Topological Properties of Benzenoid Systems. IX *. On the Sextet Polynomial

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A number of mathematical relations for the sextet polynomial are derived. A graph has been introduced (the so called C-graph), representing those properties of a benzenoid system which are essential in the sextet theory of Clar. The main structural properties of the C-graph are determined. The obtained results contribute towards a better understanding of the algebraic and combinatorial background of Clar's theory of the aromatic sextet.

Introduction

Few years ago Hosoya and Yamaguchi [1] introduced the sextet polynomial of a benzoid system B as

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

The coefficient $s(B, k)$ of this polynomial is by definition equal to the number of Clar-type resonant sextet formulas of B, in which exactly k aromatic sextets exist. In particular, $s(B, 1) = n_R$ is the number of those six-membered rings (hexagons) of B in which an aromatic sextet can be drawn in at least one Clar-type formula.

The sextet polynomial was shown to possess a number of interesting properties and to reflect the main features of Clar's resonant sextet theory [2]. Some relations between $\sigma(G)$ and the resonance theory [3] were also observed [1]. Various further developments of the sextet polynomial concept can be found elsewhere [4—8]. The fact that the sextet polynomials of some benzenoid systems are identical with the characteristic polynomials of certain acyclic graphs was first pointed out in [9]. In the present paper we shall generalize the result of [9] and, in particular, show that there exist close relations between $\sigma(B)$ and a number of graph theoretical polynomials.

For necessary details on the sextet polynomial and the numbers $s(B, k)$ the reader is refered to [1].

The C-Graph

In this section we shall define an auxiliary graph, the C-graph, associated with a benzenoid system. The close connection of the C-graph and Clar's theory will become evident in the subsequent section.

Let B be a benzenoid molecule composed of n hexagons (i.e. n six-membered rings) $h_1, h_2, \ldots, h_n$. In this paper we shall consider only benzenoid systems for which at least one Kekulé valence formula can be drawn. Then, of course, the Clar resonant sextet formalism can be applied [1, 2] and several Clar-type formulas of B can be drawn. If at least in one of such formulas there is an aromatic sextet in the hexagon h_r, we say that h_r is resonant. If at least one Clar-type formula exists in which two aromatic sextets are simultaneously located in the hexagons h_r and h_s, we say that h_r and h_s are mutually resonant. For every pair of hexagons we can decide whether they are mutually resonant or not [1].

We construct now a graph $C = C(B)$ with n vertices $v_1, v_2, \ldots, v_n$, such that the vertices v_r and v_s of C are adjacent if and only if the hexagons h_r and h_s in B are mutually not resonant.

For example, the C-graphs of anthracene (B_1), picene (B_2), perylene (B_3), pentacene (B_4), triphenylene (B_5) and coronene (B_6) are given on Figure 1. After a little exercise the construction of the C-graphs becomes a routine task. We list here some properties of C(B) which can be easily verified.

1. The C-graph of the linear polyacenes is the complete graph (examples: B_1 and B_4).
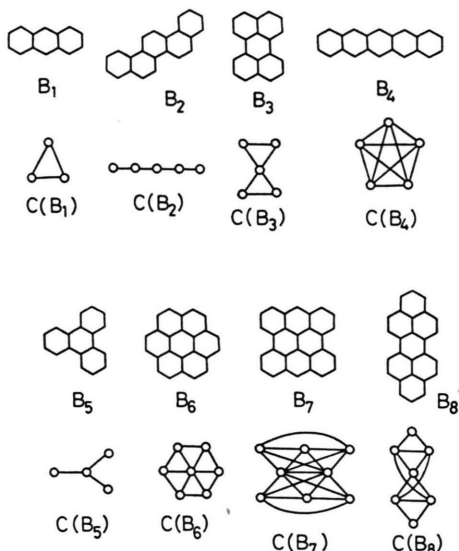
Fig. 1. Some benzenoid systems and their C-graphs.

2. The C-graph of the angular polyacenes is the path (example: B_2).

3. If all the hexagons of a benzenoid system B are resonant and if B is composed of two disconnected parts B_a and B_b, then C(B) is composed of two disconnected components $C(B_a)$ and $C(B_b)$.

If, however, not all hexagons of B are resonant, then the above statement does not hold because of the following property of the C-graph.

4. If the vertex v_r of C(B) corresponds to a hexagon which is not resonant in B, then v_r is adjacent to all other vertices of C(B). Hence the degree of v_r is $n-1$. As an example may serve the central hexagon of B_3 and the two non-resonant hexagons of B_7.

