

Two-Dimensional Arrays in the Analysis of Trends in Series of Molecules: Strongly Subspectral Molecular Graphs, Formula Periodic Tables, and Number of Resonance Structures

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Two-dimensional arrays consisting of strongly subspectral molecular graphs and formula periodic tables for polycyclic aromatic hydrocarbons are briefly reviewed. New two-dimensional arrays for free-radical benzenoid hydrocarbons are presented with general analytical expressions for counting their number of resonance structures (SC). The structural origin of the coefficients to these analytical expressions is discussed.

INTRODUCTION

The search and discovery of trends in collections of facts is one of the essential activities of empirical scientists. The common *Periodic Table of Elements* is exemplary of a two-dimensional array which orders elements into a framework that facilitates the analysis of their trends. Similarly, two-dimensional NMR gives more information than one-dimensional NMR. In our prior work, two-dimensional arrays consisting of strongly subspectral molecular graphs¹ and formula periodic tables for benzenoids,² fluorenoids/fluorantheneoids,³ and indacenoids⁴ have been put forth and numerous algorithms and molecular trends discussed; the C–C σ -bond skeleton representation of a fully conjugated polyene structure is called a molecular graph. In this paper, we will provide new examples of two-dimensional arrays which uniquely provide novel insights concerning the number of resonance structures of free-radical benzenoids. All of these two-dimensional arrays have member molecular graphs generated by repetitive attachment of specific aufbau units.

Two-Dimensional Arrays of Strongly Subspectral Molecular Graphs. Two molecular graphs are strongly subspectral if they have a preponderance of eigenvalues (HMO $p\pi$ -electronic energy levels) in common. Figures 1 and 2 are generalizations of our previously published two-dimensional arrays¹ in which there is a one-to-one matching in the eigenvalues of a molecular graph in Figure 1 and an equivalently located molecular graph in Figure 2. The weighted vertices (**X** and **Y**) can correspond to any heteroatom or polyene substituent or be deleted. As one example, the **X**s could be nitrogens and the **Y**s carbonyls. Consider the last molecular graph in both Figures 1 and 2 (third molecular graph in the third row) having 36 and 34 unweighted vertices, respectively. Regardless of the precise identity of **X** and **Y** both molecular graphs will have at least 34 eigenvalues in common.

Formula Periodic Tables. Given a particular chemical formula, the range of structures that can correspond to it can, in principle, be deduced. What is usually lacking is a known systematic process or set of algorithms by which one can

generate the structures of the corresponding isomer set. The formula periodic tables organizes the formulas of a given class of molecules according to certain structural invariants which results in sorting them into physically distinct domains having other correlated structural characteristics. Formula periodic tables provide the framework for developing strategies for producing algorithms that generate specific types of structures having a given formula.⁵

The criteria for a periodic table set are that it is a partially ordered set of elements, forming a two-dimensional array of infinite extent with a least element, and complies with the triad principle where the middle element has a metric property that is the arithmetic mean of two oppositely adjacent elements.⁵ Our formula periodic tables consist of points (x, y, z), coordinates of (d_s, N_{ic}, r) , on a plane defined by the equation $N_{ic} + d_s - r = -2$. Formula periodic tables are two-dimensional plots of d_s versus N_{ic} , where the third dimension r is not explicitly shown but can be indicated by parallel lines connecting formulas with identical r values. Formula periodic tables partition formulas into structural classes with the invariants N_{ic} and d_s identifying rows and columns, respectively, where N_{ic} is the number of internal carbon vertices and d_s is the net number of disconnections among the internal edges within the molecular graph of a polycyclic conjugated hydrocarbon; internal vertices are bounded by three rings, and internal edges are bounded by two rings. Either N_{ic} or d_s in these plots can be substituted by r without any unique organizational change that alters the information content. Various structural characteristics can be associated with the various locations or regions in these formula periodic tables. Such characteristics include constant-isomer series, the maximum number of resonant sextets, nonexistence of Hamiltonian circuits, etc. Formula periodic tables lead to hierarchical ordering and edge effects. By edge effects we mean that formulas located on the edge of the two-dimensional array correspond to structures having more unique properties.

