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Aromaticity of Polycyclic Conjugated Hydrocarbons

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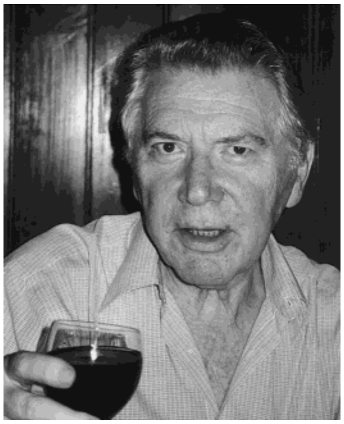
Contents



Milan Randić is a native of Croatia, born in 1930, and is a citizen of the United States and Croatia. He studied theoretical physics at the University of Zagreb (1954) under Professor Ivan Supek (a student of Werner Heisenberg). Supek introduced him to the book by Linus Pauling, *The Nature of the Chemical Bond*, with a request to get involved in quantum chemistry. He got his Ph.D. degree in Cambridge in 1958, studying high-resolution infrared molecular spectra with Dr. Norman Sheppard. At the Rudjer Bošković Institute in Zagreb, Croatia, in 1960, he founded the theoretical chemistry group. Since 1971, he has visited several U.S. universities. From 1980 to 2000, he was in the Department of Mathematics and Computer Science at Drake University, Des Moines, Iowa. Among the awards he has received are the City of Zagreb Science Award, the Boris Kidrič Science Award (of Republic of Slovenia), The Governor's Science Award (Iowa), and the Skolnik Award (American Chemical Society). He is a member of the Croatian Academy of Sciences and Arts. His continuing interest is to advance a better understanding of chemical graph theory. Since January 1, 2000, he is Professor Emeritus at Drake University, while continuing a three-months-a-year visitatation at the National Institute of Chemistry in Ljubljana, Slovenia. His other interests include development of a universal language, NOBEL.

PHOTOGRAPH CAPTION: The author is in full agreement with Plutarch (46–119 A.D.), who characterized wine as, "Of drinks — the most useful; Among medication — the most tasteful; Among food — the most enjoyable."

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PRACTICAL POINTS: Molecular structures are numbered according to the figure in which they are shown by a fraction ***x*/*X***, where ***x*** is the number of the molecule and ***X*** is the number of the figure showing its skeleton. In the list of references, in the case of review articles we have given the title of each article as this offers some information on the particular content of the review. In addition, we may have indicated the length of the review by listing the full page range of such articles.

> *If a man can preach a better sermon, write a better book, or make a better mouse-trap than his neighbor, though he build his house in the woods, the world will make a beaten path to his door.*
>
> R. W. Emerson (1803−1882),
> American essayist and poet,
> a leading figure in
> American literary history.

I. Prologue

"*Kekulé is dead. Long live Kekulé.*"

Indeed. By browsing the recent special issue of *Chemical Reviews* devoted to the topic of aromaticity,[1] one may obtain an impression that not only is Kekulé dead, but also the valence bond theory is dead. Moreover, disappointingly, one may also get the impression that Clar was never born! Among several thousand references listed in that issue, excluding historical remarks, you can count on your fingers how many times Kekulé and Clar are mentioned. In over 3200 references cited collectively in 18 articles on aromaticity, books by Clar were cited only eight times. Yet, it is difficult to look at the contributions to the discussion of the aromaticity of benzenoid hydrocarbons, which form the basis for discussion of aromaticity of non-benzenoid and heterocyclic compounds, without reference to Kekulé and Clar. Are we forgetting the shoulders on which we stand?[2]

As we will see, the four persons who made the most important contributions to our understanding of aromaticity are August Kekulé, Erik Hückel, Linus Pauling, and Eric Clar. Of the four, the least appreciated, Eric Clar, was the closest to recognizing the aromaticity of benzenoid compounds, even though his work can be characterized as intuitive. It is therefore regrettable that the pioneering work of Clar on the clarification of aromaticity has not been considered by theoretical chemists for more thorough investigation—as if it does not deserve their attention. There are few exceptions. Orchin and Jaffé, in their well-known textbook *Symmetry, Orbitals, and Spectra*,[3] devoted several pages to Clar. They recognized the merits of the Clar π-sextet, as is evident from the following quotation (from p 78), in which they draw attention to the widespread, even in these days, incorrect representation of benzenoid hydrocarbons:

