A Formula Periodic Table for Benzenoid Hydrocarbons and the Aufbau and Excised Internal Structure Concepts in Benzenoid Enumerations

Jerry Ray Dias

Department of Chemistry, University of Missouri, Kansas City, MO 64110, U.S.A.

Z. Naturforsch. **44a**, 765–771 (1989); received March 10, 1989

The genesis of two concepts of recent importance to isomeric polyhex enumeration is traced. As it will become evident from this review, the philosophy of our approach stresses the enumeration of select benzenoid groups of practical interest to chemists. These concepts were pivotal to the first published enumerations of the strictly peri-condensed, non-Kekulean, and essentially strain-free total resonant sextet benzenoid groups.

Our 1978–1980 work, dealing with the priority pollutants under the aegis of the Environmental Protection Agency, Region VII [1–3], made it evident that benzenoid hydrocarbons were ubiquitous pyrolytic pollutants which needed systematic study. When I subsequently went on a Fulbright Senior Lectureship to the University of Ljubljana, Yugoslavia, during the Winter Semester of 1981, I had the opportunity to delve into the problem of analyzing the formula/isomer relationships of benzenoid hydrocarbons. It seemed to me that a reasonable relationship must exist. At that time I was only aware of Eric Clar's two volume work [4] and Balaban and Harary's Tetrahedron paper [5]. This latter paper dealt exclusively with the enumeration of cata-condensed benzenoid hydrocarbons. Several events converged at this time. First, I developed my formula table, aufbau and excised internal structure concepts in rudimentary form. Second, I was invited by Professor Trinajstić to present a lecture on these results [6] and for a return visit to lecture on the priority pollutants. It was Professor Trinajstić who named my formula table a "periodic table." This work was the first to emphasize enumeration of peri-condensed benzenoid hydrocarbons [7].

Our work has always been concerned with the enumeration of chemically relevant benzenoid compounds rather than indiscriminant enumeration of polyhexes [8]. The first publication of the excised internal structure concept was associated with the first enumeration of strictly peri-condensed benzenoid isomers which are predicted to be among the ultimate pyrolytic products [9]. The first reported work dealing with the exclusive enumeration of non-Kekuléan benzenoids was stimulated by their presumed intermediacy in combustion processes [10]. A master structure and corresponding method for enumerating total resonant sextet benzenoids was proposed in the seminal paper [11] which inspired the subsequent work of Knop and coworkers [12]. This led to the first enumeration of essentially strain-free total resonant sextets of potential interest to analytical/environmental scientists [13–14].

Reprint requests to Prof. Dr. J. R. Dias, College of Arts and Sciences, Department of Chemistry, University of Missouri, Kansas City, Missouri 64110, U.S.A.

A Formula Periodic Table for Benzenoid Hydrocarbons

The formulas for all benzenoids are found in Table 1 which has the coordinates (d_s, N_{Ic}). Recursive construction of this table was accomplished using the aufbau principle (*vide infra*). Table 1 complies to a sextet rule analogous to the octet rule for the periodic table of elements, d_s being analogous to the outer-shell electronic configuration and N_{Ic} being analogous to the principal quantum number associated with the periodic table of elements. Thus, Table 1 can be described as being "Mendeleevian" [15]. The terminology used is summarized in the caption of Table 1.

