

Topological Properties of Benzenoid Systems. XXIV. Computing the Sextet Polynomial

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A graph-theoretical method for the calculation of the sextet polynomial is proposed. The method is easy and generally applicable. It is based on the construction of the Clar graph and on the calculation of its independence numbers.

The discovery of the sextet polynomial by Hosoya and Yamaguchi [1] gave a strong impetus to the development of Clar's theory of aromatic sextets [2, 3]. The sextet polynomial concept stimulated numerous further investigations of the topological properties of benzenoid molecules [4–8]. In spite of this, no systematic and general method for constructing the sextet polynomial was reported so far in the literature. The original procedure [1], namely trial-and-error constructing and counting the Clar formulas, becomes a very awkward and error-prone task in the case of large (or even medium size) benzenoid molecules.

Some efficient computation techniques were proposed for the sextet polynomials of cata-condensed benzenoid systems [5], but these are inapplicable in the case of peri-condensed systems.

In the present paper we offer a novel graph-theoretical method for computing the sextet polynomials, which is well applicable to both cata- and peri-condensed molecules. Our method is based on the Clar graph concept, which was elaborated in a previous communication [6]. In that paper the mathematical results, necessary for the formulation of the method can be found. Therefore we shall completely follow the terminology and symbolism used in [6] and the reader should consult [6] for necessary details.

Hence the benzenoid system under consideration will be denoted by B , its hexagons by h_1, h_2, \dots, h_n ,

its sextet polynomial by

$$\sigma(B) = \sum_k s(B, k) x^k,$$

where $s(B, k)$ is the k -th resonant sextet number of B .

Preliminaries

a) The independence polynomial

Let G be a graph with n vertices. Let these vertices be labelled by v_1, v_2, \dots, v_n . The collection of the vertices $v_{i_1}, v_{i_2}, \dots, v_{i_k}$ ($k \geq 2$) of G is said to be an independent vertex set of G , if no two among these vertices are adjacent in G . This independence set has cardinality k . The number of independent vertex sets of G with cardinality k is denoted by $o(G, k)$. Hence $o(G, k)$ is the number of selections of k independent vertices in G . This number will be called the k -th independence number of G .

In addition, we define $o(G, 1) = n$ and $o(G, 0) = 1$ for all graphs G . The independence polynomial of the graph G is then

$$\omega(G) = \sum_{k=0}^m o(G, k) x^k$$

with m being the greatest value of the index k , for which the k -th independence number is non-zero.

The independence polynomial of an arbitrary graph can be easily determined using the following two results [6]:

Lemma 1. Let v be a vertex of G and A_v be the set containing v and all vertices being adjacent to v .

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Then the independence polynomial of G conforms to the recurrence relation

$$\omega(G) = \omega(G - v) + x \omega(G - A_v). \quad (1)$$

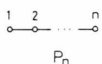
Lemma 2. Let the graph G be composed of two disjunct components G_1 and G_2 . Then

$$\omega(G) = \omega(G_1) \cdot \omega(G_2). \quad (2)$$

For the application of the above two lemmas one will often need the following independence polynomials:

$$\begin{aligned} \omega(0) &= 1, \\ \omega(P_1) &= 1 + x, \\ \omega(P_2) &= 1 + 2x, \\ \omega(P_3) &= 1 + 3x + x^2, \\ \omega(P_4) &= 1 + 4x + 3x^2, \\ \omega(P_5) &= 1 + 5x + 6x^2 + x^3, \\ \omega(P_6) &= 1 + 6x + 10x^2 + 4x^3, \end{aligned}$$

where 0 symbolizes the “empty” graph (i.e. the graph without vertices), whereas P_n is the pat with n vertices:



Note that $\omega(P_n) = \omega(P_{n-1}) + x \omega(P_{n-2})$ or, what is the same, $\omega(P_n, k) = \omega(P_{n-1}, k) + \omega(P_{n-2}, k-1)$. This recurrence relation is, of course, a special case of (1). It enables a rapid computation of $\omega(P_n)$ for arbitrary values of n .