> *There is an unfortunate misuse of the practice of depicting aromatic rings by use of a solid circle inscribed in a hexagon. In accordance with Sir Robert Robinson's original suggestion, the circle should represent only a sextet of pπ electrons. Accordingly, drawing naphthalene with two solid circles not only is aberration from the original suggestion but is misleading as well, since there are ten and not twelve pπ electrons in naphthalene. In this example only one of the two rings should be drawn with a solid circle inside it, but it is immaterial which ring is chosen. The choice, when it exists, as to which of the rings in the polycyclic system should be shown as possessing sextets (solid circles) is not completely arbitrary. Eric Clar, Polycyclic Hydrocarbons, Academic Press, Vols. 1 and 2, 1969, makes skillful use of the placement of the sextets to show chemical and spectral relationships between aromatic systems. His volumes are essential references for anyone interested in chemistry and spectra of aromatic compounds...*

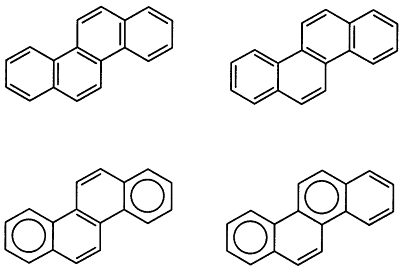


Figure 1. Clar structures (bottom) and Kekulé structures (top) of chrysene. The representations on the left are preferred to those on the right if a single structure is to be used for display.

This warning, set up over 30 years ago, apparently fell on deaf ears. A dozen years later, Belloli,[4] in an article entitled "The Misuse of the Circle Notation to Represent Aromatic Sextets" in the *Journal of Chemical Education*, again drew the attention of chemists to Clar structures, but apparently in vain. We are raising this issue again here, hoping that there may be some truth in an old Croatian saying: "Third time God helps." There is, this time, some basis for being optimistic. In a recent contact with Professor A. T. Balaban, one of the topical editors of *Polycyclic Aromatic Compounds* (The Journal of the International Society for Polycyclic Aromatic Compounds), after raising a complaint that many articles in this journal misuse the circle notation to represent aromatic sextets, I was assured that the matter will be addressed and authors will be instructed to draw either Clar structures or Kekulé structures for polycyclic benzenoid hydrocarbons but not incorrect structures with circuits (π-sextets) in adjacent rings. One of the problems that may have contributed to inertia in misrepresenting structures of benzenoids is that, just as is the case with the Kekulé valence structures, there are many benzenoid hydrocarbons that have more than one Clar structure. Which one should one draw? It does not matter much, but it is certainly better to use any such structure than to use the incorrect structure in which circles do not represent π-sextets. It may be beneficial if we could all agree to select standard structures by following some rules to reduce the number of alternative graphical representations. In the case of Kekulé valence structures, where we have a similar problem, Orchin and Jaffé suggest drawing a Kekulé structure, as shown on the left in Figure 1 for chrysene, "*that permits the maximum number of rings to have the Kekulé structure (three double bonds). Thus, for example, it is preferable to draw chrysene as in (a) rather than (b), since in the former all four rings have Kekulé structures, but in (b) only three rings are Kekulé and one is quinoidal.*"[3] As we will see later, the Kekulé valence structure with the maximal number of Kekulé benzene rings is the valence structure that, in 1927, Fries[5,6] recognized as *the most important* Kekulé valence structure. In parallel to the recommendation of Orchin and Jaffé to draw the most important Kekulé valence structure to represent benzenoid hydrocarbons, we suggest here that when more than one Clar structure is possible (as will be seen later to be often the case), we select *the most important* Clar structure, which has yet to be recognized. We suspect that this is the Clar structure in which the maximal number of rings have quinoidal form. This is the case with the Clar structure shown on the left in Figure 1, where there are two quinoidal benzene rings, in contrast to the Clar structure on the right in Figure 1, where there is only one quinoidal benzene ring. Molecules with symmetry may have more than one such "most important" Clar structure that will be symmetry-related. It is an open problem to establish whether there are two or more symmetry-unrelated Clar structures having the same number of quinoidal rings, in which case additional criteria may have to be considered to establish the most important Clar structure. A plausible route for characterizing such structures is to select the associated Clar structure that contributes maximally to molecular resonance energy.

