

Further Developments in Determining the Number of Resonance Structures in Benzenoid Free Radicals: Analytical Expressions and Elementary Substructures

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Relationships for counting the number of resonance structures (SC) of benzenoid free radicals are discussed. The structural origin of some of the coefficients to the SC analytical expressions for series of benzenoid free radicals generated by successive attachment of specific aufbau units is determined. It is shown that a proper pruning fragment for the purpose of a priori determination of the coefficient in the highest degree n term of the SC analytical expression belonging to a given radical series has the property of bond fixation when the operation is performed on every member of that series, resulting in all remnant structures having the same SC value.

INTRODUCTION

Free-radical (open-shell) benzenoid hydrocarbons are reactive intermediates that appear in every pyrolytic process, from charring of pitches to hydrocarbon flames.^{1–3} Benzenoid hydrocarbons and fullerenes are also believed to be formed in the outflows of red giant stars.⁴ They are thought to be the carriers of so-called unidentified infrared emission bands associated with these carbon stars. The possible presence of benzenoid free radicals has not yet been considered in the interstellar medium. Understanding how the number of resonance structures (SC) of benzenoid free radicals change with structure and how this affects their chemistry and photophysics is an important goal.

While mono- and diradical systems are the principal thrust of this paper, several points are worth noting. The results given herein are equally applicable to the analogous classes of carbocations, monoradicals, and carbanions. For example, phenalenyl carbocation, monoradical, and carbanion all have the same number of resonance structures; i.e., SC = 20. Electrophilic protonation in superacid medium or nucleophilic protonation by dissolving metal reduction in liquid ammonia of Kekulean benzenoid hydrocarbons, particularly at solo positions, can produce carbocations or carbanions, respectively, with structures analogous to the free radicals in this study. Only resonance structures where the maximum number of $p\pi$ -electrons are singlets coupled in pairs between nearest-neighbor sites are counted; Dewar-like canonical structures and higher degrees of excitation are not considered.³ A radical unpaired electron entity located on catacondensed appendages is tantamount to a (topological) soliton on a polyacene strip.⁴

The repeated appearance of specific substructures under different circumstances provides important clues in our quest of a unified structure theory.^{5–7} Figure 1 shows the first generation members of our C_{2v} one-isomer polyradical series and their ultimate excised internal structures in bold. These constant-isomer series are produced by repetitive circumscribing.^{8–10} The polyhex circumscribing algorithm is a construc-

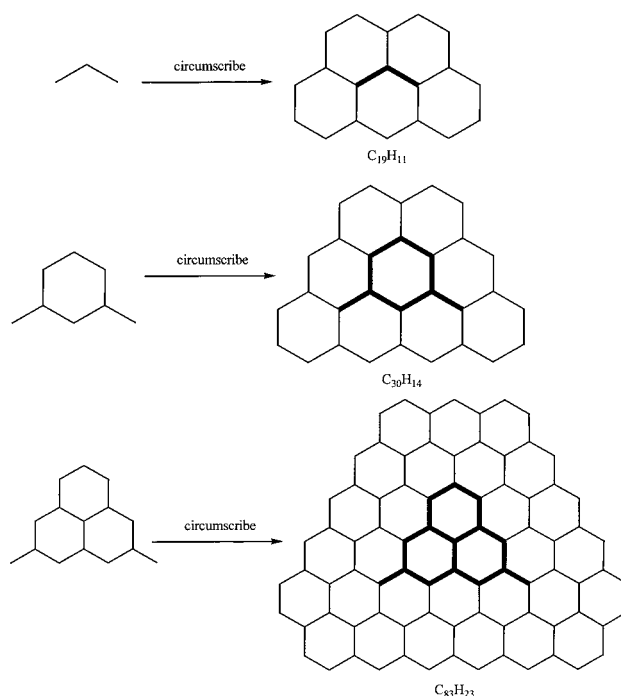


Figure 1. First generation members to the C_{2v} monoradical, diradical, and triradical one-isomer series, respectively.