5. If two hexagons h_r and h_s are adjacent in B then the vertices v_r and v_s are adjacent in C(B).

The inner dual $D = D(B)$ of a benzenoid system B is the graph with the vertices $v_1, v_2, \ldots, v_n$, such that the vertices v_r and v_s are adjacent if and only if the hexagons h_r and h_s are adjacent [10−12]. Then from the property 5 we immediately have the following result.

6. The inner dual of B is always a (spanning) subgraph of C(B).

C(B) coincides with D(B) in many cases (examples: B_2, B_3, B_5, B_6, all angular polyacenes etc.). In fact, the graphs C(B) and D(B) are isomorphic if and only if all pairs of non-adjacent hexagons in B are mutually resonant.

A full topological characterization of the benzenoid systems for which the inner dual and the

C-graph coincide seems to be not simple. Some structural requirements which are sufficient for the validity of the condition $C \neq D$ are given below.

7. Let B possess two non-adjacent hexagons h_r and h_s, such that h_r is not resonant. Then the inner dual of B differs from the C-graph (example: B_7).

B_3 is the only benzenoid molecule whose non-resonant hexagon is adjacent to all other hexagons. Therefore we have the following corollary of 7.

8. $C(B_3) = D(B_3)$. For all other benzenoid systems B which possess non-resonant hexagons, $C(B) \neq D(B)$.

The statement 8 completely solves our problem for benzenoid systems with non-resonant hexagons. Therefore in the subsequent considerations we shall focus our attention to systems whose all hexagons are resonant.

The vertices of B can be divided into two groups — external and internal [11, 13]. The external vertices form the perimeter of B. Cata-condensed systems possess only external vertices [11, 13].

9. If B has an external vertex w of degree two, such that its both neighbouring vertices are of degree three, then $C(B) \neq D(B)$.
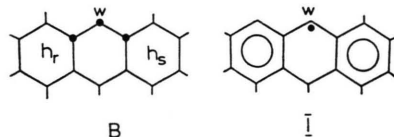
The property 9 follows from the observation that the hexagons h_r and h_s in B can not be mutually resonant since then in the pertinent Clar-type formulas (I) the vertex w would become isolated. Therefore the vertices v_r and v_s are adjacent in C(B), but, of course, are not adjacent in D(B).

In the case of cata-condensed benzenoid systems we have the following specialization of the statement 9.

10. If B is cata-condensed, then a necessary and sufficient condition for $C(B) = D(B)$ is that no three hexagons of B are annelated in a linear mode or, what is the same, that the anthracene fragment (B_1) is not contained in B.

For peri-condensed systems the requirement 9 although sufficient is not necessary. For example, the molecule B_8 has no atoms of the type w, but nevertheless $C(B_8) \neq D(B_8)$.

11. The C-graph of a peri-condensed system contains triangles. The C-graph of a cata-condensed

system contains triangles unless the C-graph and the inner dual coincide.

12. The C-graph may also contain larger cycles, but then inside every k-membered cycle ($k \geqq 4$) there are at least $k-2$ triangles. Every vertex belonging to a k-membered cycle ($k \geqq 4$) belongs also to a triangle.

13. The C-graph of a branched cata-condensed system contains a vertex of degree three which does not lie on a triangle (and therefore does not lie on any cycle).

This latter statement follows from the observation that the three hexagons which are adjacent to a branched hexagon of a branched cata-condensed system are always mutually resonant.

The properties 11—13 are important for the application of Beineke's theorem by which one can decide whether a C-graph is a line graph (see later).

The C-graph represents those relations between the hexagons of a benzenoid system which are fundamental from the point of view of Clar's resonant sextet theory. Therefore C(B) could be perhaps named the Clar graph of the benzenoid system B.

Some Graphic Polynomials and Their Relation to the Sextet Polynomial

In order to formulate the dependence of the sextet polynomial on the C-graph we need some further definitions. Let G be a graph with n vertices and m edges. Two vertices of G are said to be independent if they are not adjacent. Two edges of G are said to be independent if they are not incident.

Let the number of selections of k mutually independent vertices in G be denoted by $o(G, k)$, whereas the number of selections of k mutually independent edges be denoted by $p(G, k)$, $k = 1, 2, \ldots$. In addition we shall adopt the convention

$$o(G, 0) = p(G, 0) = 1$$

for all graphs G.

According to the above definitions, $o(G, 1) =$ number of vertices of G, and $p(G, 1) =$ number of edges of G.