Two-Dimensional Arrays of Radical Benzenoids. While numerous papers and monographs on counting the number of resonance structures for Kekulean (nonradical) benzenoid hydrocarbons are available in the literature,⁶ very few papers

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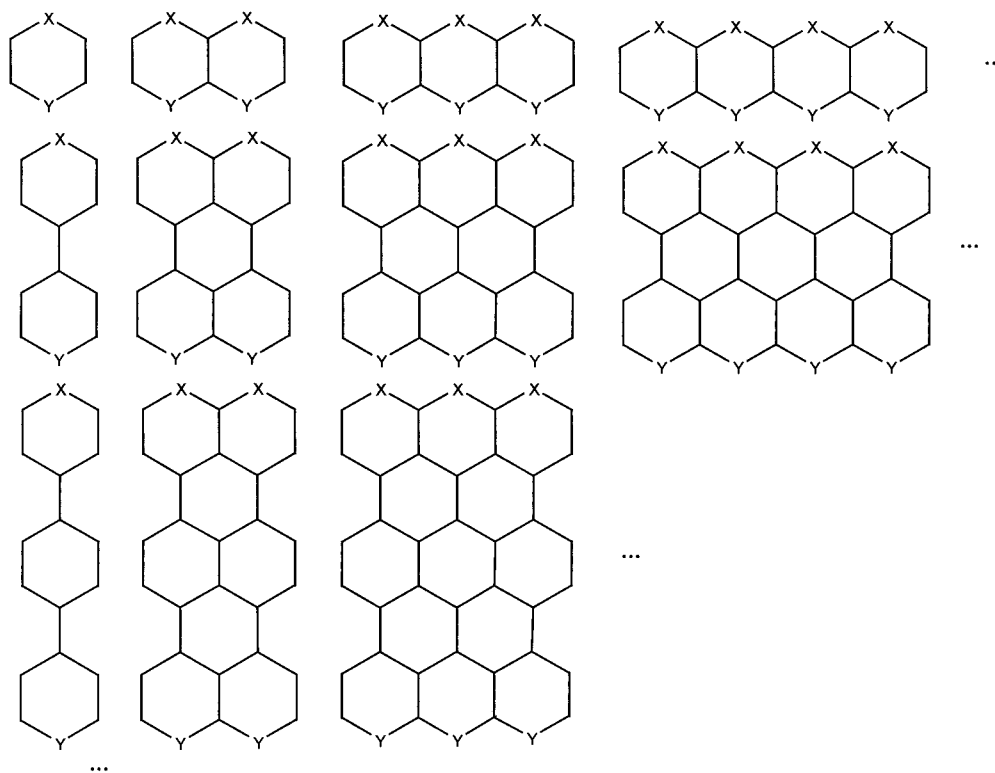


Figure 1. Two-dimensional array of molecular graphs that are strongly subspectral to the corresponding molecular graphs given in Figure 2.