tion process in which a starting conjugated polyene of formula C_nH_s ($n = N_c$ = the number of formula carbons and $s = N_H$ = the number of formula hydrogens) is encircled by a chain of carbon atoms in such a way that a perimeter of hexagonal rings is formed to give a successor benzenoid of formula $C_{n+2s+6}H_{s+6}$. For example, the D_{6h} one-isomer series is obtained by circumscribing benzene (C_6H_6) to give coronene ($C_{24}H_{12}$), circumscribing coronene to give circumcoronene ($C_{54}H_{18}$), and so forth; in a reverse fashion, coronene is the excised internal structure of circumcoronene and benzene is the ultimate excised internal structure of the D_{6h} one-isomer series. While there is only 1 $C_{19}H_{11}$ benzenoid isomer (Figure 1), there are 3 Kekulean and 1 diradical $C_{30}H_{14}$ benzenoid isomers (the latter is shown in Figure 1) and 15 monoradical and 1 triradical $C_{43}H_{17}$ benzenoid isomers. Circumscribing the sole $C_{43}H_{17}$ triradical gives the

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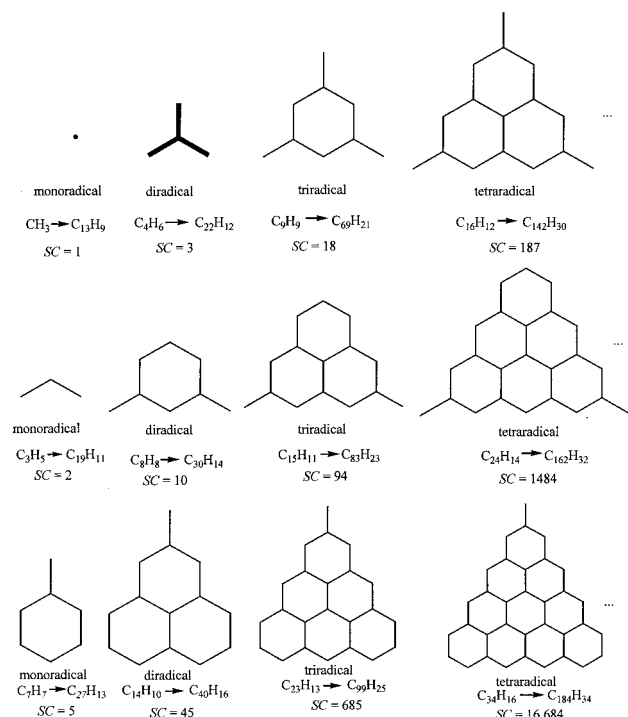


Figure 2. Smallest, most condensed polyradicals which are ultimate excised internal structures belonging to the constant one-isomer series.⁸

$C_{83}H_{23}$ triradical (Figure 1) which is the first generation member of the C_{2v} triradical one-isomer series.

Figure 2 gives the ultimate excised internal structures for the first four polyradical one-isomer series and records their SC values for the first time;^{8,11} the first formula beneath each structure coincides with the ultimate excised internal structure shown, and the second formula belongs to the corresponding first generation member of the constant-isomer series. The formulas for the first generation members of the smallest unique polyradical one-isomer series (second formula in the uppermost row of Figure 2) are determined by $n = N_c(\text{odd}) = (1/8)(3\Delta^4 + 26\Delta^2 + 75)$ or $N_c(\text{even}) = (1/8)(3\Delta^4 + 20\Delta^2 + 48)$ and $s = N_H(\text{odd}) = (3/2)(\Delta^2 + 5)$ or $N_H(\text{even}) = (3/2)(\Delta^2 + 4)$, where $\Delta = 0, 1, 2, 3, 4, \dots$ for the radical degree (or the absolute value of (no. of peaks) – (no. of valleys)). The ultimate excised internal structures in Figure 2 are the smallest possible polyradicals and, as it will be shown, are elementary substructures having importance in determining the coefficients to the analytical expressions that count the number of resonance structures (SC) of appropriate radical series.