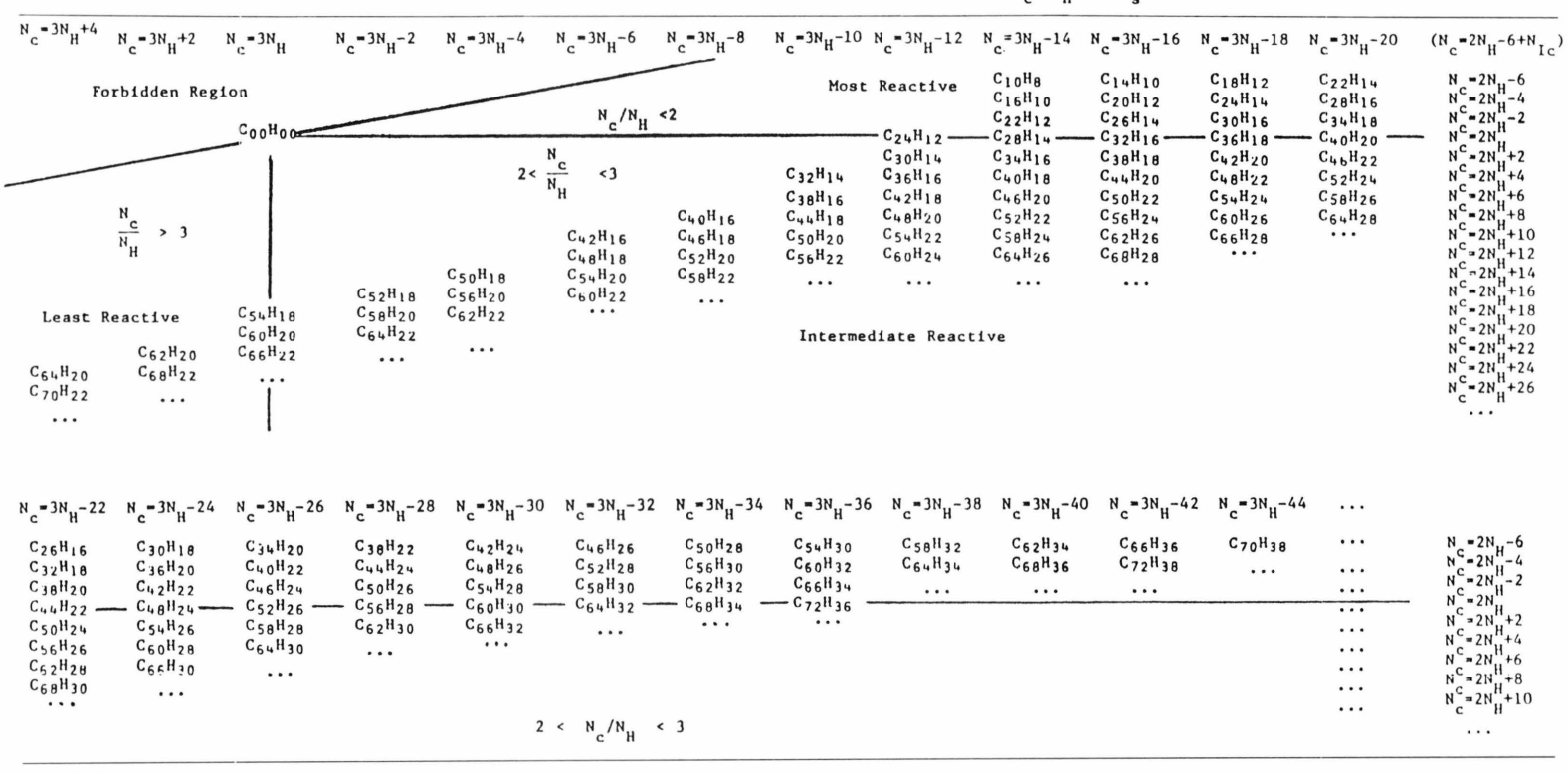
Table 1 represents a partially ordered set which sorts benzenoid hydrocarbons into isomer groups and identifies their group properties [16, 17]. The graph theoretical invariants (GI) that remain unchanged among polyhex isomers are known:

$$\mathrm{GI(PAH\,6)} = \{a_4,\ a_6 + n_0,\ a_8^c,\ d_s,\ N_{Ic},\ N_c,\ N_H,\ q,\ q_I,\ r\}\,.$$

These absolute group properties are fixed and are useful in studying differences among isomer groups. For

0932-0784 / 89 / 0800-0765 $ 01.30/0. – Please order a reprint rather than making your own copy.

