ALGEBRAIC STRUCTURE COUNT

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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

$$\text{ASC}(G) = |\,\text{ASC}(G - e) \pm \text{ASC}(G - (e))\,| \qquad (1)$$

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]:

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

$$\cdot [L(G) + L(G - (e)) - L(G - e)] \cdot [L(G) + L(G - (e)) + L(G - e)] = 0, \quad (2)$$

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
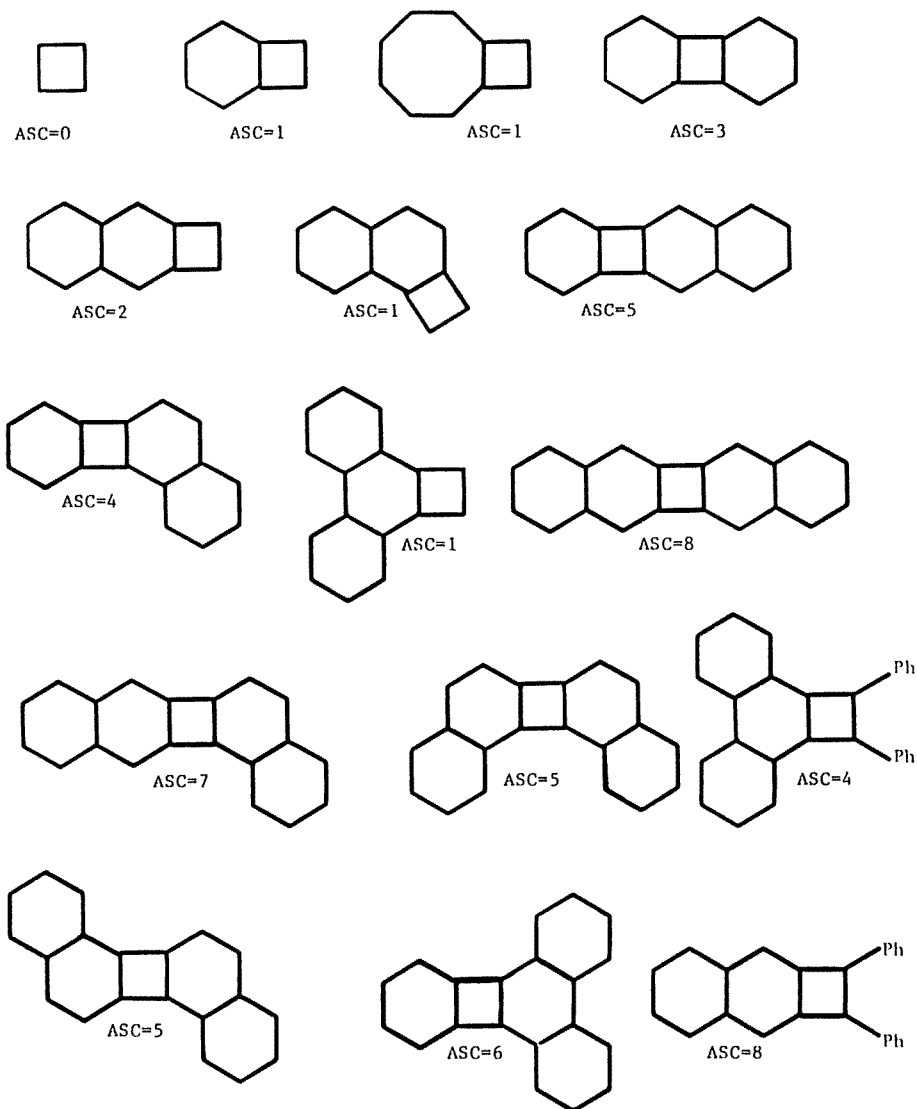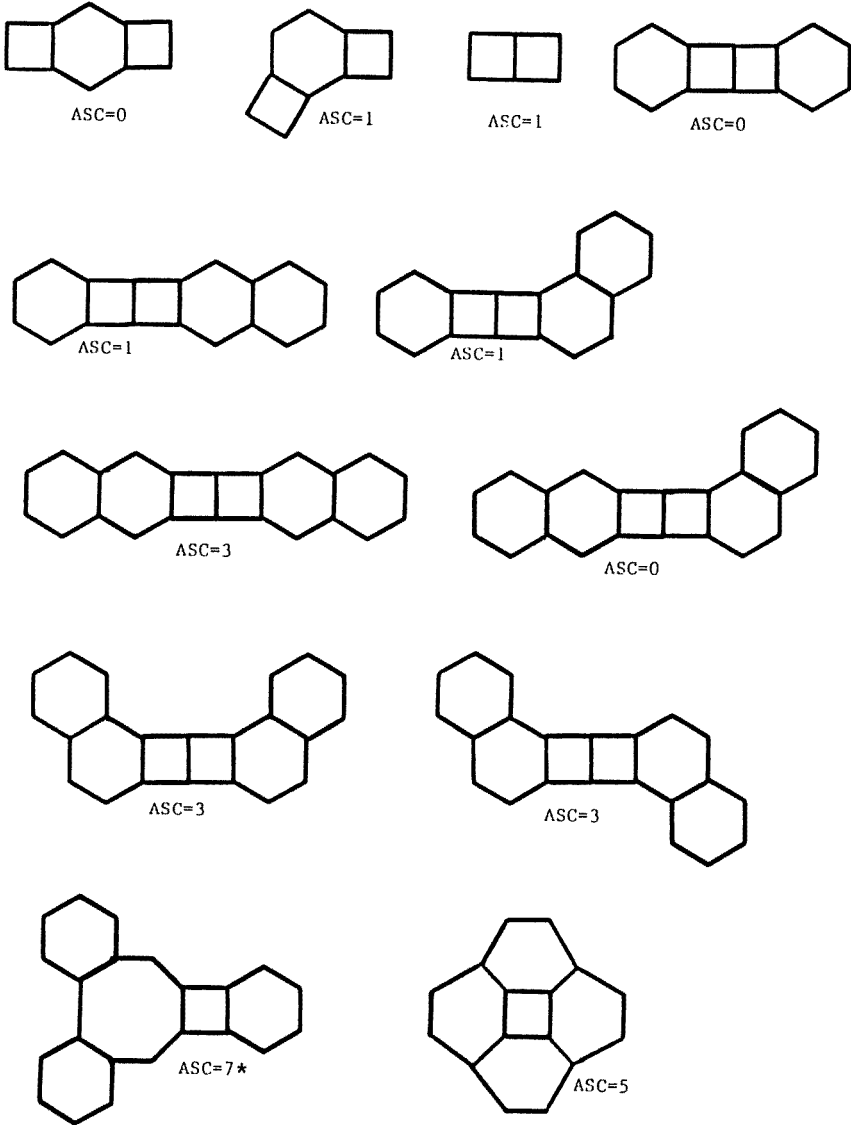
Fig. 1. (continues)