As an example we determine the independence polynomial of the graph G_1 (see Figure 1). Applying (1) to one of the central vertices of G_1 we get

$$\omega(G_1) = \omega(G_1 - v) + x \omega(G_1 - A_v)$$

An analogous argument gives

$$\omega(G_1 - v) = \omega(G_1 - v - v_1) + x \omega(G_1 - v - v_2)$$

Therefore

$$\omega(G_1) = \omega(G_1 - v - v_1) + 2x \omega(G_1 - v - v_2)$$

Here and later the vertex on which we apply Lemma 1 is being indicated by a full circle. Now, using (1) we have further

$$\begin{aligned} \omega(G_1 - v - v_1) &= \omega(G_1 - v - v_1 - v_2) + x \omega(G_1 - v - v_1 - v_3) = \\ &= \omega(G_1 - v - v_1 - v_2 - v_3) + x \omega(G_1 - v - v_1 - v_4) + x^2 \omega(G_1 - v - v_1 - v_5) + x^3 \omega(G_1 - v - v_1 - v_6) \end{aligned}$$

and by (2),

$$\omega(G_1 - v - v_1 - v_2 - v_3 - v_4 - v_5 - v_6) = \omega(P_3)^2 + 2x \omega(P_1) \omega(P_2) + x^2 \omega(P_3).$$

Hence

$$\omega(G_1) = \omega(P_3)^2 + 2x [\omega(P_1) \omega(P_2) + \omega(P_3)] + x^2 \omega(0),$$

and taking into account the above given expressions for $\omega(P_n)$ we arrive at the final result

$$\omega(G_1) = 1 + 10x + 24x^2 + 12x^3 + x^4.$$

An alternative technique for the calculation of the independence numbers is given in Appendix 1.

b) The Clar graph

According to [6], the Clar graph of the benzenoid system B is the graph $C(B)$ with n vertices. The vertices v_r and v_s are adjacent in $C(B)$ if the hexagons h_r and h_s are not mutually resonant in B . For example, the Clar graph of ovalene is G_1 , whereas the Clar graph of kekulene is G_2 (see Figure 1).

The construction of the Clar graph is explained in detail in [6]. After a little exercise the construction of $C(B)$ becomes a routine task even for benzenoid systems as large as ovalene or kekulene.

A special method for building of the Clar graph of a cata-condensed system will be presented later on.

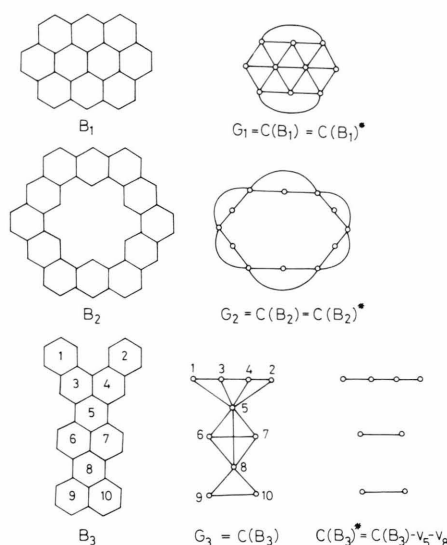


Fig. 1. Ovalene (B_1), kekulene (B_2), 2,3,4,5-dibenzoterrylene (B_3), their Clar graphs and their reduced Clar graphs.

c) The reduced Clar graph

The graph $C(B)^*$, called the reduced Clar graph of the benzenoid system B , is obtained from $C(B)$ by deleting the vertices which correspond to non-resonant hexagons of B . (A hexagon h_r of B is non-resonant if there is no Clar-type formula in which a resonant sextet is located in h_r .)

For example, the hexagons h_5 and h_8 in dibenzoterrylene (see Fig. 1) are non-resonant.

If all the hexagons in B are resonant (which is the case with the great majority of chemically relevant benzenoid systems), then

$$C(B)^* = C(B).$$

In particular, the above relation holds for all cata-condensed benzenoid systems (see Appendix 2).