Table 1. Formula Periodic Table for Benzenoid Polycyclic Aromatic Hydrocarbons (PAH6). Glossary: d_s – net tree disconnections of internal graph edges (positive values) or connections (negative values – called negative disconnection). N_c – total number of carbon atoms in a PAH. N_H – total number of hydrogen atoms in a PAH. N_{Ic} – number of internal carbons atoms in a PAH having a degree of 3. N_{Pc} – number of peripheral carbon atoms in a PAH having a degree of 3. PAH6 – polycyclic aromatic hydrocarbon containing exclusively fused hexagonal rings; also referred to as benzenoid and polyhex. $|P| = p = N_c$ – total number of graph points or carbon vertexs. P_3 – number of graph points (vertexs) having a degree of 3. $|Q| = q$ – number of graph edges (lines or C–C bonds). q_I – number of internal graph edges. q_p – number of peripheral graph edges. r – number of rings.



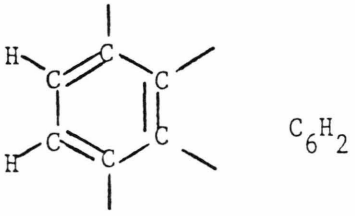
example, the average electronic $p\pi$ energy between isomer groups is principally determined by N_c and q. To study differences among PAH6 isomers, one needs graphical invariants that change from one isomer to another. No unique and simple invariant for all PAH6 isomers has yet be identified. The number of Kekulé structures is a graphical invariant which has been used to partially order the benzenoids within isomer groups [17]. This order approximates their relative order of stability. Since there are no known isospectral benzenoids, computed HMO eigenvalues appear to be unique but are not simply obtained through inspection. If the simplicity requirement could be fulfilled, this would facilitate our conceptualization and thinking processes about these systems. In the meantime, we must be satisfied with HMO eigenvalues for discerning among PAH6 isomers. If one is interested in a subset of PAH6 structures that are somehow related, as a homologous series, the hierarchial relationships among the nonisomeric homologous members are prescribed by Table 1.

Through a vector addition analog method, we previously showed that the total $p\pi$ energy (E_π^L) of a large benzenoid hydrocarbon can be estimated from the known E_π values of smaller ones [10]. Thus, when the number of carbon (N_c^L) and hydrogen (N_H^L) atoms of a large benzenoid hydrocarbon is related by $(N_c^L, N_H^L) = (N_c, N_H) + (N'_c, N'_H) = (N_c + N'_c, N_H + N'_H)$ to the number of carbon and hydrogen atoms of smaller benzenoid hydrocarbons, then $E_\pi^L = E_\pi + E'_\pi$. Since both $N_c^L = N_c + N'_c$ and $q^L = q + q'$ are overall conserved quantities, the level accuracy of the vector predicted E_π^L is better than the approximations due to McClelland [18] ($E_\pi \leq \sqrt{2qN_c}$) or Hall [19] ($E_\pi = q + \frac{1}{3}N_c$) because of the input of known E_π and E'_π values for the smaller benzenoids. For example, in the vector addition of $(10,8)+(28,14)=(38,22)$ naphthalene ($E_\pi = 13.68\beta$) plus a $C_{28}H_{14}$ isomer ($E'_\pi = 40.08-40.37\beta$) would go to a $C_{38}H_{22}$ PAH6 isomer ($E_\pi^L = 53.26-54.06\beta$) giving a better E_π^L estimate (54.1β) than $E_\pi^L = \sqrt{2 \cdot 46 \cdot 38}\beta = 59.13\beta$ or $E_\pi^L = (46 + \frac{1}{3} \cdot 38)\beta = 58.67\beta$ due to McClelland or Hall, respectively. Recently Cioslowski [20] published a new and more precise upper bound for E_π. Using his graph topological equation for the above example, one obtains $E_\pi = 58.01\beta$, which can be compared to the actual value of $E_\pi = 54.06\beta$. Though his value is better than that obtained by Halls equation, it still is inferior to our method. Our method does have its limitation since not all benzenoid formulas are accessible via the vector addition described above. Since no vector sum corresponds to a strictly peri-condensed benzenoid having a formula on the extreme edge of Table 1, these benzenoid species can not have their E_π estimated by this method. One should note the numerous papers written by Gutman on this subject alone [21]. As a final example of our vector addition method for estimating E_π of large benzenoid hydrocarbons, consider isoviolanthrene ($C_{34}H_{18}$), which has $E_\pi = 48.5320\beta$. Vector addition of $(2,4)+(32,14) = (34,18)$ using ethene ($E_\pi = 2.0\beta$) and ovalene ($E_\pi = 46.4974\beta$) gives $E_\pi = 48.4974\beta$ as an estimate for the electronic $p\pi$ energy of isoviolanthrene. Cioslowskys nodal increment method gives $E_\pi = 48.6616\beta$ for isoviolanthrene [22].