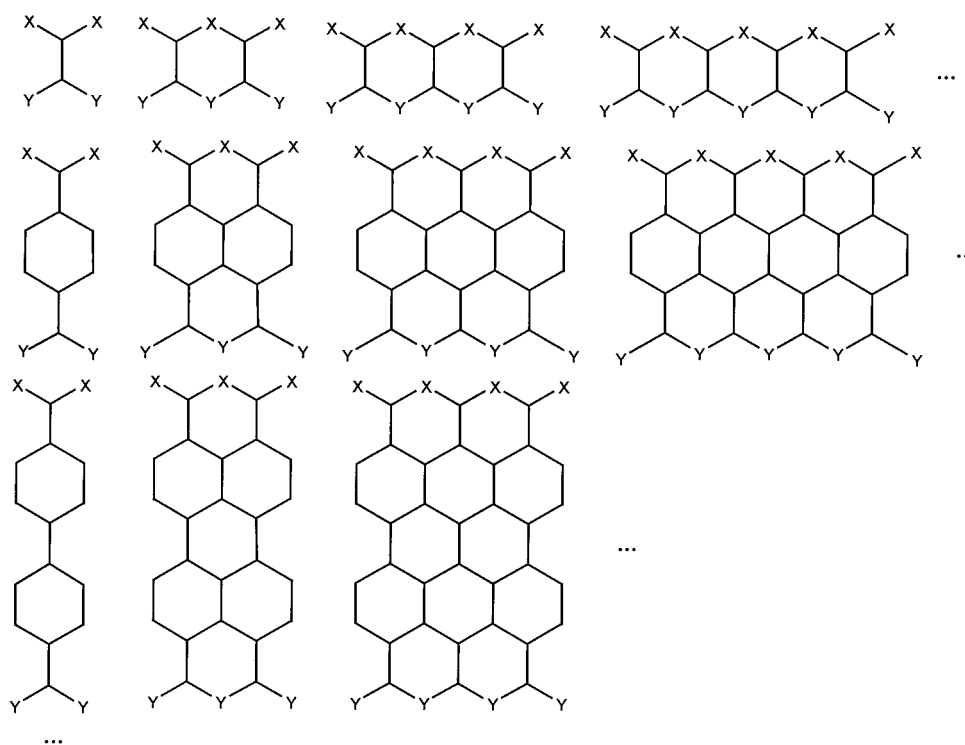


Figure 2. Two-dimensional array of molecular graphs that are strongly subspectral to the corresponding molecular graphs given in Figure 1.

have appeared in print that count the number of resonance structures for radical benzenoids.⁷ Our recent efforts have been directed toward remedying this situation for several reasons.⁸ First, recent research has produced polyradical systems of considerable interest, and radical benzenoids have been shown to be reactive intermediates in the formation of Kekulean aromatic compounds and fullerenes.⁹ Second, other

things being equal, one measure of stability of a molecule is its number of aromatic resonance structures.

Odd benzenoid radicals have antiaromatic contributions as well as aromatic ones. For example, phenalenyl mono-radical (SC = 20) has 2 antiaromatic SC contributions and 18 aromatic SC contributions; the $4n$ antiaromatic circuit is comprised of the C_{12} perimeter of phenalenyl ($n = 3$), where

