the other terminal hexagon. With these conventions, the LA-sequence[4] of a general unbranched catacondensed benzenoid system has the form

$$\mathrm{TL}^{t_0}\,\mathrm{AL}^{t_1}\,\mathrm{AL}^{t_2}\,\mathrm{A}\cdots\mathrm{L}^{t_{n-1}}\,\mathrm{AL}^{t_n}\,\mathrm{T} \tag{4}$$

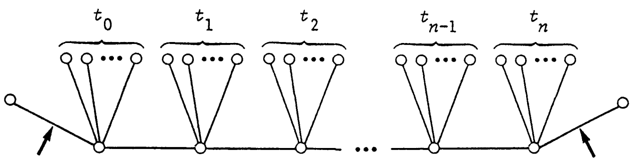
where LL, LLL, LLLL etc. is abbreviated by L^2, L^3, L^4 etc. Note that t_i may be equal to zero, which simply means that the i-th and the $(i+1)$-th hexagon of the type A are first neighbors.

For example, the below unbranched benzenoid system B_0 has $n=4$ kinks and its LA-sequence is $\mathrm{TL}^3\mathrm{A}$-$\mathrm{LAAL}^2\mathrm{AT}$; hence $t_0=3$, $t_1=1$, $t_2=0$, $t_3=2$, and $t_4=0$.



B_0

Now, the graph G in Eqs. 2 and 3 is of the form:[4]

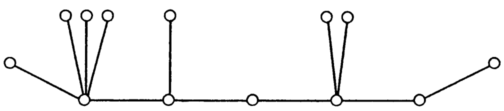


$\mathrm{G} = \mathrm{G}(t_0, t_1, t_2, \ldots, t_{n-1}, t_n)$

The graphs of the above type are called caterpillars[15,21] or sometimes[19,21] Gutman trees.

One should observe that the caterpillar G has n horizontal edges, each corresponding to a hexagon of type A. This explains why the branching points of G are numbered from 0 to n (and not from 1 to n as, at the first glance, may look more appropriate). Anyway, it should not be forgotten that the main object of the present paper are benzenoid hydrocarbons whereas their LA-sequences and the associated Gutman trees are auxiliary mathematical constructions needed only to deduce our expression for the sextet polynomial.

The caterpillar corresponding to B_0 is $\mathrm{G}(\mathrm{B}_0)$:



$\mathrm{G}(\mathrm{B}_0)$

As already mentioned, the Z-counting polynomial of $G(t_0, t_1, t_2 \cdots, t_{n-1}, t_n)$ coincides with the sextet polynomial of an unbranched catacondensed hydrocarbon whose LA-sequence is given by Eq. 4.

The properties of the matching numbers $m(G, k)$, the Z-counting polynomial $Q(G, x)$ and the closely related matching polynomial have been studied in detail.[25] In the present paper we need only two simple relations[24] for $Q(G, x)$.

(i) Let G be an arbitrary graph, e its arbitrary edge, and let e connect the vertices u and v. Then

$$Q(G, x) = Q(G\text{-}e, x) + xQ(G\text{-}u\text{-}v, x). \tag{5}$$

(ii) Let G be a graph composed of two components G_1 and G_2. Then

$$Q(G, x) = Q(G_1, x) \cdot Q(G_2, x). \tag{6}$$

The Main Result. The sextet polynomial of an unbranched catacondensed benzenoid system whose LA-sequence is given by Eq. 4 is equal to $U_{11}+U_{12}+U_{21}+U_{22}$ where

$$\begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix} = M_0 M_1 M_2 \cdots M_{n-1} M_n \begin{pmatrix} 1 & 0 \\ 0 & x \end{pmatrix} \tag{7}$$

and

$$M_i = \begin{pmatrix} 1 + t_i x & 1 \\ x & 0 \end{pmatrix}.$$

For the previous example,

$$\begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix} = \begin{pmatrix} 1+3x & 1 \\ x & 0 \end{pmatrix} \begin{pmatrix} 1+x & 1 \\ x & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ x & 0 \end{pmatrix} \begin{pmatrix} 1+2x & 1 \\ x & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ x & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & x \end{pmatrix}$$

which after simple matrix multiplication gives

$$\begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix} = \begin{pmatrix} 1+10x+29x^2+21x^3 & x+9x^2+23x^3+15x^4 \\ x + 6x^2 + 7x^3 & x^2 + 5x^3 + 5x^4 \end{pmatrix}$$

yielding the sextet polynomial of B_0:

$$\begin{aligned} \sigma(B_0, x) &= (1+10x+29x^2+21x^3) + (x+9x^2+23x^3+15x^4) \\ &\quad + (x+6x^2+7x^3) + (x^2+5x^3+5x^4) \\ &= 1 + 12x + 45x^2 + 56x^3 + 20x^4. \end{aligned}$$

Two special cases of Eq. 7 are worth mentioning. If on the left-hand side from the first kink there are no L-type hexagons (i.e. $t_0=0$), then

$$\begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix} = \begin{pmatrix} 1 & 1 \\ x & 0 \end{pmatrix} M_1 M_2 \cdots M_n \begin{pmatrix} 1 & x \\ 0 & x \end{pmatrix}.$$