The main "tool" in our approach to aromaticity is the concept of conjugated circuits that this author introduced over 25 years ago. As will be argued and demonstrated in this review, this "tool" is immensely suitable for the intended job, which includes classification of polycyclic conjugated hydrocarbons, characterization of aromaticity, and calculation of molecular resonance energy (RE). It will be shown how polycyclic conjugated hydrocarbons can be discriminated into those that qualify as "fully aromatic", those that are aromatic, and those that are less aromatic or not aromatic at all. The "theory of conjugated circuits", as this model is sometimes referred to, is quite simple to understand and use, and one could say it to be elegant, yet it is not simplistic. Apparently, this model has captured all the most important structural features of polycyclic conjugated hydrocarbons that are of interest when one considers their aromatic characteristics or lack thereof. One of the reviewers of this paper commented that "(the conjugated circuits) *model is more or less an empirical and parametric one*", which can be interpreted as a sign of deficiency. However, the same can be said of many important concepts of chemistry, starting with van't Hoff's tetrahedral model of the carbon atom, the notion of bond dipoles of Langeven, and Pauling hybridization and Pauling bond orders — all very simple concepts but of profound importance for chemistry. Conjugated circuits may well qualify for a similar distinction, but of course in a narrow field of chemistry — that of conjugated polycyclic hydrocarbons.

On the other hand, if a model is simple, empirical, and parametric, that does not necessarily means that it has no firm, apparently hidden link to generally accepted fundamental laws, such as those of quantum chemistry. Just as the opposite may be the case, a model that is thought to be based on basic axioms may turn out not to reflect this "deep" connection with quantum chemistry. It thus was found, mostly through the work of D. J. Klein,[7−10] that the conjugated circuits model has a quite firm foundation in quantum chemical principles, while as we all know, the Hückel molecular orbital (MO) model that started as a quantum chemical model turned out to be a consequence of molecular topology, rather than an intricate interaction of π-electrons governed by the Schrödinger equation.

The conjugated circuits model, as will be seen, offers insight into aromaticity that has been so far missing, and in that sense in our view it will be found indispensable. However, it should be kept in mind that this model, just as is the case with many other models, has limited applicability. Most chemists are aware of futile attempts to generalize the Hückel $4n + 2$ rule to polycyclic systems — for which it was not designed! The conjugated circuits model has been "designed" to discriminate among Kekulé valence structures, and hence applies wherever Kekulé valence structures play a role. As will be seen, this includes aromaticity, local aromaticity, molecular resonance energy, Clar structures, and Clar's aromatic π-sextet.

This article may be found in some way unusual and non-traditional. First, it approaches the "problem of aromaticity" from the chemical graph theory point of view rather than the traditional approaches based on experimental evidence as the support for the notion of aromaticity and theoretical approaches based on molecular orbital (MO) theory or valence bond (VB) theory. The article challenges non-structural approaches (both experimental and theoretical) as contributing to the confusion rather than clarification of aromaticity. The presentation is focused on the aromaticity of benzenoid and non-benzenoid hydrocarbons, almost "ignoring" 99% or more of the chemistry involving heteroatoms.

The article is "self-contained" in the sense that the most important basic concepts and approaches are fully outlined so as to allow the reader uninterrupted reading of the main body of the article without necessarily looking for clarifications elsewhere, in cited references or source publications. An effort was made to give credit to those who made important contributions in this area and to mention alternatives, even if not pursued in detail. Moreover, the article includes a number of original auxiliary contributions that help to clarify the material. It is hoped that these contributions will illustrate similarities and differences between the traditional and the standard approaches on one side and the graph theoretical (combinatorial and topological) approaches on the other side. In order to illustrate better the nature of graph theoretical methods, many notions of graph theory are outlined, even if some may be only marginally related to the central topic of the review — the aromaticity of conjugated hydrocarbons.