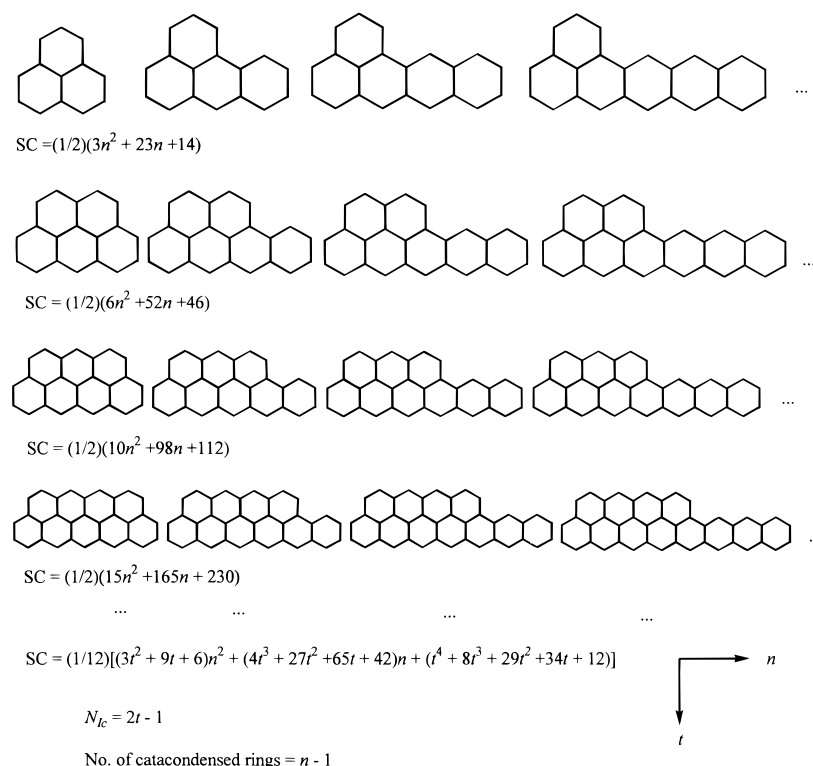


Figure 3. Two-dimensional array of monoradical series with analytical expressions for counting their number of resonance structures.

the radical electron is localized at its center carbon. The smallest antiaromatic circuit that can exist in a radical benzenoid is C_{12} . Using the conjugated circuit theory of Randić on phenalenyl, we get $RE = (1/20)(24R_1 + 12R_2 + 2Q_3) = (1/20)(23.808 - 0.3) = 1.18$ eV.¹⁰ Thus, the antiaromatic depreciation of the resonance energy (RE) in phenalenyl only amounts to 1.3%, which is the largest expected depreciation for a typical benzenoid radical. In general, it is presupposed that the aromatic contributions to benzenoid radicals are dominant and that SCs can be used as a measure of relative stability. The SCs of this work were derived by a combination of graph theoretical decompositions and the use of the Pascal matching polynomial program of Ramaraj and Balasubramanian,¹¹ as described in our prior paper.⁸

Figures 3 and 4 present two-dimensional infinite arrays of molecular graphs of radical benzenoid hydrocarbons with row-by-row (function of n only) and overall general (function of n and t) analytical expressions for counting their number resonance structures. The coordinate system used is shown at the bottom of Figure 3, where n locates the position in a given row and t the position in a given column in both arrays; i.e., n denotes the column and t denotes the row. The first molecular graph in each row is the core structure, and catacondensed appendages commence with the second molecular graph of each row. Successively attaching the C_4H_2 aufbau unit to the first column member (core structure) in Figures 3 and 4 generates all the catacondensed members of the respective series. All the molecular graphs in Figure 3 correspond to monoradical benzenoids and all the molecular graphs in Figure 4 to diradical benzenoids. The structural origin of some of the coefficients to these series will now be discussed.

If the right-hand corner to the molecular graphs in the first column of Figures 3 and 4 are pruned off, the molecular

graphs in Figure 5 are obtained. Comparing the SC values in the first row of Figure 5 with the first coefficient in the analytical expressions of the corresponding series of Figure 3 and comparing the SC values in the second row of Figure 5 with the value of the first coefficient in the analytical expressions of the corresponding series of Figure 4, it is seen that they are identical. If deattachment of a C_4H_2 aufbau unit from the core structures is performed, the zero generation members of these series are produced as given in Figure 6. Multiplying the SC values of these zero generation members by 2 gives the value of the last coefficient in the analytical expressions of the respective series in Figures 3 and 4.

To understand the structural origin of these coefficients, the fragmentation of the molecular graphs in the first row of Figure 3 presented in Figure 7 will be illustrative. The three lower two-component series in Figure 7 give SCs that are the product of the component fragments which sum to the SC of the upper most molecular graph. The presence of the naphthalene molecular graph ($K = 3$) in every member of the second series of Figure 7 explains the origin of the coefficient 3 in the analytical expression of the first series above (and in Figure 3), and the presence of the zero generation molecular graph ($SC = 7$) in every member of the fourth series explains the origin of the last coefficient of $2 \times 7 = 14$. The n^2 term only appears in the first fragment series (the second series in Figure 7), and the constant numerical term only appears in the last fragment series. The n term appears in both the first and second fragment series (the third series in Figure 7), and the origin of the second coefficient depends on both of these modes of fragmentation. Figure 8 illustrates this for the origin of the second overall general coefficient for the two-dimensional array in Figure 3 which depends on the two modes of fragmentation illustrated by the middle two series in Figure 7.