RESULTS AND DISCUSSION

Catacondensed Radical Series. Using the molecular graph of the phenalenyl moiety, Figure 3 illustrates a general method of fragmentation of all benzenoid free radicals having catacondensed appendages (not explicitly shown but would be fused to the bold edge) for the purpose of counting the number of resonance structures. All possible $p\pi$ -bond/unpaired electron arrangements at the catacondensed juncture are shown and their graph theoretical equivalents given. Summing the structure count of the subgraphs gives the SC of the precursor molecular graph. As it will be shown (vide infra), the subgraph placing the greatest number of unpaired

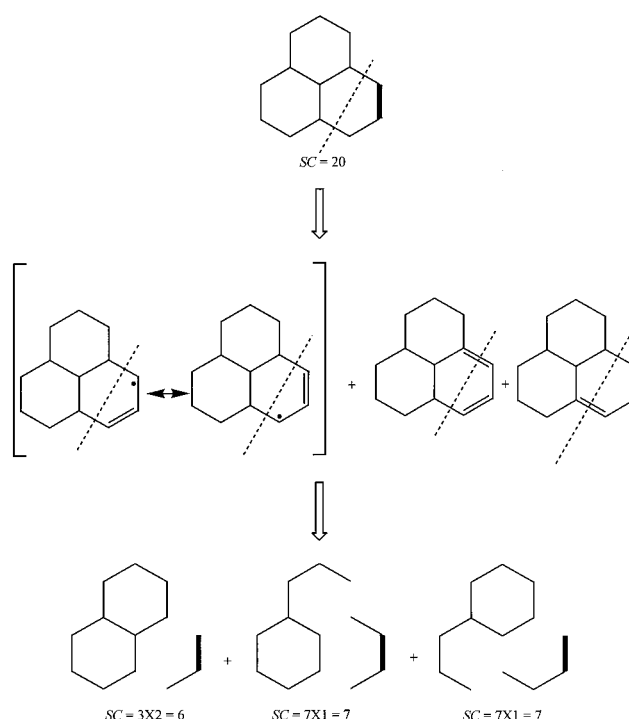


Figure 3. Method of fragmentation of the phenalenyl moiety appended with catacondensed extensions from the bold edge.

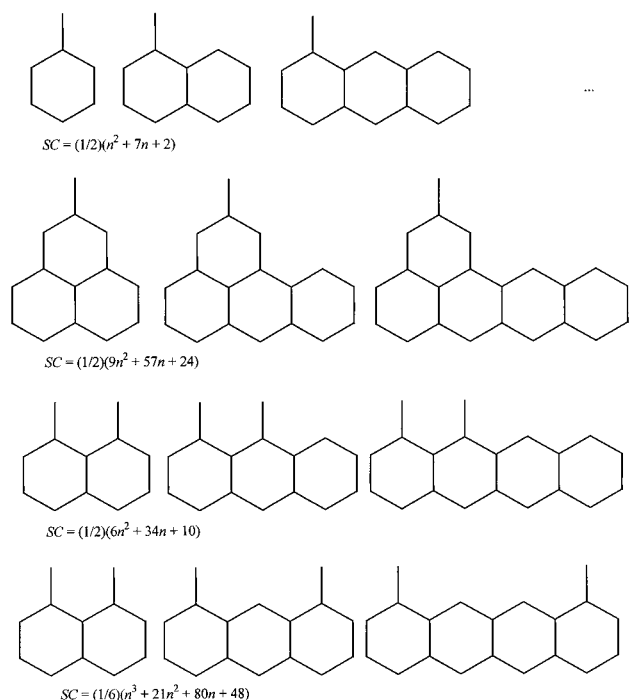
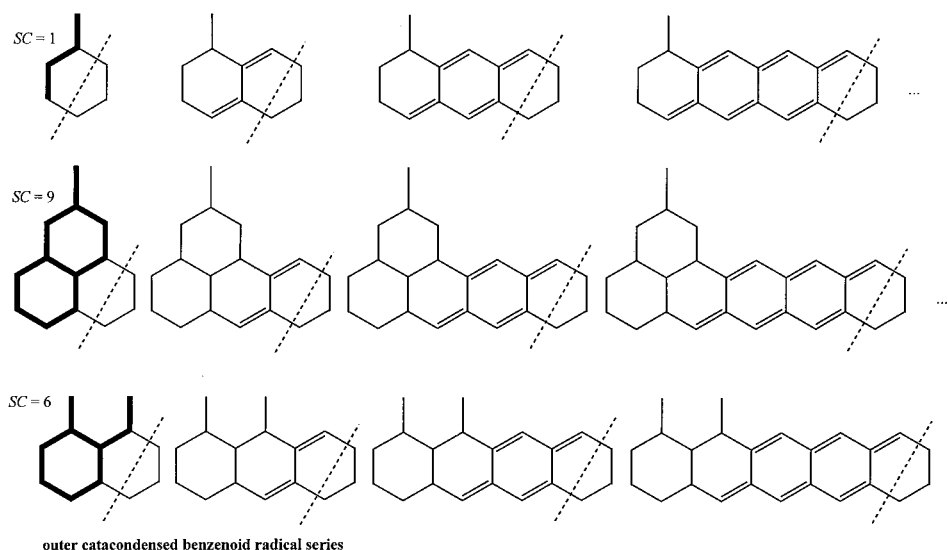