It would be too much to expect that the arguments presented would be generally accepted and generally understood. "*I have found you an argument; I am not obliged to find you an understanding.*" This was the answer that Samuel Johnson[11] gave after a prolonged argument with "*a pertinacious gentleman*" when he to one of Johnson's points had responded: "*I don't understand you, Sir.*" Understanding may require prior knowledge of various details, including various aspects of theory and experiments, and some individuals may be better or not so well equipped to fully understand various subtle points. But there is nothing abnormal about chemical graph theory that any *well-intentioned* person could not grasp. In fact, graph theory is so close to chemical descriptions of molecules that many may be surprised to find out how much of chemical graph theory they already know, without knowing it! However, I have to add a word of caution. The opposite also is often the case with some critics of chemical graph theory. Some of those who think that they know chemical graph theory may be surprised to find out how little they know. As Confucius said over 2500 years ago, "*Those who don't know that they do not know are dangerous, avoid them!*"

Apparently, often these days we do not give proper credit to the originators of important scientific ideas, except when a contribution relates to historical details. To mention but a few illustrations: How many of those who may have daily used Gaussian programs refer to S. F. Boys,[12,13] who initiated ab initio quantum chemical calculations based on Gaussian functions? How many of those who teach introductory courses on molecular orbital theory give credit to F. Hund[14−17] and R. Mulliken[18−21] (Nobel Prize for Chemistry in 1966) for initiating MO calculations? How many of those playing with Hückel molecular orbitals are aware that it was F. Bloch[22,23] who introduced (0,1) matrices (to which the Hückel Hamiltonian is reduced by suitable scaling) as an effective Hamiltonian for the interaction of electrons? How many of those who use principal component analysis (PCA) have heard of H. Hotelling?[24] How many chemists using X-ray computer software to report on molecular geometry are aware that it was J. Karle and H. A. Hauptmann[25] (Nobel Prize for Chemistry 1985) who solved the inverse problem for X-ray dispersion and made possible the calculation of atom coordination from X-ray data? How many of those involved in isomer enumeration and conformer studies are aware that it was Flavitskii[26,27] who made the first *chemical* enumeration? Renowned English mathematician Cayley, who has been often credited as reporting the first enumeration of isomers, was the first to consider enumeration of graphs.[28] His paper on enumeration of isomers appeared four years after Flavitskii published some of his isomer enumeration in the same journal.[29,30]

In order to pay due respect to those who have made seminal contributions to aromaticity, we have listed them in Table 1. A longer and more detailed list can be found in a paper by Balaban, entitled "Is Aromaticity Outmoded?".[31] The first paper on the VB model is the historical paper by Heitler and London[32] which explained the mystery of the so-called "chemical forces", characterized by unusual properties that are absent in electromagnetic and gravitational forces: the short range, the direction, and the saturation. As Heitler and London showed by calculations on the H_2 molecule, these "chemical forces" turned out to be nothing but interactions of electrons and atomic nuclei as governed by Coulomb potential and the Schrödinger equation. Their paper, which opened a new branch of chemistry, quantum chemistry, defined the VB approach. Browsing through chemical literature may give a wrong impression that the VB method is dying, if not already dead. Nothing can be more incorrect. Valence bond is alive and well, as is illustrated by numerous publications dealing with developments of VB theory.[7−10,33−35] One is reminded of the quotation from Mark Twain: "*The report of my death is an exaggeration.*"