Let us now define the graphic polynomials $\omega(G)$ and $\pi(G)$ as follows:

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

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

Note that $\pi(G)$ is just what Hosoya called the Z-counting polynomial [14, 15]. There exists a close relation between $\pi(G)$ and the so called matching polynomial $\alpha(G)$, namely

$$\alpha(G, x) = x^n \pi(G, x^{-2}).$$

On the other hand, the mathematical theory of the matching polynomial is nowadays very well elaborated [16—20] because of its numerous applications in physics and chemistry. In the following we will show that the sextet polynomial of certain benzenoid systems can be reduced to the matching polynomial. This will enable the application of results which are already known for the matching polynomials, in Clar's resonant sextet theory. For the purpose of the subsequent considerations we shall need the following properties of $\alpha(G)$.

Let $L(G)$ denote the line graph of the graph G. (Details on line graphs can be found in every textbook of graph theory, e.g. [21].)

Lemma 1. $\pi(G) = \omega(L(G))$.

Lemma 2 [19]. The zeros of $\alpha(G)$ are real. Therefore the zeros of $\pi(G)$ are real and negative.

Let $\Phi(G)$ be the characteristic polynomial of the graph G. (For the theory of the characteristic polynomial see [22].)

Lemma 3. $\alpha(G) = \Phi(G)$ if and only if G is acyclic.

For further elements of the theory of the matching polynomial see the reviews [17, 20].

The basic properties of $\omega(G)$ are summarized in the Appendix.

Theorem 1. If in a benzenoid molecule B with n hexagons there are n_R resonant hexagons, then

$$\sigma(B, x) = \omega(C(B), x) - (n - n_R) x. \qquad (1)$$

In particular, if all the hexagons are resonant ($n_R = n$), then the polynomials $\sigma(B)$ and $\omega(C)$ coincide.

Proof. From the definition of the C-graph follows immediately that for $k \geqq 2$ the number of Clar-type sextet formulas with exactly k resonant sextets is just equal to the number of selections of k independent vertices in C(B). In other words, for $k \geqq 2$,

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

For $k = 1$, however, $s(B, k) = n_R$ whereas

$o(C(B), k) = n$. Taking this into account we arrive to the formula (1).

Although Theorem 1 is a more or less direct consequence of the definition of C(B) and $\omega(G)$, we find this result important. Namely, Eq. (1) provides a connection between the basic concepts of Clar's theory and the purely graph theoretical ω-polynomial. In other words, Theorem 1 provides a precisely defined graph theoretical basis for Clar's resonant sextet theory.

If G is the line graph of a graph H, we shall write either $G = L(H)$ or $H = L^{-1}(G)$. If G is not a line graph, then $L^{-1}(G)$ does not exist. For example, $C(B_5)$, $C(B_6)$ and $C(B_7)$ are not line graphs (i.e. $L^{-1}(C(B_i))$, $i = 5, 6, 7$ do not exist), whereas $C(B_i)$, $i = 1, 2, 3, 4$ and 8 are line graphs. Using standard graph theoretical methods [21] it is not difficult to construct $L^{-1}(C)$. Some examples are given in Figure 2.

Theorem 2. If $C = C(B)$ is a line graph, then

$$\sigma(B, x) = \pi(L^{-1}(C), x) - (n - n_R) x$$

and

$$x^N \sigma(B, x^{-2}) = \alpha(L^{-1}(C), x) - (n - n_R) x^{N-2},$$

where N is the number of vertices of $L^{-1}(C)$. In particular, if all the hexagons of B are resonant, then $\sigma(B)$ and $\pi(L^{-1}(C))$ coincide.

Proof. Combine Theorem 1 with Lemma 1.

Theorem 3. If all the hexagons of the benzenoid system B are resonant and its C-graph is a line graph, then all the zeros of the sextet polynomial are real and negative.

Proof. Combine Theorem 2 with Lemma 2.

The above result is of great importance for the calculation of Aihara's resonance energy [4—6], namely it guarantees its reality. If C(B) is not a line graph, then the zeros of the sextet polynomial

Fig. 2. Graphs whose line graphs are given on Figure 1.

may be complex, what has already been noticed in [4].

Theorem 4. If $L^{-1}(C(B))$ exists and is acyclic, then

$$x^N \sigma(B, x^{-2}) = \Phi(L^{-1}(C), x) \\ - (n - n_R) x^{N-2}. \quad (2)$$

Proof. Combine Theorem 2 with Lemma 3.

This latter theorem is a generalization of the result of the paper [9]. Namely, in [9] a statement has been proved which is equivalent to the special case of Eq. (2) for cata-condensed benzenoid molecules (for which necessarily $n_R = n$). In [9] was in fact noticed that the right hand side of Eq. (2) is the characteristic polynomial of a certain graph, but not that this graph is $L^{-1}(C(B))$. As a consequence a rather cumbersome method was proposed for the construction of the respective graph.