Figure 4. Catacondensed radical series and their analytical expressions for counting the number of resonance structures.

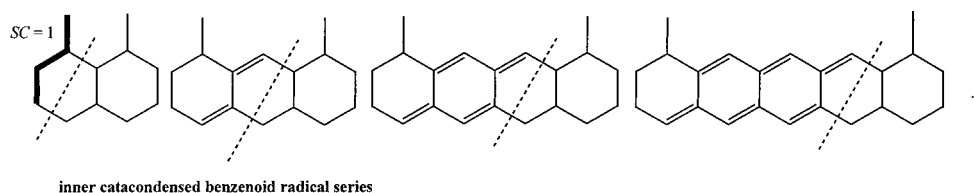
electrons on the extended moiety will determine the value of the first coefficient in the SC analytical expression for benzenoid free-radical series.

Figure 4 gives four catacondensed radical series and their corresponding analytical expressions which count the number of resonance structures; we define the first three series as *outer* catacondensed and the latter as *inner* catacondensed. Benzyl and 2-methylenephthalenyl are C_{2v} ultimate excised internal structures from Figure 2. The two middle series in Figure 4 have been previously analyzed.¹² The first coef-



outer catacondensed benzenoid radical series

Figure 5. Pruning off an allyl (L_3) from the right-handed catacondensed corner to the members of the first three series given in Figure 3, generating successor structures all having the same number of resonance contributors which coincides with the value of the first coefficient to the analytical expression for that original series. The SC values shown are for the substructures in bold and all series members pruned of L_3 .



inner catacondensed benzenoid radical series

Figure 6. Pruning off *m*-quinodimethane from the right-handed catacondensed corner to the members of the last series given in Figure 3, generating successor structures all having the same number of resonance contributors which coincides with the value of the first coefficient to the analytical expression for that original series. The SC value shown is for the substructures in bold and all series members pruned.

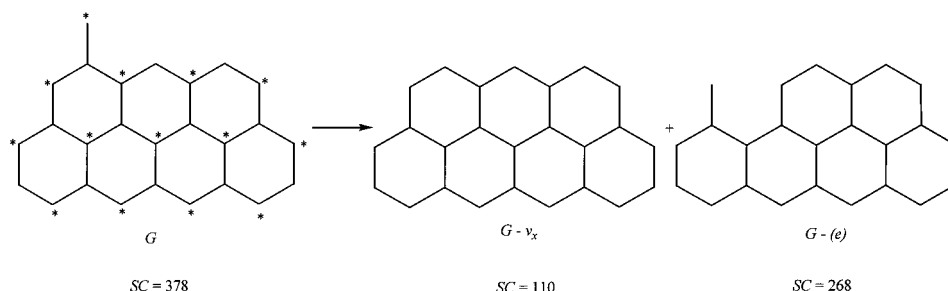


Figure 7. Fragmentation of a molecular graph to smaller ones by operating on a starred position per $SC(G) = SC(G - v_x) + \sum SC(G - (e))$.

efficient of the upper three series in Figure 4 is given by the SC of the substructure that remains after pruning off allyl (L_3) from the lower right-hand corner of these structures (Figure 5). Pruning allyl from all members of these series give successor structures having the same SC value which equals the numerical value of the coefficient in front of the highest power of n in the analytical expression when the denominator of the fraction before the left-hand parenthesis has a factorial value corresponding to the highest power of n . Thus pruning off allyl from benzyl gives 1,3-butadiene, which has a $SC = 1$; from 2-methylenephthalenyl gives 2-methylenenaphthalene, which has a $SC = 9$; and from 1,8-dimethylenenaphthalene gives 2-vinylbenzyl, which has a $SC = 6$ all coinciding with the coefficients in front of the n^2 terms of the respective analytical expression. Note that 1,3-butadiene, 2-methylenenaphthalene, and 2-vinylbenzyl are shown in bold in Figure 5 and that the allyl fragments are joined to these bold fragments through their unstarred sites.