The Aufbau Principle

The aufbau principle was anticipated by Clars annellation method for correlation UV absorption spectral trends for various series of benzenoid compound in which the number of bay regions and resonant sextets were generally held fixed [2]. In 1981, two postulates were stated [5]. First, the formula for any benzenoid hydrocarbon is found in my formula periodic table for benzenoid polycyclic aromatic hydrocarbons (Table 1). Second, all possible isomers are enumerated by all combinatorial attachments of C=CH−CH=C units to the immediately preceding row series homologue isomers and by all combinatorial attachments of C=CH−C=CH−C=C or two C=CH−C units to the immediately preceding column homologues (Scheme II). Since the cata-condensed benzenoids have no formula in Table 1 above them, the first attachment mode gave the complete set of isomers. Similarly, since many of the strictly peri-condensed benzenoids have no formula in Table 1 at their left, either of the second attachment modes gave the complete set of isomers. For benzenoids having formulas located away from the upper or diagonally left sloping boundaries of Table 1 all attachment modes were needed to generate all the isomers; duplicates had to be discarded for those benzenoids having inner located formulas. Strictly peri-condensed benzenoid isomers having formulas in Table 1 with no formulas either immediately above or to their left were generated attaching a C=C unit to a bay region of the benzenoid structures having a formula located diagonally to the upper right (Scheme II). For example attachment of a C=C unit to the bay region of

benzo[*ghi*]perylene ($C_{22}H_{12}$) gives coronene ($C_{24}H_{12}$). For benzenoid structures having inner Table 1 formulas, this latter attachment mode led to no new isomers. Also, no new isomers were generated by attaching the following unit (Scheme I) to the bay region of a benzenoid having a formula immediately above the target enumeration formula [7]. In a formal sense, the formulas of C_2H_4 (ethene) and C_6H_6 (benzene) might be considered $N_{Ic}=0$ row members of Table 1 since the aufbau attachment of a C_4H_2 unit to C_2H_4 gives C_6H_6, and another successive attachment of C_4H_2 gives $C_{10}H_8$ (naphthalene).



Scheme I

One benzenoid growth mechanism involved acetylene addition to bay regions. As the simplest example, the main route to benzenoids in benzene pyrolysis is the formation of biphenyl by addition of phenyl to benzene followed by sequential addition of two acetylene molecules concomitant with loss of two H_2 to form pyrene, the smallest strictly peri-condensed benzenoid [23]. In general, strictly peri-condensed benzenoids have formulas on the left-hand diagonal of Table 1, are without coves or fjords on their perimeters, and have a minimum number of bay regions for a given number of carbons (N_c); pyrene, coronene, ovalene, and their circum benzenoid derivatives have no bay regions. Thus, acetylene addition growth of strictly peri-condensed benzenoids is topologically thwarted relative to other peri-condensed benzenoids. It should be noted that this acetylene growth process is equivalent to the aufbau attachment of a C_2 unit to the bay region of a benzenoid hydrocarbon.

