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The Gutman formulas for algebraic structure count

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The concept of ASC (algebraic structure count) is introduced into theoretical organic chemistry by Wilcox as the difference between the number of so-called "even" and "odd" Kekulé structures of a conjugated molecule. Precisely, algebraic structure count (ASC-value) of the bipartite graph G corresponding to the skeleton of a conjugated hydrocarbon is defined by $ASC\{G\} = \sqrt{|\det A|}$ where A is the adjacency matrix of G. In the case of bipartite planar graphs containing only circuits of the length of the form $4s+2$ ($s = 1, 2, \ldots$) (the case of benzenoid hydrocarbons), this number is equal to the number of the perfect matchings (K-value) of G. However, if some of circuits are of the length $4s$ ($s = 1, 2, \ldots$) then the problem of evaluation ASC-value becomes more complicated. The theorem formulated and proved in this paper gives a simple and efficient algorithm for calculation of algebraic structure count of an arbitrary bipartite graphs with $n + n$ vertices. Three recurrence formulas for the algebraic structure count – the *Gutman formulas*, which are closely analogous to the well-known recurrence formula $K\{G\} = K\{G - e\} + K\{G - (e)\}$ for the number of perfect matchings ($G - e$ is the subgraph obtained from the graph G by deleting the edge e and $G - (e)$ is the subgraph obtained from G by deleting both the edge e and its terminal vertices) are obtained as a simple corollary of the theorem.

KEY WORDS: algebraic structure count, Kekulé structure

AMS subject classification: 05C70, 05C50, 05B50, 05A15

1. Introduction

The *algebraic structure count* (ASC-value) of a bipartite graph G is defined by

$$ASC\{G\} := \sqrt{|\det A|},$$

where A is the adjacency matrix of G. This concept was introduced into theoretical organic chemistry by Wilcox [1,2], following earlier work of Dewar and Longuet-Higgins [3]. It is based on the idea that each individual perfect matching (*Kekulé structure*) of the graph corresponding to a conjugated molecule has a "parity". Then ASC is equal to the difference between the number of "even" and the number of "odd" perfect matchings.

The thermodynamic stability of an alternant hydrocarbon is related to the ASC-value (*ASC*) for the bipartite graph which represents its skeleton. The basic application of *ASC* is in the following. Among two isomeric conjugated hydrocarbons (whose related graphs have an equal number of vertices and an equal number of edges), the one having greater *ASC* will be more stable. In particular, if $ASC = 0$, then the respective hydrocarbon is extremely reactive and usually does not exist [4,5].

In the case of the bipartite planar graphs containing only circuits of the length of the form $4s + 2$ $(s = 1, 2, \dots)$ (benzenoid hydrocarbons) all perfect matchings are of the same parity. Consequently, in this case *ASC* coincides with the number of perfect matchings, i.e., K-value.

The enumeration of perfect matchings (Kekulé structures) is a classical problem in the theoretical chemistry of polycyclic conjugated molecules with a plethora of known counting formulae and several hundreds of published papers [6]. This can be attributed to the fact that simple and powerful recursive method exists for the calculation of K-values which is based on the formula

$$K\{G\} = K\{G - e\} + K\bigl\{G - (e)\bigr\}.$$

In this and what following $G - e$ stands for the subgraph obtained from the graph G by deleting the edge e of G and $G - (e)$ stands for the subgraph obtained from G by deleting both the edge e and its terminal vertices.

On the other hand, there are very few works dealing with ASC. Ten years ago prof. Ivan Gutman with his colleagues started the systematic study of the algebraic structure count (ASC) [9–16]. The graphs of interest were bipartite planar graphs with at least one face-boundary (cell) of length of the form $4s$ $(s = 1, 2, \dots)$ (nonbenzenoid alternant conjugated hydrocarbons). Let us mention some of the more interesting results (in our subjective opinion).