Pruning off *m*-quinodimethane from the lower right-hand corner of the members in the last series in Figure 4 gives successor structures (Figure 6) all having $SC = 1$ which is the coefficient in front of n^3 in the corresponding analytical expression. This result shows that we need to differentiate between outer catacondensed, like the first three series and inner catacondensed like the last series in Figure 4. In Figures 5 and 6 all the fixed double bonds that result from the pruning process are explicitly shown. The important result here is that pruning off a *proper fragment* from all members of a radical series will lead to remnant structures all having the same SC value because of bond fixation. The exploitation of this property will allow one to determine the proper pruning fragment for the purpose of deducing the coefficient to the highest power n term in the corresponding SC analytical expression for that radical series.

Perinaphthocondensed Radical Series. The following fragmentation relations can be used to decompose a molec-

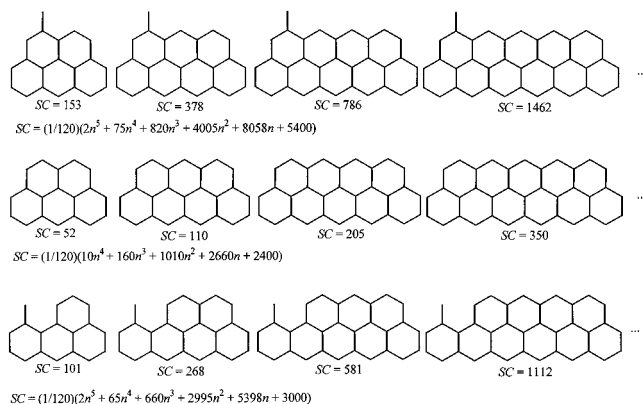


Figure 8. Three series of molecular graphs, each of which is derivable from the other two. Note that, for a given power of n , the sum of the coefficients of the lower two series is equal to that of the uppermost one. Confer with Figure 1.

ular graph of any benzenoid radical into smaller ones. For the set of all resonance structures of a mono- and polyradical system, a given starred site will either contain an unpaired electron or belong to a double bond emanating, one at a time, from each attached unstarred carbon. This leads to the relation $SC(G) = SC(G - v_x) + \sum SC(G - (e))$, where $G - v_x$ is the subgraph resulting from the deletion of the starred carbon site in graph G . This fragmentation process is illustrated in Figure 7. On the basis of this result, one can see that the three series in Figure 8 are interrelated. Pruning m -quinodimethane from the lower right-hand corner of the first structures in these series gives a substructure (on the left-hand) whose $SC \times 2$ predicts the value of the first coefficient in the corresponding analytical expressions for only the uppermost and lowermost series but not for the middle series. A similar analysis of the three radical series in Figure 9 leads to the same observation; the middle series, common to both Figures 8 and 9, which was derived previously is a monoradical series, whereas the others are diradical series.¹³

To more fully understand the perinaphthocondensed phenalenyl (middle series in Figures 8 and 9), we decompose each member shown into five two component subgraphs

which give five corresponding series presented in Figure 10. The right-hand component of the first generation subgraphs must have the edges marked in bold in common. If the five analytical expressions below these series are summed, we obtain the analytical expression for the original parent series. The second decomposition series (third series down in Figure 10) is a constant and a function of the zero generation member (benzyl) of the parent series shown at the very top of Figure 10. The styrene ($SC = 2$), benzyl ($SC = 5$), 2-vinylpentadienyl ($SC = 3$), heptatrienyl ($SC = 4$), and octatetraene ($SC = 1$) fragments are present in every member of the first, second, third, fourth, and fifth decomposition series, respectively, and account for the initial constant factor in the corresponding analytical expressions. The last decomposition series is the only one which has a n^4 term.

