Abstract

Further studies of an efficient graphical algorithmic method for determining algebraic structure count of polycyclic polyene systems possessing $4n$ rings are presented.

Numerous methods for determining the number of Kekulé structures (isomorphic with 1-factor subgraphs) of benzenoid hydrocarbons have been published [1–4]. For alternant (no odd-sized rings) molecular systems having exclusively $4n + 2$ ($n = 1, 2, \ldots$) rings, the algebraic structure count (ACS) [5] or corrected structure count (CSC) [4] is identical to the number of Kekulé (K) structures. Limited work on alternant molecular systems possessing $4n$ rings or nonalternant molecular systems has been pursued [4–7]. Herein, we present a clarification of the generalization of the method of Randić [2] which permits one to decompose larger molecular systems into smaller ones of known CSC for the purpose of determining the CSC of the larger system.

Our previous note [8] on the rapid graphical determination of the algebraic structure count (ASC) of alternant molecular graphs is expanded and our selection rules are made more explicit. Recently, we uncovered [9] an exception to our generalization of the Randić recursion [2], which is discussed together with numerous other examples.

It was previously demonstrated that the proposed formula

$$ASC(G) = |ASC(G - e) \pm ASC(G - (e))|$$  \hspace{1cm} (1)

led to the rapid determination of ASC for two very diverse systems when the negative sign was chosen only when edge $e$ belonged solely to a $4n$ ring of graph $G$; $G - e$ denotes the subgraph obtained by deleting an arbitrary edge $e$, and $G - (e)$ denotes the subgraph obtained from $G$ by the deletion of two vertices incident to $e$ in $G$. Use of the negative sign in (1) for edges on $4n$ rings agrees with our intuition, since these rings are antiaromatic and must make negative contributions to the overall stability of the polyene molecular system containing them.
Proof of (1) for two special cases

It can be easily demonstrated that if an alternant system has a single $4n$ ring among otherwise hexagonal rings, then operating on this $4n$ ring (a selection rule) is more convenient since $K = ASC$ for benzenoids are better known and are easily deducible by the Randić equation of $K(G) = K(G - e) + K(G - (e))$. It can be easily proved that eq. (1) with the negative sign is always true for alternant systems with a single $4n$ ring if this ring is decomposed to give hexagonal fragments. Consider the following equation, derived in Gutman’s paper [7]:

$$[L(G) - L(G - (e)) - L(G - e)] \cdot [L(G) - L(G - (e)) + L(G - e)] \cdot [L(G) + L(G - (e)) - L(G - e)] \cdot [L(G) + L(G - (e)) + L(G - e)] = 0,$$

where $L(G) = ASC(G)$. Since the last factor of (2) is nonzero, then one of the three remaining factors must equate to zero. If one operates on an edge of the sole $4n$ ring in $G$ among otherwise hexagonal rings and obtains fragments possessing only hexagonal-containing components, then the first factor of (2) cannot equate to zero since in this case $ASC(G - e) = K(G - e)$ and $ASC(G - (e)) = K(G - (e))$ would imply that $ASC(G) = K(G)$, which is a contradiction. Thus, either the second or third factor must equate to zero, which proves the applicability of (1) with the negative sign when it is applied to an edge of the sole $4n$ ring in alternant systems having otherwise hexagonal rings. Figures 1 and 2 give several diverse examples of molecular graphs having a single $4n$ ring. The author has used (1) as a cross-check for his computations on several families of alternant hydrocarbons possessing a single $4n$ ring among otherwise hexagonal ones [10]. When two $4n$ rings are joined, their common bond should be selected for application of (1) with the negative sign. It can be proved that (1) with the negative sign is always true for alternant systems with two joined $4n$ rings if these rings are simultaneously decomposed to give hexagonal fragments. The proof is exactly the same as the one given above for alternant systems with a single $4n$ ring. Figure 1 gives several examples of such alternant systems.

Algorithm for the application of (1)

Figure 1 presents all the alternant molecular graphs and their ASC values previously studied by Herndon and Wilcox [4,5,11]. Application of (1) to all the edges of all these structures except the three marked with asterisks gives the correct ASC values. The ASC values for the structures in fig. 2 were originally obtained by computation of their characteristic polynomials using $|a_n| = ASC(G)^2$ for the tail coefficient.

Figure 3 details the application of (1) to all the edges of a molecular graph which is isomeric to anthracene/phenanthrene. Operating on edges $a$, $b$, and $c$ of the tetragonal rings leads to exceptions of (1). Similarly, operating on the edges of the