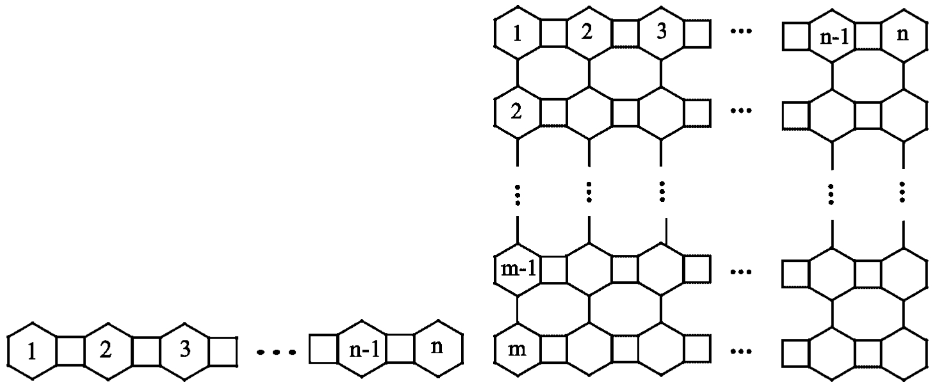
The formula for the *ASC*-number for the linear $[n]$-phenylene (figure 1(a)) is $ASC(X_{1,n}) = n + 1$ [9], and the one for the multiple phenylenes (figure 1(b)) is

$$ASC(X_{m,n}) = \frac{1}{R}\left[\left(\frac{n+1+R}{2}\right)^{m+1} - \left(\frac{n+1-R}{2}\right)^{m+1}\right],$$

where $R = \sqrt{2n+1}$ if n is even and $R = \sqrt{2n+2}$ if n is odd [11,12].

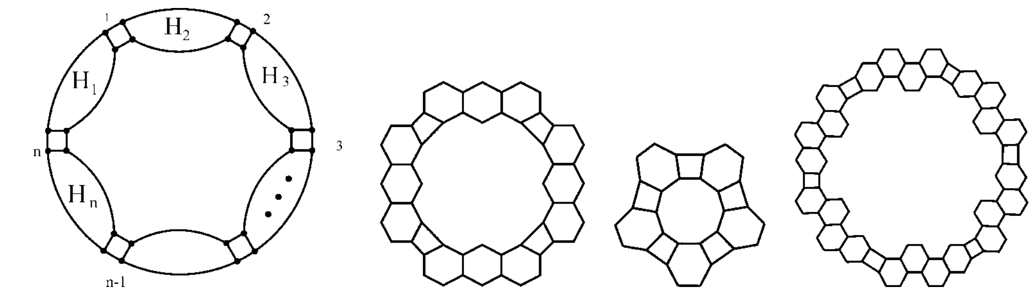
The formula for the ASC the cyclic hexagonal-square chain C_n consisting of n mutually isomorphic hexagonal chains $H_1, H_2, \dots, H_n$ cyclically concatenated by circuits α_i of length 4 (figure 2(a)) was obtained in [15]. In special cases depicted in figures 2(b)–(d) we have $ASC(C_4) = 0$, $ASC(C_5) = 11$ and $ASC(C_6) = 54756$.

In [8] Gutman proved the following theorem.



(a) $X_{1,n}$ (b) $X_{m,n}$

Figure 1. (a) Linear [n]-phenylene, (b) multiple phenylenes.



(a) $C_n = C_n(H_1, H_2, \ldots, H_n)$ (b) C_4 (c) C_5 (d) C_6

Figure 2. (a) The cyclic hexagonal-square chain C_n consisting of n mutually isomorphic hexagonal chains $H_1, H_2, \ldots, H_n$, cyclically concatenated by circuits α_i of length 4, (b) C_4, (c) C_5, (d) C_6.