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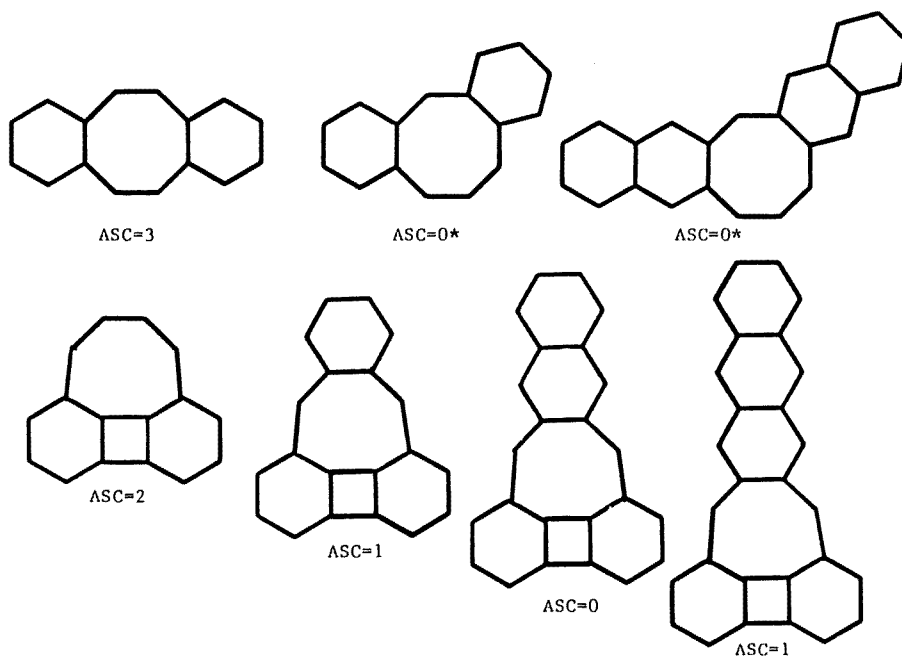
Fig. 1. Herndon and Wilcox's ASC results.