Pauling and Wheland[36] initiated expansion of the VB method to benzenoids and other organic compounds almost 70 years ago, and although for a while the VB method was overshadowed by a fast development of various MO methodologies, it still remains a useful alternative approach for characterization of molecules. In recent years it has even seen a lively resurgence. Very accurate VB calculations based on 10^6 and more configurations are quite feasible.[37−39] In contrast to various semi-empirical MO schemes, such as the "extended Hückel" method,[40] the Pariser−Parr−Pople self-consistent field (SCF) MO method,[41,42] and modified intermediate neglect of differential overlap (MINDO) variants reported by Dewar and coworkers,[43−45] which tend to fade away with the development of ab initio calculations (based on Gaussian orbitals), this is not the case with various semi-empirical VB approaches. The reason may be that interpretations of VB models are more natural to chemistry, while efforts to digest the abundant numerical details of a typical MO ab initio calculation often fail to improve our insight into subtle aspects of molecular structures. For example, rigorous MO calculations of the geometry, say, of triphenylene will undoubtedly give fairly accurate estimates of various CC bond lengths in this molecule but will not tell us why the central CC bonds are much longer than the peripheral CC bonds. To "understand" this, one needs to construct appropriate bond orders (e.g., in the case of HMO theory the Coulson bond orders[46]), often forgetting that quantities such as bond orders, bond dipoles, atom−atom and atom−bond polarizabilities, atomic charges, etc. are non-observable. Dirac, in his treatise *The Principles of Quantum Mechanics*,[47] defined an observable as a quantity that can be calculated from the first principles. Thus, any quantity that is computed by not using the total molecular wave function is non-observable. Such, for example, are the Kekulé valence structures, the Pauling bond orders,[48] the Clar structures,[49,50] and the conjugated circuits[51−53] on one side, and on the other side various molecular descriptors (the so-called topological indices),[54−57] such as the path numbers of Platt,[58] the Wiener index W,[59] the Hosoya Z topological index,[60] the connectivity index χ,[61−67] Balaban's J index,[68,69] etc. All of these quantities have equal legitimacy or illegitimacy, although some may appear more "fundamental" than others (at least in the eyes of some) — they are at an equal footing.

What keeps various graph theoretical and semi-empirical VB models alive is that the concepts involved in these models are expressed by a language that is commonly understood in chemistry, which includes such basic structural elements as atoms, bonds, rings, and various molecular fragments, such as the bay region or the pharmacophores, which are of interest in structure−bioactivity studies. In this article we will focus on aromaticity in hydrocarbons, and in particular the aromaticity of benzenoid hydrocarbons, and will see that there is some theoretical justification to expect the "fully benzenoid" $6n$ π-electron systems of Clar to be the most aromatic polycyclic hydrocarbons. The reason that we have confined our attention to conjugated hydrocarbons is