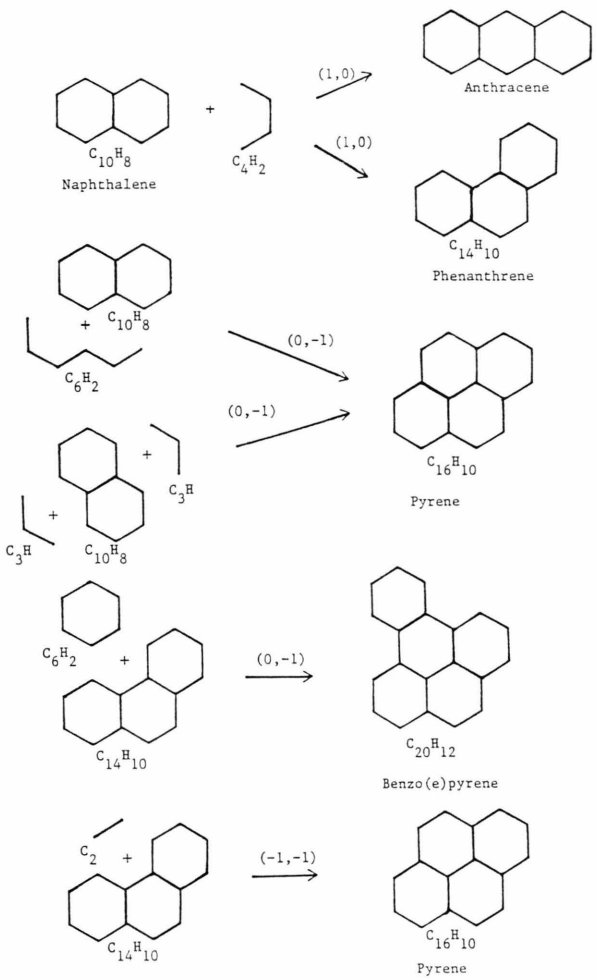
The elementary aufbau units are C_2, C_3H, and C_4H_2 [7]. All other aufbau units are appropriate combinations of these. A rudimentary construction of a new benzenoid from another involves attaching a C_2 unit to a bay region, two C_3H units to two vee regions, or a C_4H_2 unit to an edge of a precursor benzenoid. Consecutive attachment of a C_2 unit to a bay region followed by attaching a C_4H_2 to the edge generated is equivalent to attaching a benzo C_6H_2 unit to a bay region, and attaching three consecutive C_4H_2 units can be made equivalent to attaching a biphenyl $C_{12}H_6$ to an edge of a benzenoid [7].

Some aspects of our aufbau construction process were previously proposed in the excellent thermodynamic work of Stein [24]. Stein used successive C_4H_2 edge and C_2 bay region attachments to trace the thermodynamically most favourable high temperature PAH6 polymerization route for coronene, circumcoronene, etc. Here we note that successive C_4H_2 edge and C_2 bay region attachments are in some examples equivalent to our C=CH−C=CH−C=C attachment. According to Stein's work the smallest soot particle corresponds to hexacircum(30,42,54,66,78,90)coronene ($C_{384}H_{48}$). For a given number of carbons strictly peri-condensed benzenoids are among the more stable ones. This is a generalization of Stein's results. This Stein paper [24] also showed that for direct benzene polymerization, essentially strain-free total resonant sextets were thermodynamically favored. Thus it is now apparent that our aufbau construction process may be related to the mechanism of pyrolysis, and a premise implied in our work is that our enumeration process which follows the thermodynamics of the structure being generated will also be the more efficient one. Indubitably, it is the one of greatest interest and utility to experimental chemists.