The Main Result

According to Theorem 1 of [6],

$$\sigma(B) = \omega(C(B)) - (n - n_R)x,$$

where n_R is the number of resonant hexagons of B . Now, if a hexagon h_r is not resonant in B , then v_r — the corresponding vertex of $C(B)$ — is adjacent to all other vertices of $C(B)$. Therefore v_r will not be the element of any independent vertex set of $C(B)$. Then the deletion of the vertex v_r from $C(B)$ will not affect the independence numbers of $C(B)$. Thus we conclude:

$$o(C(B), k) = o(C(B)^*, k)$$

for all $k \geq 2$. On the other hand,

$$o(C(B), 1) = n \quad \text{whereas} \quad o(C(B)^*, 1) = n_R.$$

Since by Theorem 1 from [6],

$$s(B, k) = o(C(B), k)$$

for $k \geq 2$ and

$$s(B, 1) = n_R,$$

we immediately see that

$$\sigma(B) = \omega(C(B)^*) \quad (3)$$

for all benzenoid systems B . Equation (3) can be understood as the main result of the present paper.

The importance of (3) lies in the fact that the problem of the calculation of the sextet polynomial of B is now transformed to the much easier problem

of the calculation of the independence polynomial of the reduced Clar graph. Since the independence polynomials are obtained by straight-forward graph-theoretical reasoning, we have an efficient and general algorithm for computing the sextet polynomials.

In particular, our algorithm requires the following three steps.

- (i) Construction of the Clar graph of B .
- (ii) Construction of the reduced Clar graph.
- (iii) Determination of the independence polynomial of the reduced Clar graph.

By (3), the polynomial obtained in step (iii) is the sextet polynomial of B .

Since $C(B_1)^* = G_1$, we have already determined the sextet polynomial of ovalene:

$$\sigma(B_1) = 1 + 10x + 24x^2 + 12x^3 + x^4.$$

The sextet polynomial of 2,3,4,5-dibenzoterrylene (B_3) is immediately obtained using (2):

$$\sigma(B_3) = \omega(C(B_3)^*) = \omega(P_4) \cdot \omega(P_2) \cdot \omega(P_2).$$

Thus

$$\sigma(B_3) = 1 + 8x + 23x^2 + 28x^3 + 12x^4.$$

As a third illustration we compute the sextet polynomial of kekulene.

$$\begin{aligned} \sigma(B_2) &= \omega\left(\text{Diagram 1}\right) = \\ &= \omega\left(\text{Diagram 2}\right) + x \cdot \omega\left(\text{Diagram 3}\right) = \\ &= \omega\left(\text{Diagram 4}\right) + x \cdot \omega\left(\text{Diagram 5}\right) + \\ &\quad + x \cdot \omega\left(\text{Diagram 6}\right) + x^2 \cdot \omega\left(\text{Diagram 7}\right) \end{aligned}$$

Since

$$\begin{aligned} \omega\left(\text{Diagram 8}\right) &= \omega(\text{Diagram 9}) + x \cdot \omega(\text{Diagram 10}) = \\ &= \omega(P_1) \omega(P_3) + x \cdot \omega(P_1) = 1 + 5x + 5x^2 + x^3 \end{aligned}$$

we obtain finally

$$\begin{aligned} \sigma(B_2) &= (1 + 5x + 5x^2 + x^3)^2 \\ &\quad + 2x(1 + 3x + x^2)^2 + x^2(1 + x)^2, \end{aligned}$$

i.e.

$$\begin{aligned} \sigma(B_2) &= 1 + 12x + 48x^2 + 76x^3 + 48x^4 \\ &\quad + 12x^5 + x^6. \end{aligned}$$

Note that the calculation of $\sigma(B_2)$ by the previously known enumeration method [1] would be an enormously cumbersome task – one would have to draw 198 Clar-type formulas of kekulene, i.e. more than two thousand hexagons. On the other hand, the present technique requires only a few minutes of work and just one sheet of paper.

Cata-Condensed Systems

In this section we consider an important special case, namely the cata-condensed benzenoid molecules. For these systems the general algorithm described in the previous section can be significantly simplified. First of all, for all cata-condensed systems the Clar graph and the reduced Clar graph coincide (see Appendix 2). Hence step (ii) can be omitted.

a) Non-branched cata-condensed systems

The hexagons h_1, h_2, \dots, h_n of a non-branched cata-condensed benzenoid (NBCCB) molecule can be labelled so that h_r and h_{r+1} are adjacent for $r = 1, \dots, n-1$. The hexagons h_1 and h_n are thus terminal.

The non-terminal hexagons in a NBCCB system can be annelated in just two ways, viz.