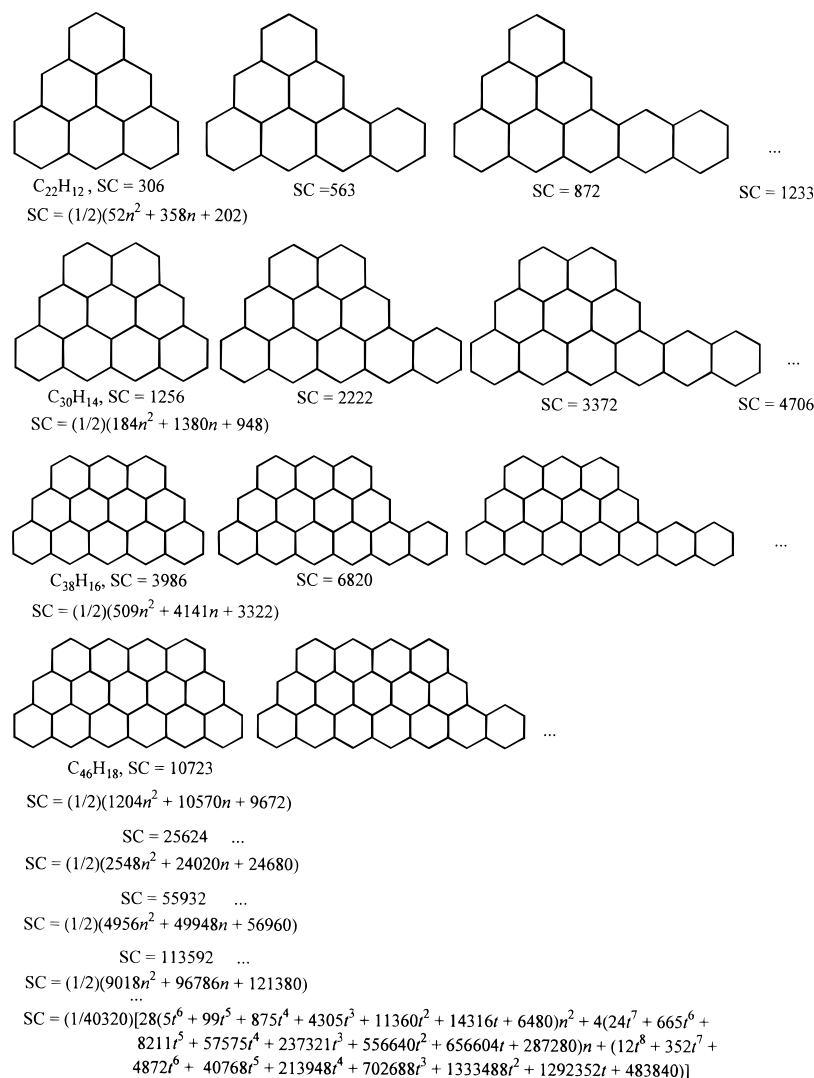


Figure 4. Two-dimensional array of diradical benzenoid series with analytical expressions for counting their number of resonance structures.

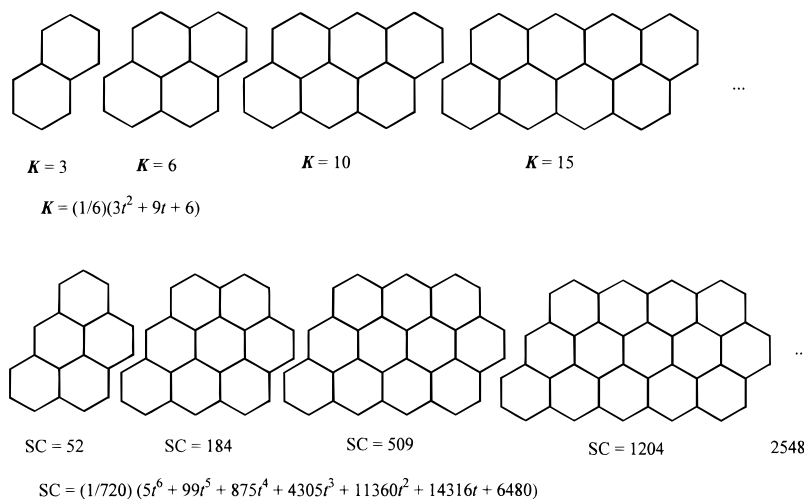


Figure 5. Structural origin of the first coefficient to the analytical expressions for the series in Figures 3 and 4, respectively.