Essentially stain-free total resonant sextets were enumerated by attachment of the above C_6H_2 unit to a bay region (Scheme II) or attachment of a $C_{12}H_6$ biphenyl unit to a sterically unencumbered perimeter edge of a smaller total resonant sextet benzenoid [13, 14]; this latter attachment mode is equivalent to attaching three successive C_4H_2 units in a manner which duplicates the biphenyl arrangement. We end this section by a quote from the work of Trinajstić and coworkers [15]. "The Dias (aufbau/Table 1) method obviously becomes very complicated for systems with many isomeric forms because of the enormous combinatorial possibilities. However, if combined with our computer procedure, it can be used for an efficient generation of all isomeric ... benzenoid hydrocarbons of a particular CH composition [15].

Excised Internal Structure Concept

Like the aufbau principle, the excised internal structure concept was preluded by spectroscopic ideas, by Platts perimeter rule [25] for data-condensed benzenoids and the subsequent spectroscopic distinction



Scheme II. Recursive aufbau construction of benzenoid hydrocarbons.

of the insular orbitals in peri-condensed benzenoids [26]. The conceptual jump to excising the insular structure out from peri-condensed benzenoids and studying the conserved properties and uses of the corresponding excised internal structures in enumeration was made in [9].

The excised internal structure of a benzenoid hydrocarbon consists of all its connected internal third degree vertices that remain after stripping off all the peripheral carbon vertices. A strictly peri-condensed benzenoid hydrocarbon has no cata-condensed appendages or disconnected internal vertices. Benzo[a]-pyrene and perylene are not strictly peri-condensed because the former has a cata-condensed appendage (the benzo moiety) and the latter has disconnected internal vertices. Pyrene is a strictly peri-condensed benzenoid with an ethene excised internal structure. Since ethene is incapable of having isomers, pyrene has no other benzenoid isomer since it has only one arrangement of its internal third degree vertices. There are three isomers of the formula C_4H_6: *s-cis*-1,3-butadiene, *s-trans*-1,3-butadiene, and trimethylenemethane diradical (Figure 1). If an 18-carbon-atom perimeter is circumscribed about each of these C_4H_6 isomers with the resulting species being incremented with six hydrogens, one obtains the only three $C_{22}H_{12}$ benzenoid isomers possible for this formula, i.e., benzo[*ghi*]perylene, anthanthrene, and triangulene. If these three latter strictly peri-condensed benzenoids are circumscribed by a 30-carbon-atom perimeter followed by incrementation with 6 H's, one obtains the only three benzenoid isomers possible for $C_{52}H_{18}$. Because trimethylenemethane is a diradical, triangulene and its $C_{52}H_{18}$ successor are also diradicals as well as all benzenoids built up from these cores by attaching successive C_4H_2 units in an aufbau fashion. Thus, the concept of excised internal structure has been useful in simplified enumeration of benzenoids and in the identification of one type of non-Kekuléan benzenoid species.

Whenever a benzenoid structure can have a succession of edges bisected with a straight line drawn from one side of the molecule to the other with the terminal rings being symmetrically convex relative to the line, then those rings intersected by the line can be embedded with a perpendicular succession of ethene substructures, and the benzenoid structure as a whole will have at least one eigenvalue pair of plus and minus one. This straight line will be called a selective lineation [27], and Fig. 1 shows several examples.

If a benzenoid excised internal structure is 1-factorable, 2-factorable, strictly peri-condensed, has one or more bay regions, and/or has one or more selective lineations, then the corresponding larger daughter PAH 6 structure formed by circumscribing a perimeter of carbon atoms around the excised internal structure and incrementing it with six hydrogens will also have these attributes.