Theorem 1. For the arbitrary bipartite graph with $n + n$ vertices and for every edge e of G the values $ASC(G)$, $ASC(G-e)$ and $ASC(G-(e))$ conform to one of the following tree formulas:

$$\begin{aligned} ASC\{G\} &= ASC\{G-e\} + ASC\big\{G-(e)\big\}, \\ ASC\{G\} &= ASC\{G-e\} - ASC\big\{G-(e)\big\}, \\ ASC\{G\} &= ASC\big\{G-(e)\big\} - ASC\{G-e\}. \end{aligned} \tag{1}$$

He deduced these recurrence formulas using some (more complicated) formulas relating to characteristic polynomials of corresponding graphs. These techniques does not make possible to determine the conditions to predict which of three formulas in (1) will apply for a given edge e of a given graph G.

In this paper we obtain the same formulas with a much simpler explanation which enable us in some cases with an simple and applicable “paper-and-pencil” method for the calculation of ASC.

2. Preliminaries

Let G be an (undirected) bipartite graph with $2n$ vertices with n vertices of each colour: white vertices $w_1, w_2, \dots, w_n$ and black vertices $b_1, b_2, \dots, b_n$, and every edge of G connects vertices of different colours.

Let H be a digraph, obtained from G by replacing every edge of G by two directed edges of opposite orientations between the same pair of vertices.

A spanning directed subgraph of H such that exactly one arc goes out from every white (black) vertex and exactly one arc terminates in every black (white) vertex is called a *white* (*black*) *separation*. Every white (black) separation can be represented as a permutation $\mathcal{P}$: $j_1 j_2 \dots j_n$ by a permutation of indexes of black (white) vertices. The labels $j_1, j_2, \dots, j_n$ denote indexes of black (white) vertices on which the arcs, going out from the white (black) vertices $r_1, r_2, \dots, r_n$ $(b_1, b_2, \dots, b_n)$ terminate. *The parity of the white* (*black*) *separation* is defined as the parity of corresponding permutation $\mathcal{P}$ of numbers $1, \dots, n$, i.e., as the quantity $(-1)^{Inv(\mathcal{P})}$, where $Inv(\mathcal{P})$ is the number of inversions in the permutation $\mathcal{P}$ [7].

A regular spanning subgraph of G of degree 1 is called a *perfect matching* of G. Let M be a perfect matching of G and W and B be the corresponding white and black separation in H, respectively. If we denote the parity of the separation X by *par* X then it can easily be seen that *par* $W =$ *par* B (the corresponding permutations are inverse). Now, we can define the parity *par* K of the perfect matching K by

$$par\ K \stackrel{\text{def}}{=} par\ W = par\ B.$$

Let K_+^G be the number of perfect matchings of positive parity and K_-^G be the number of perfect matchings of negative parity in the graph G. It can be proved [7] that

$$\det A = (-1)^n \left| K_+^G - K_-^G \right|^2,$$

where A is the adjacency matrix (the Dewar and Longuet–Higgins theorem). Thus, from the definition of the value ASC we obtain

$$ASC(G) = \left| K_+^G - K_-^G \right|. \tag{2}$$

Let G' be a graphical representation of the considered bipartite graph G obtained in such way that all vertices are aligned in two rows: the upper one consisting of $w_1, w_2, \dots, w_n$ and the lower one consisting of vertices $b_1, b_2, \dots, b_n$ (figure 3). For every $i = 1, \dots, n$ the vertex b_i is positioned bellow the vertex w_i. The edges of G' are represented by linear segments.

For example, a bipartite graph G and its corresponding representation G' are plotted in figure 3. For the perfect matching of this graph labeled by bold lines in figure 3, corresponding permutation of black vertices is $\mathcal{P}$: 12485673.