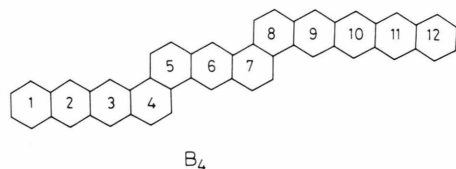
Therefore, an ordered n -tuple of symbols L, A, the so called L,A-sequence, can be associated to every NBCCB molecule [7]. The L,A-sequence of the molecule B will be denoted by $\langle B \rangle$. Hence

$$\langle B \rangle = (S_1, S_2, \dots, S_n),$$

where $S_1 = S_n = L$, and $S_r = L$ if the hexagon h_r of B is annelated in L-mode, and $S_r = A$ if the hexagon h_r is annelated in A-mode ($r = 2, 3, \dots, n-1$). The general form of an L,A-sequence is

$$\langle B \rangle = L^{t_1} A L^{t_2} A L^{t_3} \dots A L^{t_m},$$

where L^2 means LL, L^3 means LLL etc. E.g., the hexagons of B_4 are labelled as follows:



Therefore

$$\langle B_4 \rangle = LLLAALAALLL = L^3 A L^0 A L^1 A L^0 A L^4,$$

which means that $t_1 = 3$, $t_2 = 0$, $t_3 = 1$, $t_4 = 0$, $t_5 = 4$ and $m = 5$.

We distinguish the following m subsequences of $\langle B \rangle$:

$$\langle B | 1 \rangle = L^{t_1} A,$$

$$\langle B | k \rangle = A L^{t_k} A, \quad k = 2, \dots, m-1,$$

$$\langle B | m \rangle = A L^{t_m}.$$

In order to transform the L,A-sequence of B into the corresponding Clar graph we have to apply the following rules.

i) The vertices of $C(B)$ correspond to the symbols L, A of $\langle B \rangle$.

ii) The vertices corresponding to each $\langle B | k \rangle$, $k = 1, 2, \dots, m$, form a complete graph, i.e. every two vertices corresponding to the same $\langle B | k \rangle$ are connected.

iii) The vertices which do not simultaneously correspond to any subsequence $\langle B | k \rangle$ are not connected.

The above rules are the consequence of the fact that no two hexagons of B, corresponding to the same $\langle B | k \rangle$ are mutually resonant, whereas hexagons corresponding to different $\langle B | k \rangle$'s are necessarily mutually resonant.

For example, in the case of B_4 :

$$\langle B_4 | 1 \rangle = (S_1, S_2, S_3, S_4),$$

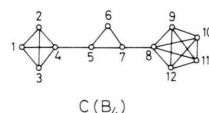
$$\langle B_4 | 2 \rangle = (S_4, S_5),$$

$$\langle B_4 | 3 \rangle = (S_5, S_6, S_7),$$

$$\langle B_4 | 4 \rangle = (S_7, S_8),$$

$$\langle B_4 | 5 \rangle = (S_8, S_9, S_{10}, S_{11}, S_{12}),$$

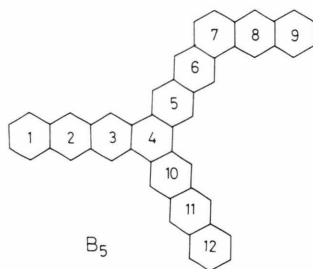
and therefore $C(B_4)$ has the following structure



b) Branched cata-condensed systems

We may still use the L,A-sequence formalism with an additional convention that a hexagon which is fused simultaneously to three other hexagons (i.e. a branched hexagon) is assigned the symbol A.

Thus for the benzenoid system B_5 we have $S_4 = S_7 = A$ and $S_r = L$ otherwise:



We have the subsequences

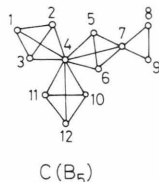
$$\langle B_5 | 1 \rangle = (S_1, S_2, S_3, S_4),$$

$$\langle B_5 | 2 \rangle = (S_4, S_5, S_6, S_7),$$

$$\langle B_5 | 3 \rangle = (S_7, S_8, S_9),$$

$$\langle B_5 | 4 \rangle = (S_4, S_{10}, S_{11}, S_{12}),$$

from which the construction of the Clar graph is immediate:



Appendix 1

An Alternative Method for the Calculation of the Independence Numbers

We present here a pruning method as an alternative to the recurrence relation (1). The method is efficient for graphs with moderate number of vertices (eight vertices or less).