The second component in these fragment series are general to all catacondensed series regardless of the identity of the core structure. Thus, if one has SC analytical expressions for a series of core structures and the constant component fragments, then one can determine the overall general analytical expressions such as those at the bottom of Figures 3 and 4 which depend on both n and t .

SUMMARY

In addition to the construction of the Periodic Table of Elements per se,¹² Mendeleev's legacy was his demonstration that organizing chemical information into a two-dimensional array reveals unique insights not made evident by other organizational schemes. Structure/property trends are pre-

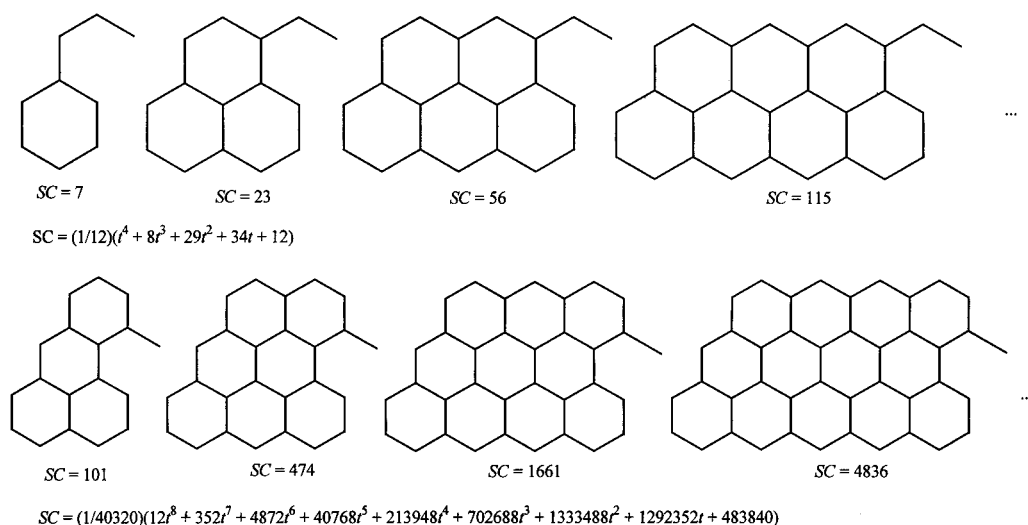


Figure 6. Structural origin of the last coefficient to the analytical expressions for the row series in Figures 3 and 4, respectively.