Recall that the parity of an arbitrary permutation $\mathcal{P}$ can be determined as $(-1)^{p(\mathcal{P})}$ or $(-1)^{n-q(\mathcal{P})}$ where $p(\mathcal{P})$ is the number of (oriented) circuits of even length and $q(\mathcal{P})$ is the number of all (oriented) circuits in the digraph of permutation $\mathcal{P}$. For the permutation

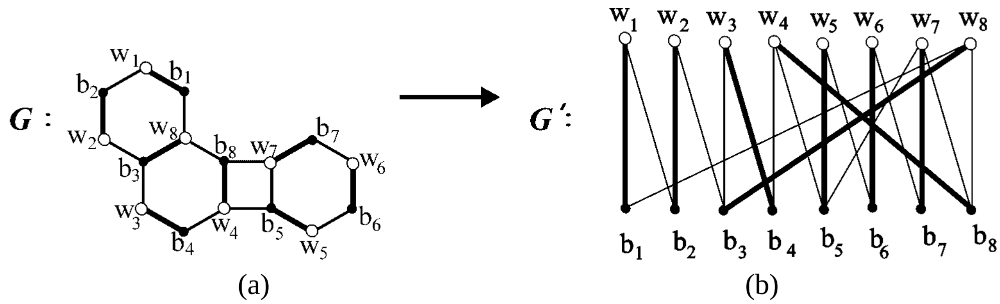


Figure 3. A bipartite graph G and its corresponding representation G'.

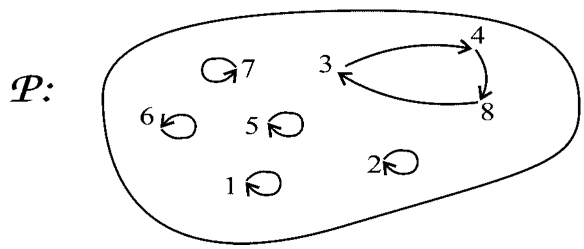


Figure 4. The permutation $\mathcal{P}$: 12485673 is even.

from the above example the values $p(\mathcal{P}) = 0$ and $q(\mathcal{P}) = 6$ (figure 4), so we can conclude that $\mathcal{P}$ is even.

On the other hand, observe that the parity of a perfect matching of the graph G is determined by parity of the number of intersections of line segments belonging the perfect matching (bold lines in figure 3) in corresponded representation G' of the graph G. Namely, every such intersection of two line segments corresponds to exactly one inversion of the black (white) separation. In our example in figure 3 the number of the line segments intersections in G' equals to 8 (even) so we obtain again that the perfect matching in the example is even.

Recall [7] that the property of two perfect matching "being of the same parity" depends neither on the labeling of the vertices nor on the choice of colours in the graph coloring. This binary relation is an equivalence relation and, in a natural way, subdivides the set of perfect matchings into two equivalence classes. However, the parity of a perfect matching depends on the labeling of the vertices.

Thus, we introduce a new value which depends on the vertex labeling in the bipartite graph. Let $\mathcal{L}$ be a starting (fixed) numbering of vertices of G, i.e., $\mathcal{L}(w_i) = i$, $i = 1, \ldots, n$; $\mathcal{L}(b_j) = j$, $j = 1, \ldots, n$. Then

$$\mathcal{D}_{\mathcal{L}}(G) \stackrel{\text{def}}{=} K_+^{G,\mathcal{L}} - K_-^{G,\mathcal{L}}, \tag{3}$$

where $K_+^{G,\mathcal{L}}$ is the number of perfect matchings of positive parity and $K_-^{G,\mathcal{L}}$ is the number of perfect matchings of negative parity in the graph G with respect to the labeling $\mathcal{L}$.