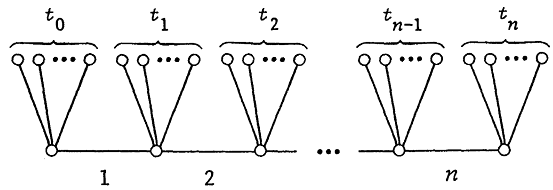
If on the right-hand side from the last kink there are no hexagons of the type L (i.e. $t_n=0$), then

$$\begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix} = M_0 M_1 \cdots M_{n-1} \begin{pmatrix} 1 & x \\ x & 0 \end{pmatrix}.$$

Verification of Equation 7. We first apply Eqs. 5 and 6 to the two edges of $G(t_0, t_1, t_2, \cdots, t_{n-1}, t_n)$ which on the previous diagram are indicated by arrows. Bearing in mind that for the graph E_p with p vertices but without edges $Q(E_p)\equiv 1$, we straightforwardly obtain:

$$\begin{aligned} &Q[G(t_0, t_1, t_2, \cdots, t_{n-1}, t_n), x] \\ &\quad = Q[F(t_0, t_1, t_2, \cdots, t_{n-1}, t_n), x] \\ &\quad + xQ[F(t_0, t_1, t_2, \cdots, t_{n-1}), x] \\ &\quad + xQ[F(t_1, t_2, \cdots, t_{n-1}, t_n), x] \\ &\quad + x^2 Q[F(t_1, t_2, \cdots, t_{n-1}), x] \end{aligned} \tag{8a}$$

where the caterpillar F is defined as follows:



$F(t_0, t_1, t_2, \ldots, t_{n-1}, t_n)$

It is expedient to use the shorthand notation

$$Q[F(t_0, t_1, t_2, \cdots, t_{n-1}, t_n), x] \equiv (0, n).$$

Then Eq. 8a is simplified as

$$\begin{aligned} &Q[G(t_0, t_1, t_2, \cdots, t_{n-1}, t_n), x] \\ &\quad = (0, n) + x \cdot (0, n-1) + x \cdot (1, n) + x^2 \cdot (1, n-1). \end{aligned} \tag{8b}$$

Another way to deduce the identity Eq. 8 is to apply the inclusion and exclusion principle to the Q polynomial. Let a and b denote the edges of G indicated by arrows. Then the first term on the right-hand side of either Eq. 8a or 8b corresponds to the subgraph of G from which both a and b are excluded. The second term in Eqs. 8a and 8b corresponds to the subgraph of G in which a is included, but b is excluded; the third term corresponds to the subgraph from which a is excluded, but b is included. Finally, the last term in Eqs. 8a and 8b corresponds to the subgraph to which both a and b are included. The authors are indebted to the referee for pointing out this observation.

Applying Eqs. 5 and 6 to the i-th horizontal edge of $F(t_0, t_1, t_2, \cdots, t_{n-1}, t_n)$ we arrive at

$$(0, n) = (0, i)(i+1, n) + x \cdot (0, i-1)(i+2, n)$$

and in a fully analogous manner:

$$\begin{aligned} (0, n-1) &= (0, i)(i+1, n-1) + x \cdot (0, i-1)(i+2, n-1) \\ (1, n) &= (1, i)(i+1, n) + x \cdot (1, i-1)(i+2, n) \\ (1, n-1) &= (1, i)(i+1, n-1) + x \cdot (1, i-1)(i+2, n-1). \end{aligned}$$

These four equations can be written in a matrix form as

$$\begin{pmatrix} (0, n) & (0, n-1) \\ x \cdot (1, n) & x \cdot (1, n-1) \end{pmatrix} = \begin{pmatrix} (0, i) & (0, i-1) \\ x \cdot (1, i) & x \cdot (1, i-1) \end{pmatrix} \begin{pmatrix} (i+1, n) & (i+1, n-1) \\ x \cdot (i+2, n) & x \cdot (i+2, n-1) \end{pmatrix}. \tag{9}$$

The above relations hold for $2 \leqq i \leqq n-3$. They can easily be extended to apply for all values of i, i=0, 1, ⋯, $n-1$ if one sets $(j,j-1)\equiv 1$ and $(j+1,j-1)\equiv 0$. One should recall that $(j,j)=1+t_j x$.