In order to make the Theorems 2, 3 and 4 more efficient, we need to establish when a C-graph is a line graph. As the previous examples indicate, $L^{-1}(C)$ exists in some cases and does not exist in other cases. There are both cata-condensed (examples: B_1, B_2, B_4) and peri-condensed systems (examples: B_3, B_8) for which the C-graph is a line graph and both cata-condensed (example: B_5) and peri-condensed systems (examples: B_6, B_7) for which the C-graph is not a line graph.

In graph theory the necessary and sufficient structural conditions for line graphs are well known [21]. Applying Beineke's theorem [21] it is not difficult to determine whether any particular C-graph is or is not a line graph. (In Beineke's theorem nine graphs $G_1, \ldots, G_9$ are determined. If the graph G is a line graph, then none of G_i, $i = 1, \ldots, 9$ can be maximal subgraphs of G.) For peri-condensed benzenoid systems we observed that the C-graphs are usually line graphs. In the present moment, however, we are able to formulate a general result only for cata-condensed systems.

Theorem 5. Let B be a cata-condensed benzenoid system. Then $L^{-1}(C(B))$ exists and is acyclic, and $\sigma(B) = \Phi(L^{-1}(C(B)))$, if and only if B is non-branched.

For example, B_1, B_2 and B_4 are non-branched and B_5 is a branched cata-condensed molecule. Note that all hexagons in cata-condensed systems must be resonant, $n_R = n$. In [9] the "if" part of Theorem 5 has been observed only.
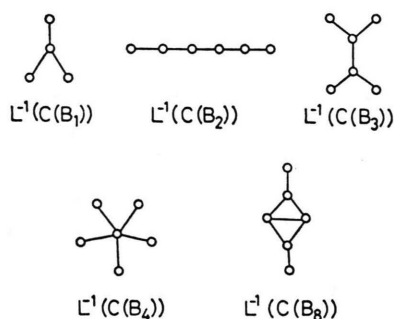
Proof of Theorem 5 is based on the application of Beineke's theorem. If B is a branched cata-condensed system, then according to property 13, C(B) contains a triplet of mutually non-adjacent vertices which are all adjacent to a fourth vertex. From Beineke's theorem we know that this is a forbidden subgraph for line graphs. Hence C(B) is not a line graph.

If B is a non-branched cata-condensed system, then C(B) is composed of linearly arranged blocks, each block being a complete graph. Thus none of the nine forbidden subgraphs is contained in C(B) and hence C(B) is a line graph.

The construction of $L^{-1}(C(B))$ in this latter case is now straightforward.

Concluding this paper we would like to point at some problems for which in the present moment we are not able to obtain a general solution. First, under which conditions are the graphs C(B) and D(B) isomorphic? Second, under which conditions is C(B) a line graph? A third related question is the characterization of those benzenoid systems for which $L^{-1}(C)$ is acyclic.

In this work all these problems have been fully solved for cata-condensed, but only partially for peri-condensed benzenoid systems.

Appendix

Whereas the mathematical properties of $\pi(G)$ have been extensively investigated [14—20], it seems that the ω-polynomial has not yet been considered in the literature. Nevertheless, problems concerning the sets of independent vertices of a graph belong to the classical topics of graph theory.

Furthermore, a chemical application of the numbers $o(G, k)$ has been recently reported [23]. In the following some elementary facts about the ω-polynomial will be mentioned.

1. Let O_n, K_n and $K_{a, b}$ be the graph with n vertices and without edges, the complete graph with n vertices, and the complete bipartite graph with $a + b$ vertices, respectively. Then

$$\omega(O_n) = (1 + x)^n,$$
$$\omega(K_n) = 1 + nx,$$
$$\omega(K_{a, b}) = (1 + x)^a + (1 + x)^b - 1.$$

2. If the graph G is composed of two disconnected parts G_a and G_b, then $\omega(G) = \omega(G_a)\,\omega(G_b)$.

3. Let v be a vertex of G and let A_v be the set containing the vertex v and all the vertices adjacent to v. Then we have the recurrence relation

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

This formula enables a straightforward evaluation of the ω-polynomial. Having in mind Theorem 1, the same result provides a recursive technique for the computation of the sextet polynomials.

4. $$(\mathrm{d}/\mathrm{d}x)\,\omega(G) = \sum_v \omega(G - A_v),$$

with the summation going over all vertices of the graph G.

5. $$\omega(L(G)) = \pi(G).$$

6. If G is a line graph, then all the zeros of $\omega(G)$ are real and negative. If, however, G is not a line graph, then it can occur that the zeros of $\omega(G)$ are complex.

A more detailed study on the ω-polynomial will be reported elsewhere [24].

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