From (2) we obtain

$$ASC(G) = \big|\mathcal{D}_{\mathcal{L}}(G)\big|. \tag{4}$$

3. Recurrence formula for $\mathcal{D}_{\mathcal{L}}(G)$ and the Gutman formulas

Theorem 2. Let $\mathcal{L}$ be the given numbering of vertices of G ($\mathcal{L}(w_i) = i$, $i = 1, 2, \ldots, n$; $\mathcal{L}(b_j) = j$, $j = 1, 2, \ldots, n$), and e be an edge of G concatenating the vertices w_i and b_j. Then

$$\mathcal{D}_{\mathcal{L}}(G) = \mathcal{D}_{\mathcal{L}}(G-e) + (-1)^{i+j}\mathcal{D}_{\mathcal{L}'}\big(G-(e)\big), \tag{5}$$

where $\mathcal{L}'$ is the numbering of vertices of graph $G-(e)$ obtained from $\mathcal{L}$ in the following way:

$$\mathcal{L}'(w_k) = \begin{cases} \mathcal{L}(w_k), & \text{if } k < i, \\ \mathcal{L}(w_k) - 1, & \text{if } i < k \leqslant n-1 \end{cases} \tag{6}$$

and

$$\mathcal{L}'(b_k) = \begin{cases} \mathcal{L}(b_k), & \text{if } k < j, \\ \mathcal{L}(b_k) - 1, & \text{if } j < k \leqslant n-1. \end{cases} \tag{7}$$

Proof. Observe the representation G' of the considered graph G and a perfect matching K of G' containing the edge e. If we delete the edge e in G' and renumber all white vertices of G' on the right-hand side of the vertex w_i and all black vertices of G' on the right-hand side of the vertex b_j in the manner shown in (6) and (7), then we obtain the graphical representation of the graph $G-(e)$ described in section 2. Note that in this way the number of line segments intersection of K is reduced just for the number of these points belonging to the edge e (if there exists any).

Thus, for the case $i \equiv j \pmod 2$ this number is even because there are even numbers of vertices of G' on both of the sides of the straight line determined with w_i and b_j. Otherwise, for the case $i \not\equiv j \pmod 2$ this number is odd because there are odd numbers of vertices of G' on both of the considered sides. From above we can conclude the following.

If $i \equiv j \pmod 2$, then

$$\begin{aligned} K_+^{G,\mathcal{L}} &= K_+^{G-e,\mathcal{L}} + K_+^{G-(e),\mathcal{L}'}, \\ K_-^{G,\mathcal{L}} &= K_-^{G-e,\mathcal{L}} + K_-^{G-(e),\mathcal{L}'}. \end{aligned} \tag{8}$$

If $i \not\equiv j \pmod 2$, then

$$\begin{aligned} K_+^{G,\mathcal{L}} &= K_+^{G-e,\mathcal{L}} + K_-^{G-(e),\mathcal{L}'}, \\ K_-^{G,\mathcal{L}} &= K_-^{G-e,\mathcal{L}} + K_+^{G-(e),\mathcal{L}'}. \end{aligned} \tag{9}$$

From (3), (8) and (9) we obtain the formula (5). □

Using (4) and the statement of theorem 2 we obtain the Gutman formulas (theorem 1) for ASC as a simple corollary.

4. Remark

In some cases (like in the example below) when the considered graph contains as its subgraphs some of graphs for which we know the value ASC and for which we know at least one representative of the larger class of perfect matchings (the class of even or odd perfect matchings) (in [13] this is every so-called "good" Kekule structures of graph B_n) the procedure of determination ASC-value can be reduced. If it is the case, for the graphs $G-(e)$ and $G-e$ we can establish which of the Gutman formulas is valid for the edge e.

Example. Let $G_{\mathcal{L}}$ be the graph with a numbering $\mathcal{L}$ of its vertices depicted in figure 5. For the emphasized edge e the following two graphs represent its subgraphs $G-e$ and $G-(e)$ with corresponded numbering of edges, respectively.

Note that the graph $G-e$ has the only one perfect matching (whose edges are labeled in the picture by bold lines) corresponding to permutation (of black vertices) $\mathcal{P}$: 2 1 5 8 3 4 7 11 6 9 10 (figure 6(a)) that is odd because $(-1)^{Inv(\mathcal{P})} = (-1)^{11-4} = -1$.