Summary

In summary, the aufbau principle, excised internal-structure concept, and concept of strictly peri-condensed benzenoids were evolved in conjunction with the formula periodic table for the enumeration of ben-

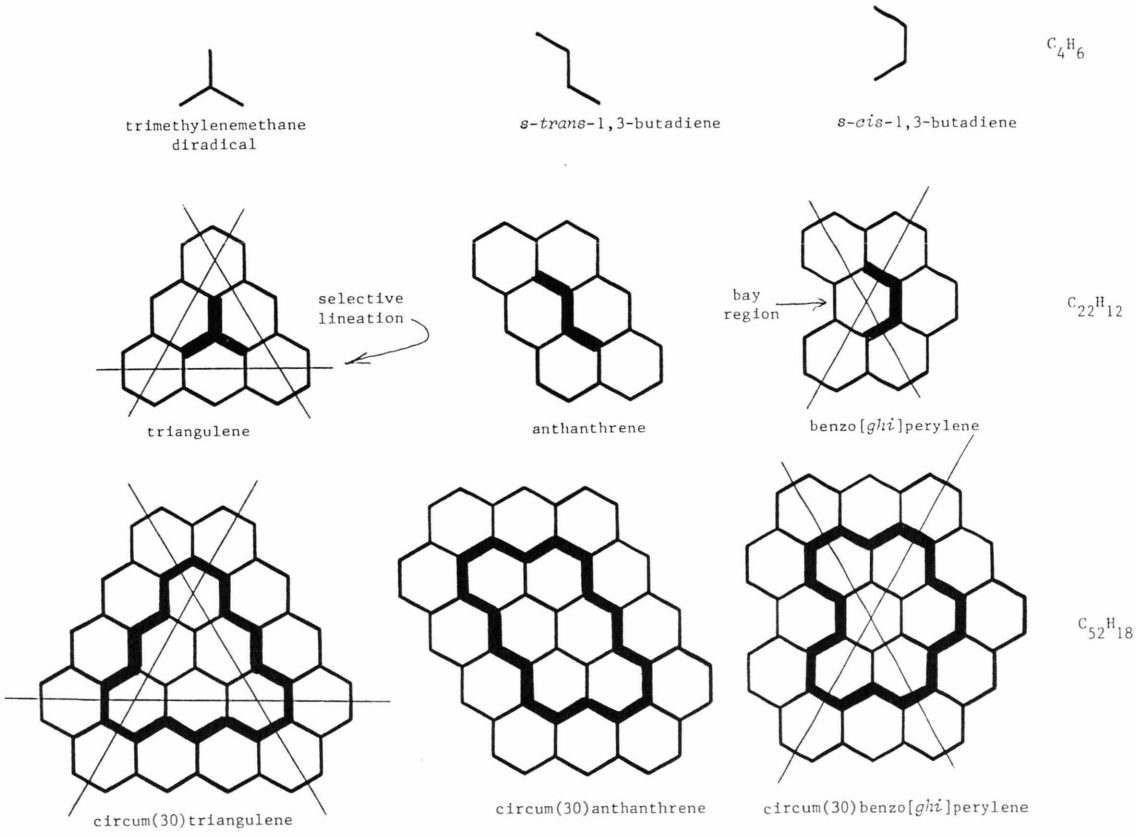


Fig. 1. Illustration of the excised internal structure concept in enumeration of all the benzenoid isomers of $C_{22}H_{12}$, $C_{52}H_{12}$, $C_{94}H_{24}$, ...

zenoids (Table 1). These fundamentals led to the first examples of enumeration of strictly peri-condensed, non-Kekuléan, and total resonant sextet (all-benzenoid systems) benzenoid groups which are of potential interest to experimental chemists [23, 24]. According to Hall [28]. "The periodic table of Dias is a very helpful device for this purpose [28]."

This review is ended with the same acknowledgement that appears in my Part B book [29]. The reader should note that the excised internal structure is incorrectly called inner dual and the aufbau principle is used in a paper which does not give proper credit to this work [30].

Acknowledgement

This work has been greatly inspired by the research and tutelage of Professors A. T. Balaban, G. G. Hall, W. C. Herndon, M. Randić, and N. Trinajstić.