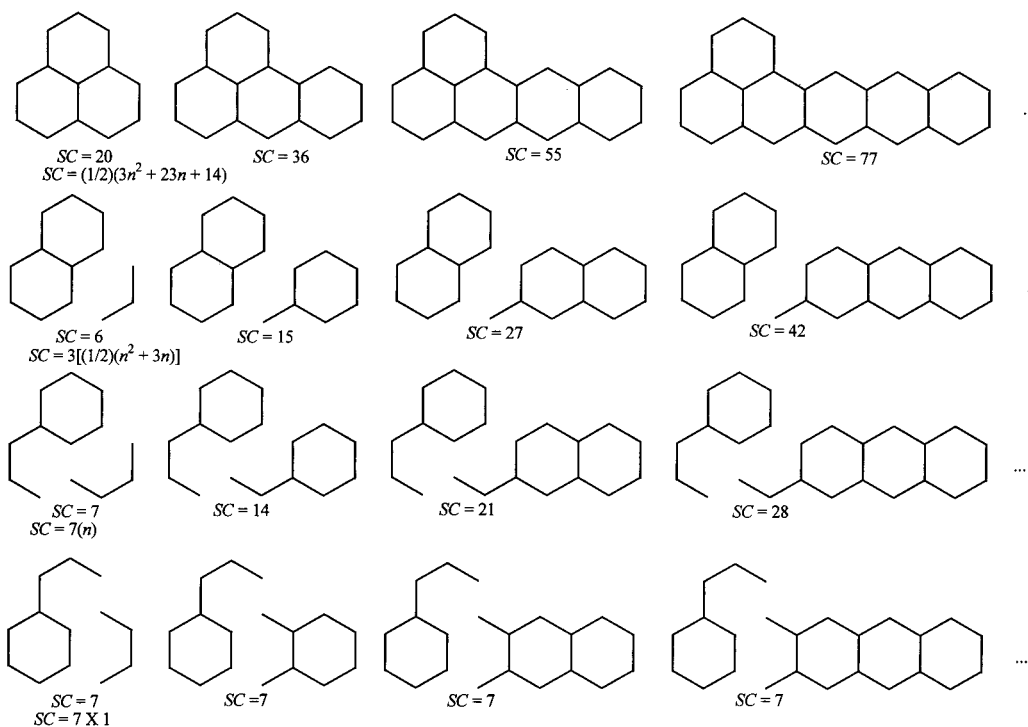


Figure 7. Fragmentation of the first series in Figure 3 gives three two-component series illustrating the origin of the coefficients to all series having progressively increasing catacondensed appendages. Summing the SC of the lower three series gives the SC of the upper most series.

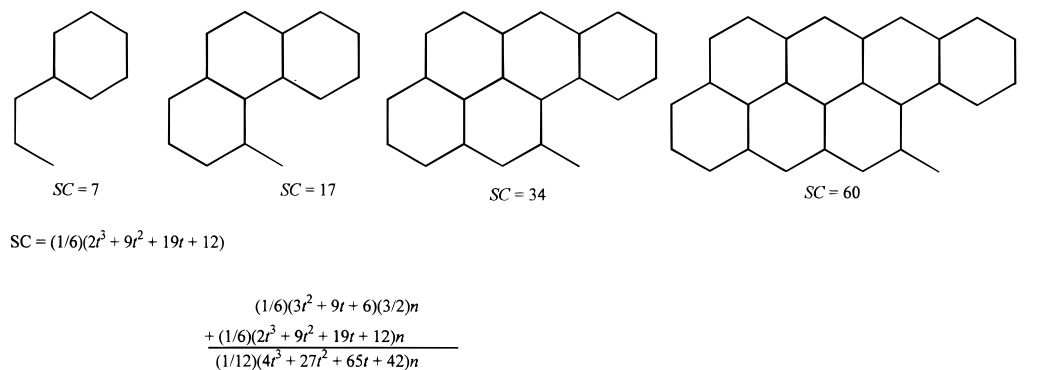


Figure 8. Combining the analytical expression of the first series in Figure 5 with the one above per the decomposition illustrated in Figure 7, leading to the second coefficient in the general expression in Figure 3.

sented nicely in a pictorial manner by our two-dimensional formula periodic tables for various classes of polycyclic conjugated hydrocarbons.

The two-dimensional arrays in Figures 3 and 4 present analytical expressions for the number of resonance structures for many monoradical and diradical benzenoids systems for the first time. The method by which these results were obtained provides a strategy for producing other two-dimensional arrays of benzenoid radicals and their SC relationships.