The methylene-1,3-butadiene (2-vinylallyl) fragment in the last decomposition series can be pruned from every member of the parent series leading to successors all having bond fixation resulting in the same SC value per Figure 11. The reason this is important is that all the fixed bonds can be trimmed off to give the first generation fragment of octatetraene which determines the initial constant factor mentioned above. Since only this fragment series contains the n^4 term, this initial constant gives the first coefficient to the SC analytical expression of the parent series. The unreduced polynomial for the middle series common to Figures 8 and 9 is $SC = (1/4!)(2n^4 + 32n^3 + 202n^2 + 532n + 480)$, which shows that the two coefficient to n^4 was carried over from the fragment series because the octatetraene remnant structure has a $SC = 1$. Pruning off pentadienyl from every member of the parent series, as was done in Figure 11 with methylene-1,3-butadiene, does not result in remnant structures all having the same SC value, showing that it is not a proper pruning fragment for determining the coefficient to the highest power n term.

We now compare the decomposition of the upper series in Figure 8 with that of the middle perinaphthocondensed phenalenyl series (Figures 8 and 9). For this purpose, we only decompose the first member of the upper series, as shown in Figure 12. Because this is a diradical series while

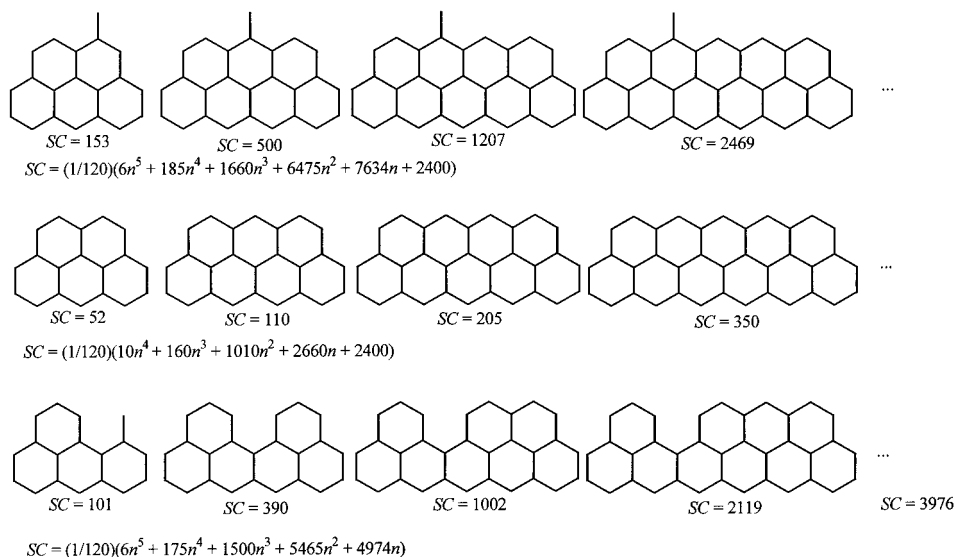


Figure 9. Three series of molecular graphs, each of which is derivable from the other two. Note that, for a given power of n , the sum of the coefficients of the lower two series is equal to that of the uppermost one. Confer with Figure 7.

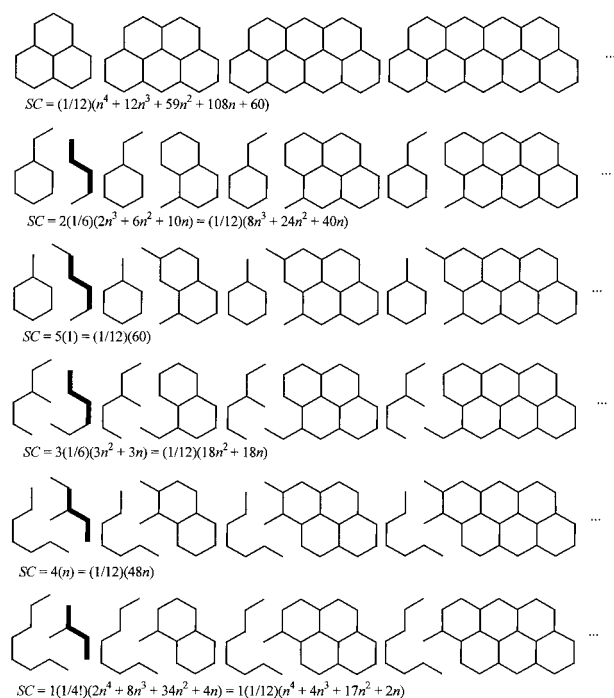


Figure 10. Decomposition of the uppermost series with the resulting five two-component series below, illustrating the origin of the coefficients in the analytical expression of the parent series. Summing the SC expressions of the lower five series gives the uppermost SC expression.