Setting $i=n-1$ in Eq. 9 we obtain

$$\begin{pmatrix} (0,n) & (0,n-1) \\ x\cdot(1,n) & x\cdot(1,n-1) \end{pmatrix} = \begin{pmatrix} (0,n-1) & (0,n-2) \\ x\cdot(1,n-1) & x\cdot(1,n-2) \end{pmatrix} \begin{pmatrix} 1+t_n x & 1 \\ x & 0 \end{pmatrix}$$

i.e.

$$\begin{pmatrix} (0,n) & (0,n-1) \\ x\cdot(1,n) & x\cdot(1,n-1) \end{pmatrix} = \begin{pmatrix} (0,n-1) & (0,n-2) \\ x\cdot(1,n-1) & x\cdot(1,n-2) \end{pmatrix} M_n$$

from which is immediately seen that

$$\begin{pmatrix} (0,n) & (0,n-1) \\ x\cdot(1,n) & x\cdot(1,n-1) \end{pmatrix} = M_0 M_1 M_2 \cdots M_{n-1} M_n \ .$$

Equation 7 follows now from the fact that

$$\begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix} = \begin{pmatrix} (0,n) & (0,n-1) \\ x\cdot(1,n) & x\cdot(1,n-1) \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & x \end{pmatrix} .$$

Discussion

Another form in which we can express our main result is

$$\sigma(\mathrm{B}, x) = \begin{pmatrix} 1 \\ 1 \end{pmatrix}^T M_0 M_1 \cdots M_n \begin{pmatrix} 1 \\ x \end{pmatrix} . \tag{10}$$

For $x=1$ the sextet polynomial reproduces the number of Kekulé structures.[1,3] Therefore Eq. 10 provides an expression for the Kekulé structure count of unbranched catacondensed benzenoid systems, viz.

$$K\{\mathrm{B}\} = \begin{pmatrix} 1 \\ 1 \end{pmatrix}^T L_0 L_1 \cdots L_n \begin{pmatrix} 1 \\ 1 \end{pmatrix} \tag{11}$$

where

$$L_i = \begin{pmatrix} t_i+1 & 1 \\ 1 & 0 \end{pmatrix} .$$

Formulas of this type, but not Eq. 11, are previously known.[26]

We wish to point at a property of the matrix elements U_{ij}, Eq. 7, whose meaning and possible significance are not understood. We have seen that $U_{11}+U_{12}+U_{21}+U_{22}$ is the sextet polynomial. In addition,

$$U_{11}U_{22}-U_{12}U_{21}=(-1)^n x^{n+1}. \tag{12}$$

The above relation is obtained if one calculates the determinants of the left- and right-hand sides of Eq. 7, taking into account that det $M_i=-x$. The special case of Eq. 12 for $x=1$ was observed previously.[27]

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References

1) H. Hosoya and T. Yamaguchi, *Tetrahedron Lett.*, **1975**, 4659.
2) J. Aihara, *Bull. Chem. Soc. Jpn.*, **50**, 2010 (1977).
3) I. Gutman, H. Hosoya, T. Yamaguchi, A. Motoyama, and N. Kuboi, *Bull. Soc. Chim. Beograd*, **42**, 503 (1977).
4) I. Gutman, *Theor. Chim. Acta*, **45**, 309 (1977).
5) I. Gutman, *Bull. Chem. Soc. Jpn.*, **51**, 2729 (1978).
6) I. Gutman, *Z. Naturforsch., A*, **33**, 840 (1978).
7) N. Ohkami, A. Motoyama, T. Yamaguchi, H. Hosoya, and I. Gutman, *Tetrahedron*, **37**, 1113 (1981).
8) I. Gutman, *Match*, **11**, 127 (1981).
9) I. Gutman, *Z. Naturforsch., A*, **37**, 69 (1982).
10) N. Ohkami and H. Hosoya, *Theor. Chim. Acta*, **64**, 153 (1983).
11) S. El-Basil, *Bull. Chem. Soc. Jpn.*, **56**, 3152 (1983).
12) I. Gutman and S. El-Basil, *Chem. Phys. Lett.*, **94**, 188 (1983).
13) I. Gutman and S. El-Basil, *Z. Naturforsch., A*, **39**, 276 (1984).
14) I. Gutman and S. El-Basil, *J. Serb. Chem. Soc.*, **50**, 25 (1985).
15) I. Gutman and S. El-Basil, *Z. Naturforsch., A*, **40**, 923 (1985).
16) F. J. Zhang and R. S. Chen, *Match*, **19**, 179 (1986).
17) W. C. He and W. J. He, *Theor. Chim. Acta*, **70**, 43 (1986).
18) S. El-Basil, *Theor. Chim. Acta*, **70**, 53 (1986).
19) S. El-Basil, *J. Chem. Soc., Faraday Trans. 2*, **82**, 299 (1986).
20) I. Gutman, *Bull. Soc. Chim. Beograd*, **47**, 453 (1982).
21) S. El-Basil, *J. Math. Chem.*, **1**, 153 (1987).
22) N. Trinajstić, "Chemical Graph Theory," CRC Press, Boca Raton (1983), Vol. II, pp. 44—46.
23) I. Gutman and S. J. Cyvin, "Introduction to the Theory of Benzenoid Hydrocarbons," Springer-Verlag, Berlin (1988).
24) H. Hosoya, *Bull. Chem. Soc. Jpn.*, **44**, 2332 (1971).
25) D. Cvetković, M. Doob, I. Gutman, and A. Torgašev, "Recent Results in the Theory of Graph Spectra," North-Holland, Amsterdam (1988), Chaps. 4 and 5.
26) D. Cvetković and I. Gutman, *Croat. Chem. Acta*, **46**, 15 (1974).
27) S. J. Cyvin, *Chem. Phys. Lett.*, **147**, 384 (1988).