1, $C_{16}H_{10}$
K=6
ASC=2
E_π=21.7765
HOMO=0.2090

2, $C_{18}H_{12}$
K=6
ASC=4
E_π=24.7886
HOMO=0.2657

3, $C_{20}H_{12}$
K=9
ASC=1
E_π=27.0368
HOMO=0.1101

4, $C_{22}H_{12}$
K=13
ASC=5
E_π=30.5435
HOMO=0.2717

5, $C_{22}H_{14}$
K=11
ASC=7
E_π=30.4424
HOMO=0.3142

Fig. 2. (continues)

6, $C_{22}H_{14}$
K=12
ASC=4

E_π=30.2012
HOMO=0.1808

7, $C_{24}H_{16}$
K=17
ASC=15
E_π=33.5439
HOMO=0.4450

8, $C_{24}H_{18}$
K=ASC=9
E_π=32.7223
HOMO=0.4568

9, $C_{26}H_{14}$
K=19
ASC=7
E_π=36.2300
HOMO=0.2280

10, $C_{26}H_{14}$
K=21
ASC=3
E_π=35.8258
HOMO=0.1586

11, $C_{28}H_{16}$
K=26
ASC=24

E_π=39.6916
HOMO=0.4689

12, $C_{30}H_{16}$
K=30
ASC=4
E_π=41.5081
HOMO=0.1367

13, $C_{32}H_{16}$
K=45
ASC=27
E_π=45.5941
HOMO=0.2607
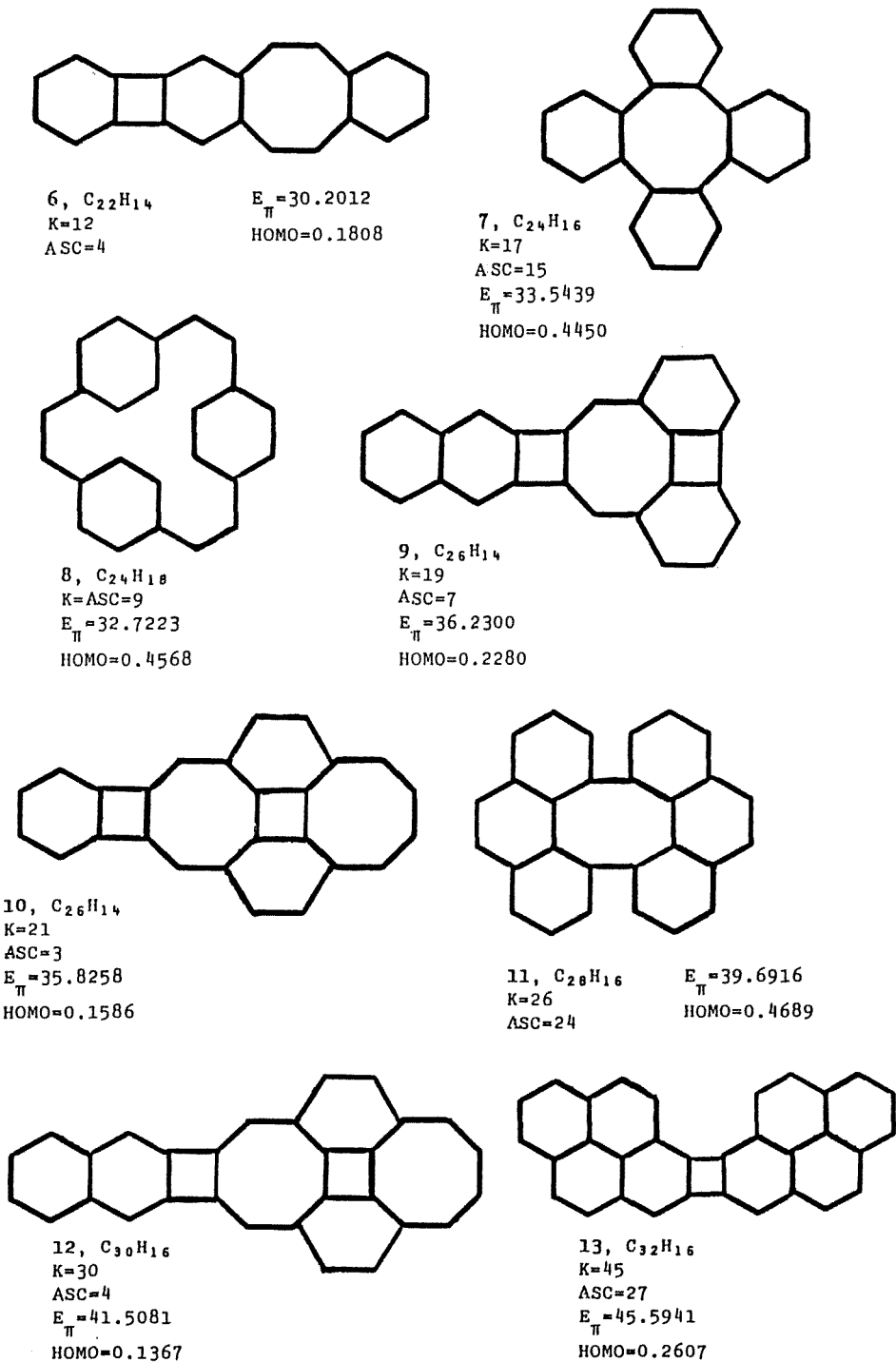
Fig. 2. Known alternant hydrocarbons with 4*n* rings.
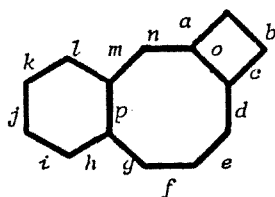
Edge	K(G − e)	K(G − (e))	K(G)	CSC(G − e)	CSC(G − (e))	CSC(G)
a	3	1	4	1	1	0
b	1	3	4	1	1	0
c	3	1	4	1	1	0
d	2	2	4	0	2	2
e	2	2	4	2	0	2
f	2	2	4	0	2	2
g	2	2	4	2	0	2
h	3	1	4	1	1	2
i	1	3	4	1	1	2
j	3	1	4	1	1	2
k	1	3	4	1	1	2
l	3	1	4	1	1	2
m	2	2	4	2	0	2
n	2	2	4	0	2	2
o	3	1	4	3	1	2
p	3	1	4	1	1	2

Fig. 3. Application of $ASC(G) = |ASC(G − e) \pm ASC(G − (e))|$ to all edges of an isomer of anthracene/phenanthrene.

analogous tetragonal ring of structures **4, 5, 9, 10,** and **12** in fig. 2 containing this same substructure also led to exceptions, whereas operating on all other edges of these structures gives the correct values. These results lead to our second selection rule: Apply (1) preferentially to the edges of octagonal rings before operating on tetragonal or hexagonal rings. Since all the structures in fig. 2 have been synthesized [12], their HMO parameters are also listed.

In summary, our general procedure is to recursively apply (1) to alternant molecular graphs operating first on edges belonging to octagonal rings and then tetragonal rings until only hexagonal components are obtained. At each step, essential single and double bonds are trimmed from the fragment graphs and the negative sign is chosen only for $4n$ rings. In this way, all the ASC values for the molecular

graphs in figs. 1–3 were rapidly and reliably obtained. Although we know of no exception to the applicability of the current algorithm, no general proof of its validity is given. As a final note, we have recently discovered a publication which presents an approach to ASC that has features very similar to the one espoused herein [13].

The concept of algebraic structure count has not yet been demonstrated to be a completely useful concept compared to Kekulé structure count. If one examines the ASC values for Wilcox's hydrocarbons (the last four structures in fig. 1) arranged in homologous order, the ASC values first decrease and then increase. If one assumes that the first two values of 2 and 1 have negative signs, then the amended ASC values would correlate with the observed chemical stabilities of these compounds. Thus, this author believes that our inability to associate a negative sign to ASC values is probably a shortcoming for some series of compounds.

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