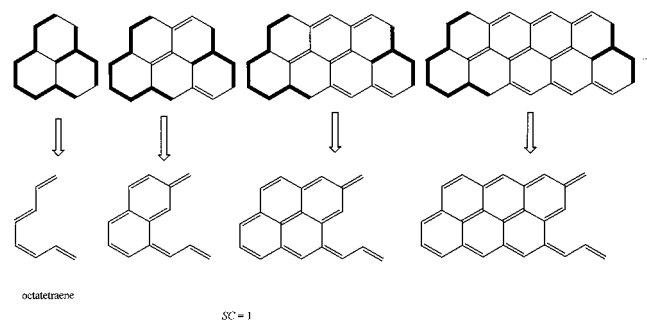


Figure 11. Pruning out methylene-1,3-butadiene from all members of the phenalenyl series, leading to successors all having the same SC. This bond fixation shows that methylene-1,3-butadiene is the proper pruning fragment for determining the coefficients of the highest power n term. Compare with the lower fragment series in Figure 10.

the phenalenyl series is monoradical, an additional decomposition to give the molecular graph of *m*-quinodimethane is necessary. However, the subgraphs in Figure 12 are not mutually independent as they were in Figure 10. The right-hand monoradical subgraphs and the molecular graph of *m*-quinodimethane both count some of the same resonance structures. Nevertheless, as the *m*-quinodimethane series shown in Figure 13 demonstrate, the value of the coefficient to higher power term of the SC analytical expression to the upper series in Figure 8 is still predicted by $2 \times SC$ of the left-hand fragment remaining after pruning off *m*-quinodimethane which is invariably also equal to constant difference value. By pruning off *m*-quinodimethane from every member of the upper series in Figure 8, it can be verified that all the remnant structures have the same SC value.

Algorithm for Finding SC Analytical Expressions for Radical Series. From the results given in Figure 13, the

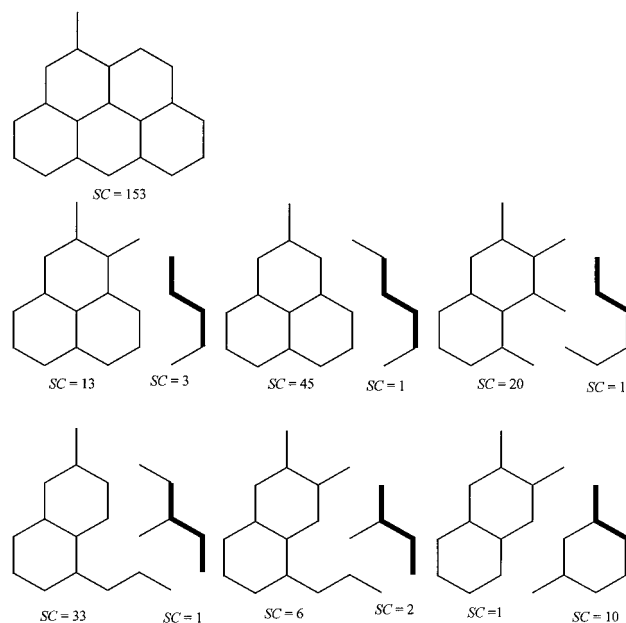


Figure 12. Decomposition of the uppermost molecular graph from the upper series in Figure 8 for comparison with Figure 10.