[1] R. D. Kleopfer, J. R. Dias, and B. J. Fairless, In Chemistry in Water Reuse; W. J. Cooper, Editor; Ann Arbor Sci. Publishers: Ann Arbor, MI, 1981; pp. 207–227.
[2] B. J. Fairless, J. R. Dias, R. D. Kleopfer; 179th ACS National Meeting: Houston, Texas 1980, March 23–28; ENVR 29.
[3] J. R. Dias, Proc. MO Acad. Sci. **15,** 181 (1981).
[4] E. Clar, Polycyclic Hydrocarbons; John Wiley & Sons, New York, 1964; Vol. 1 and 2.
[5] A. T. Balaban and F. Harary, Tetrahedron **24,** 2505 (1968).
[6] Cited in [21] of J. Knop, K. Szymanski, Z. Jericević, and N. Trinajstić, J. Comput. Chem. **4,** 23 (1983).
[7] J. R. Dias, J. Chem. Inf. Comput. Sci. **22,** 15 (1982).
[8] A. T. Balaban, J. Brunvoll, J. Cioslowski, B. Cyvin, S. Cyvin, I. Gutman, He Wenchen, He Wenjie, J. Knop, M. Kovacevic, W. Müller, K. Szymanski, R. Tosić, and N. Trinajstić, Z. Naturforsch. **42A,** 863 (1987).
[9] J. R. Dias, J. Chem. Inf. Comput. Sci. **24,** 124 (1984); Can. J. Chem. **62,** 2914 (1984).
[10] J. R. Dias, J. Molec. Struct. (THEOCHEM) **137,** 9 (1986).

[11] J. R. Dias, Nouv. J. Chim. **9,** 125 (1985).
[12] J. Knop, W. Müller, K. Szymanski, and N. Trinajstić, J. Comput. Chem. **7,** 547 (1986).
[13] J. R. Dias, Thermochim. Acta, **122,** 313 (1987).
[14] J. R. Dias, J. Molec. Struct. (THEOCHEM) **185,** 57 (1989).
[15] J. Knop, W. Müller, K. Szymanski, and N. Trinajstić, Computer Generation of Certain Classes of Molecules; SKTH/Kemija u industriji: Zagreb 1985, page 145.
[16] J. R. Dias, Acc. Chem. Res. **18,** 241 (1985).
[17] J. R. Dias, Handbook of Polycyclic Hydrocarbons, Part A; Elsevier Sci. Publishers, Amsterdam 1987.
[18] B. McClelland, J. Chem. Phys. **54,** 640 (1971).
[19] G. G. Hall, Trans. Faraday Soc. **53,** 573 (1957); Molec. Physics **33,** 551 (1977); Inst. Math. Appl. **17,** 70 (1981).
[20] J. Cioslowski, Int. J. Quantum Chem. **34,** 217 (1988).
[21] I. Gutman, MATCH **22,** 269 (1987); J. Cioslowski and I. Gutman, Z. Naturforsch. **41A,** 861 (1986).
[22] J. Cioslowski, Theoret. Chim Acta **68,** 315 (1985).
[23] M. Frenklach, T. Yuan, and M. Ramachandra, Energy & Fuels **2,** 462 (1988).
[24] S. E. Stein, J. Phys. Chem. **82,** 566 (1978).
[25] J. R. Platt, J. Chem. Phys. **22,** 144 (1954).
[26] E. Clar, J. Robertson, R. Schlogl, and W. Schmidt, J. Amer. Chem. Soc. **103,** 1320 (1981).
[27] J. R. Dias, J. Molec. Struct. (THEOCHEM) **149,** 213 (1987).
[28] G. G. Hall, Theoret. Chim. Acta **73,** 425 (1988).
[29] J. R. Dias, Handbook of Polycyclic Hydrocarbons, Part B; Elsevier Sci. Publishers, Amsterdam 1988.
[30] J. Brunvoll, B. Cyvin, S. Cyvin, and I. Gutman, Z. Naturforsch. **43a,** 889 (1988).

Verantwortlich für den Inhalt: A. KLEMM
Satz und Druck: Konrad Triltsch, Würzburg