1. Define two operators \hat{P}_1 and \hat{P}_2 , such that \hat{P}_1 prunes a vertex (any vertex) in G plus all other vertices connected to it, and \hat{P}_2 prunes that vertex upon which \hat{P}_1 operated. The operations \hat{P}_1 and \hat{P}_2 must follow one another.

2. A pruning sequence is performed on G until a terminal graph G_T is reached. A terminal graph is defined as

$$\hat{P}_1 G_T = 0 \quad \text{and} \quad \hat{P}_1 \hat{P}_2 G_T = 0,$$

with 0 denoting the empty graph.

3. The graph resulting in the first pruning sequence will be denoted as PG , its order (i.e. the number of its vertices) being $|PG|$. Observe that

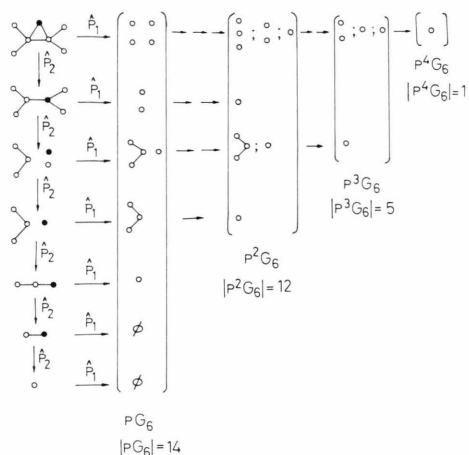


Fig. 2. Calculation of the independence numbers of the Clar graph of tetrabenzoanthracene using the pruning method.

PG is a disconnected graph. It can be shown that

$$|PG| = o(G, 2).$$

4. The graph PG is subjected to another pruning sequence to give P^2G , the order of which is $|P^2G|$. Then

$$|P^2G| = o(G, 3).$$

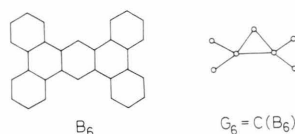
5. A third pruning sequence is performed on P^2G to give P^3G , and so on until all components of a P^kG are terminal graphs. Then $P^{k+1}G = 0$. In general, for $k \geq 1$,

$$|P^kG| = o(G, k+1)$$

and, in addition,

$$|P^0G| = |G| = o(G, 1).$$

The pruning method is illustrated on Fig. 2 on the example of G_6 , the Clar graph of tetrabenzoanthracene, B_6 .



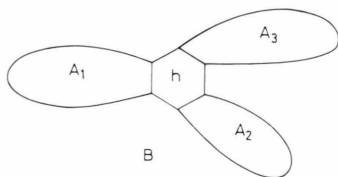
Whence

$$(G_6) = 1 + 7x + 14x^2 + 12x^3 + 5x^4 + x^5.$$

The order of the pruned graph is independent of the sequence of pruning.

Appendix 2

We prove that for cata-condensed benzenoid systems the Clar graph coincides with the reduced Clar graph. In order to do this it is sufficient to show that all hexagons in a cata-condensed benzenoid molecule are resonant. Let h be a hexagon in a cata-condensed system B . In the general case B has the following structure:



Here A_1 , A_2 and A_3 denote three benzenoid subsystems attached to h . A_i is a cata-condensed system with, say, n_i hexagons, $i = 1, 2, 3$.

If $n_i = 0$, then the respective side group is, of course, missing. A_i has $4n_i + 2$ vertices, all of which belong to the perimeter of A_i and two of which belong also to h . Let the vertices of A_i be labelled by $v_{i,1}, v_{i,2}, \dots, v_{i,4n_i}, v_{i,4n_i+1}$ and $v_{i,4n_i+2}$ so that $v_{i,r}$ and $v_{i,r+1}$ are adjacent for all $r = 1, 2, \dots, 4n_i + 1$ and so that $v_{i,1}$ and $v_{i,4n_i+2}$ belong to h . In order to demonstrate that h is resonant, we have to verify that $B-h$ has at least one Kekulé structure. This is indeed the case. Such a Kekulé structure is obtained if we set double bonds between $v_{i,r}$ and $v_{i,r+1}$ for $r = 2, 4, \dots, 4n_i$ and $i = 1, 2, 3$.

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