following paradigm can now be stated. First, all mono- and polyradical series constructed by repetitive attachment of a given aufbau unit have polynomial SC analytical expressions with the n variable corresponding to the membership generation. Second, the denominator factorial is given by the exponent of the highest degree of the n variable. Third, the numerator coefficient to the highest degree n variable equals the constant difference value. Fourth, this constant difference value is equal to the SC of the remnant structure (subgraph) produced by pruning off allyl from lower right-hand corner of any outer catacondensed radical series (as shown in Figure 5) or is equal to two times the SC value of the remnant structure produced by pruning off *m*-quinodimethane from any member of the polyradical perinaphthocondensed series (confer with Figure 13). For monoradical perinaphthocondensed series, this constant difference is also equal to two times the SC of the remnant structures produced by pruning off a proper monoradical fragment, like methylene-1,3-butadiene for the middle series common to Figures 8 and 9 or the lower series in Figure 10 or pentadienyl for the second series in Figure 10; a proper pruning monoradical must lead to bond fixation in every member of the series resulting in remnant structures all having the same SC value. All currently known catacondensed and perinaphthocondensed radical series follow this paradigm.¹²⁻¹⁵

CONCLUSION

The reason for the different behavior of the last series in Figure 4 and the middle series common to both Figure 8 and Figure 9 have been determined. The a priori determination of the coefficient to the highest n term any catacondensed and perinaphthocondensed radical series reduces the need for the number of known SC values by one, thereby streamlining the determination of their corresponding SC analytical expressions. Various structural properties and correlations have been demonstrated. Whenever any radical series is constructed by successive attachment of a specific

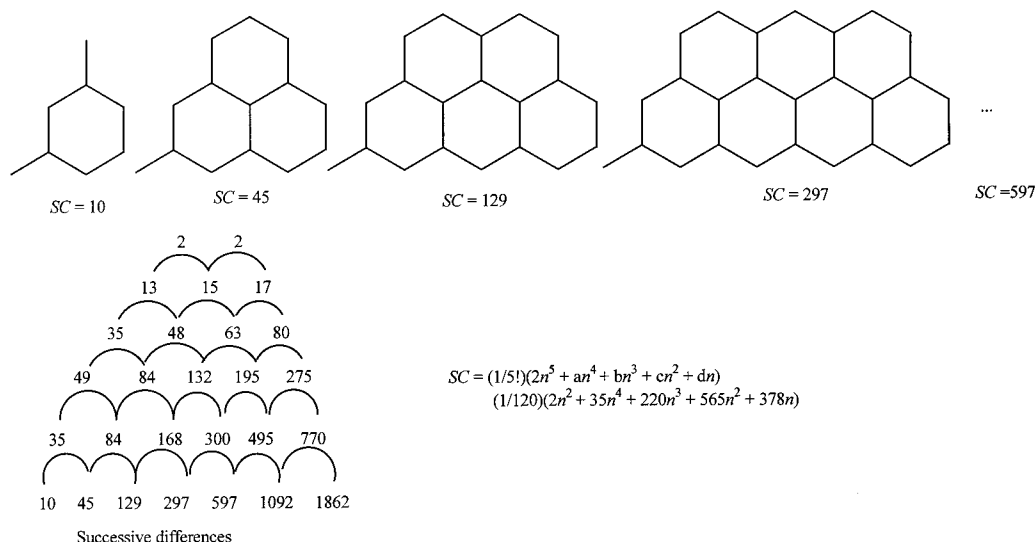


Figure 13. Method for deriving SC analytical expressions. (1) The SC's are determined for the member of a series. (2) Successive subtraction is performed until the difference becomes constant. (3) The highest power term equals the number of subtraction iterations. (4) The coefficient of the term of highest power equals the constant difference value. (5) The denominator is the factorial of the highest power value. (6) Other coefficients are determined by matrix algebra.

aufbau, then its corresponding SC analytical expression is derivable as illustrated in Figure 13, and this constitutes an important paradigm.

Some general rules for the decompositions illustrated in Figures 3, 10, and 12 can be summarized as follows. First, all fragments must contain the edges bounded by the vertices to which the aufbau units are attached. Second, the radical degree of any decomposition fragment cannot exceed that of the parent. Otherwise, one should seek all possible fragments within these constraints.

New SC data and analytical expressions for seven new radical series have been summarized. The derivation of SC analytical expressions using known SC data for a few members of a radical series is an expedient method for calculating this parameter for larger members which would be more difficult to solve directly.

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