This implies

$$\mathcal{D}_{\mathcal{L}}(G-e) = K_{+}^{G-e,\mathcal{L}} - K_{-}^{G-e,\mathcal{L}} = 0 - 1 = -1. \tag{10}$$

On the other hand, the graph $G-(e)$ is well-known graph [13] for which we know both the value of ASC and some of perfect matchings (so-called "good" perfect matchings) in the larger class. In our case, the $ASC(G-(e)) = 7$. The perfect matching of $G-(e)$ emphasized in figure 5 belongs to the class having numbers (is a "good" perfect matching). With respect to the numbering $\mathcal{L}'$ of vertices the permutation (of black vertices) $\mathcal{P}'$: 1 4 2 3 5 7 10 8 6 9 (figure 6(b)) corresponded to the perfect matching is odd because $(-1)^{Inv(\mathcal{P}')} = (-1)^{10-5} = -1$. This implies

$$\mathcal{D}_{\mathcal{L}'}\big(G-(e)\big) = K_{+}^{G-(e),\mathcal{L}'} - K_{-}^{G-(e),\mathcal{L}'} = -ASC\big(G-(e)\big) = -7. \tag{11}$$

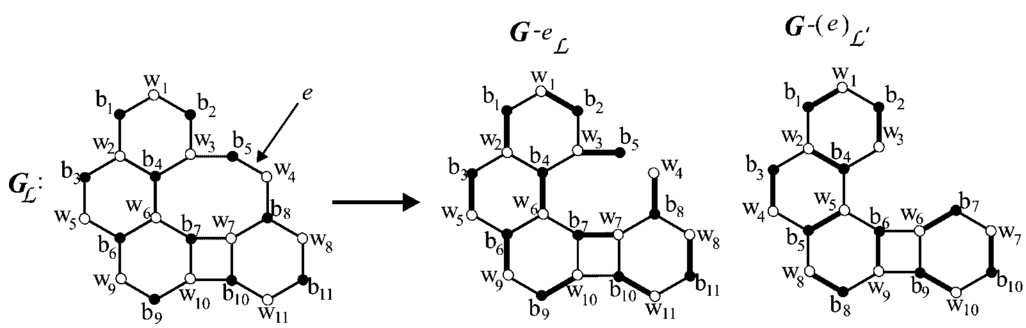
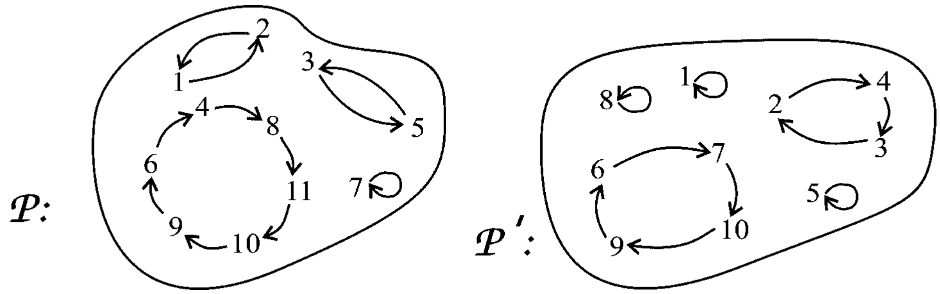


Figure 5. A graph $G_{\mathcal{L}}$ and its subgraphs $G-e_{\mathcal{L}}$ and $G-(e)_{\mathcal{L}'}$.



(a) (b)

Figure 6. Both permutations $\mathcal{P}$ and $\mathcal{P}'$ are odd.

Finally, from (10) and (11) we obtain $\mathcal{D}_{\mathcal{L}}(G) = \mathcal{D}_{\mathcal{L}}(G-e) + (-1)^{4+5}\mathcal{D}_{\mathcal{L}'}(G-(e)) = -1-(-7) = 6$, which implies $ASC(G) = |\mathcal{D}_{\mathcal{L}}(G)| = 6$.

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