REFERENCES AND NOTES

- (1) Dias, J. R. Strongly Subspectral Conjugated Molecular Systems. From Small Molecules to Infinitely Large π -Electronic Networks. *J. Phys. Chem. A* **1997**, *101*, 7167–7175. Dias, J. R. Directed toward the Development of a Unified Structure Theory of Polycyclic Conjugated Hydrocarbons: The Aufbau Principle in Structure/Similarity Studies. *J. Chem. Inf. Comput. Sci.* **1999**, *39*, 197–203.
- (2) Dias, J. R. Setting Benzenoids to Order. *Chem. Br.* **1994**, *30*, 384–386. Dias, J. R. The Formula Periodic Table for Benzenoid Hydrocarbons and the Unifying Theory of a Periodic Table Set. *Polycyclic Aromat. Compd.* **1994**, *4*, 87–106. Dias, J. R. Current Status of Isomer Enumeration of Practical Benzenoids. *J. Mol. Struct. (THEOCHEM)* **1991**, *230*, 155–190. Dias, J. R. A Periodic Table for Polycyclic Aromatic Hydrocarbons. Isomer Enumeration of Fused Polycyclic Aromatic Hydrocarbons. *J. Chem. Inf. Comput. Sci.* **1982**, *32*, 15–22. Cyvin, S. J.; Cyvin, B. N.; Brunvoll, J. Enumeration of Benzenoid Chemical Isomers with a Study of Constant-Isomer Series. *Top. Curr. Chem.* **1993**, *166*, 67–119.
- (3) Dias, J. R. Studies in Deciphering the Information Content of Chemical Formulas: A Comprehensive Study of Fluorenes and Fluoranthenes. *J. Chem. Inf. Comput. Sci.* **1992**, *32*, 2–11. Cyvin, S. J. Graph-Theoretical Studies on Fluoranthenoids and Fluorenoids. Part 1. *J. Mol. Struct. (THEOCHEM)* **1992**, *262*, 219–231. Cyvin, S. J.; Cyvin, B. N.; Brunvoll, J. Graph-Theoretical Studies on Fluoranthenoids and Fluorenoids. Part 2. *J. Mol. Struct. (THEOCHEM)* **1993**, *281*, 229–236.
- (4) Dias, J. R. Deciphering the Information Content of Chemical Formulas: Chemical and Structural Characteristics and Enumeration of Indacenes. *J. Chem. Inf. Comput. Sci.* **1992**, *32*, 203–209. Brunvoll, J.; Cyvin, B. N.; Cyvin, S. J.; Brinkmann, G.; Bornhoft, J. Enumeration of Chemical Isomers of Polycyclic Conjugated Hydrocarbons with Six-Membered and Five-Membered Rings. *Z. Naturforsch.* **1996**, *51a*, 1073–1078.
- (5) Dias, J. R. Notes on Constant-Isomer Series. *J. Chem. Inf. Comput. Sci.* **1993**, *33*, 117–127.
- (6) Cyvin, S. J.; Gutman, I. *Kekulé Structures in Benzenoid Hydrocarbons*; Springer-Verlag: Berlin, 1988. Gutman, I.; Cyvin, S. J. A New Method for Enumeration of Kekulé Structures. *Chem. Phys. Lett.* **1987**, *136*, 137–141. Røgsi, C.; Cyvin, B. N.; Brunvoll, J.; Klein, D. J. Methods of Enumerating Kekulé Structures. *Top. Curr. Chem.* **1990**, *153*, 227–253.
- (7) Herndon, W. C. Enumeration of Resonance Structures. *Tetrahedron* **1973**, *29*, 3–12.
- (8) Dias, J. R. Resonance Structures of Benzenoid Conjugated Radicals. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5081–5086.
- (9) Homann, K.-H. Fullerenes and Soot Formation—New Pathways to Particles in Flames. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2434–2451.
- (10) Randić, M.; Trinajstić, N. Conjugation and Aromaticity of Corannulenes. *J. Am. Chem. Soc.* **1984**, *106*, 4428–4434.
- (11) Ramaraj, R.; Balasubramanian, K. Computer Generation of Matching Polynomials of Chemical Graphs and Lattices. *J. Comput. Chem.* **1985**, *6*, 122–141.
- (12) Scerri, E. R. The Evolution of the Periodic System. *Sci. Am.* **1998**, *78*–83.

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