Table 1. Important Contributions to the Evolution of the Notion of Aromaticity

author(s)	year	work on
M. Faraday	1825	discovery of benzene
A. Kekulé	1865	benzene cyclic formula
J. Dewar	1867	Dewar benzene formula
A. Ladenburg	1869	benzene prizmane formula
A. Claus	1882	benzene Claus formula
J. Thiele	1900	$C_5H_5^-$
R. Robinson and T. W. Armitt	1925	aromatic π-sextet
K. Fries	1927	Fries rule
E. Hückel	1931	Hückel molecular orbital theory
E. Hückel	1937	benzene benzvalene formula
W. C. Lothrop	1941	biphenylene synthesis
T. J. Sworski	1948	tridehydro[12]annulene
P. L. Pauson	1951	ferrocene
W. von E. Doering and L. H. Knox	1954	tropylium ion
E. Clar and M. Zander	1958	aromatic π-sextet resurrected
K. Hafner and J. Schneider	1958	aceheptylene derivative
W. E. von Doering and E. A. Matzner	1958	fulvalene
F. Sondheimer and R. Wolovsky	1959	[18]annulene
F. Sondheimer and R. Wolovsky	1959	[24]annulene
S. Winstein	1959	homo-aromaticity
T. J. Katz	1960	cyclooctatetraene dianion
F. Sondheimer, R. Wolovsky, and Y. Gaoni	1960	[30]annulene
F. Sondheimer and Y. Gaoni	1960	[14]annulene
F. Sondheimer and Y. Gaoni	1961	[16]annulene
F. Sondheimer and Y. Gaoni	1961	[20]annulene
E. E. van Tamelen	1963	Dewar benzene synthesis
G. Schröder	1964	bullvalene
E. Vogel	1964	bridged $4n + 2$ π-electron systems
E. Heilbronner	1964	Möbius annulene
T. J. Katz	1965	aromatic anions
A. L. Chung and M. J. S. Dewar	1965	anti-aromaticity
W. E. Barth and R. G. Lawton	1966	corannulene
K. E. Wilzhach	1967	benzvalene synthesis
W. H. Okamura and F. Sondheimer	1967	hexadehydro[18]anulene
R. H. Martin and M. J. Marchant	1972	large helicenes
E.Clar and B. A. McAndrew	1972	tetrabenzoperylene
E.Clar and B. A. McAndrew	1972	tetrabenzocoronene
T. J. Katz	1973	prizmane synthesis
D. M. Jerina	1976	bay region
G. Olah, J. S. Staral, and L. A. Paquette	1976	cyclooctatetraene dication
H. A. Staab and F. Diedrich	1978	kekulene
C. F. Wilcox and E. N. Farley	1984	dicycloocta[*def:jfk*]biphenylene
H. W. Kroto, R. F. Curl, and R. E. Smalley	1985	buckminsterfullerene C_{60}
K. Müllen	1997	giant benzenoids
L. T. Scott	2002	C_{60} synthesis
K. P. C. Vollhardt	2002	helical [*n*]phenylenes
A. Vij and K. O. Christe	2002	cyclo-N_5^-
P. W. Fowler, R. W. A. Havenith, L. W. Jenneskens, A. Soncini, and E. Steiner	2002	flattened cyclooctatetraene
J. E. Dahl, S. G. Liu, and R. M. Carlson	2003	poly-adamantanes
E. Nakamura, K. Tahara, Y. Matsuo, and M. Sawamura	2003	[10]cyclophenacene

that, if we are to better understand aromaticity in a general case, we ought first to understand the aromaticity of hydrocarbons, benzenoid and non-benzenoid. Only after that should we try to embark on the more complex task of characterizing the degree of aromaticity of heterocyclic aromatic compounds. We also believe that, among chemists, there is hardly disagreement that the "fully benzenoid" $6n$ π-electron systems of Clar are the most aromatic benzenoid hydrocarbons — so they offer a good starting point in our effort to clarify the concept of aromaticity. We will address this topic in more detail later.

Chemical graph theory[70−85] has also its "strengths". This can be seen when considering not only *interpretation* of some quantum chemical results but also *interpretation* of statistical and other data on molecules. In this article in particular we will see how graph theoretical concepts, such as the conjugated circuits, the innate degree of freedom of Kekulé valence structures, and the Clar structures, can all be combined to characterize the local and overall aromaticity of benzenoid hydrocarbons, "fully benzenoid" hydrocarbons, and "fully aromatic" compounds. In addition, we will see that these approaches that lead to the quantification of Clar's π-sextets model can be justified using chemical arguments.[86,87]

We will present three independent arguments that support the notion of the local aromaticity of benzenoid hydrocarbons as advocated by Clar: (1) We

Table 2. Types of Aromaticity

type of aromaticity	described by	year
pseudo-aromaticity	W. v. E. Doering et al.	1956
homo-aromaticity	S. Winstein	1959
quasi-aromaticity	D. Lloyd and E. R. Marshall	1964
anti-aromaticity	A. L. Chung and M. J. S. Dewar	1965
	R. Breslow	1968
super-aromaticity	Clar	1972
3-D aromaticity	R. B. King and D. H. Rouvray	1977
	D. M. P. Mingos	1977
	J.-i Aihara	1978
spherical aromaticity	H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley	1985, 1990
σ-aromaticity	V. I. Minkin, M. N. Glukhovtsev, and B. Ya. Simkin	1994

will show that graph theoretically calculated ring resonance energies in benzenoid hydrocarbons (that parallel Clar's notion of the π-aromatic sextet, the notion of the "fully benzenoid" hydrocarbons, and the concept of "empty" rings and the migrating sextets) correlate well with the quantum chemically computed contributions of individual rings to the molecular resonance energy (RE). (2) We will see that quantum chemically computed RE values better agree with the graph theoretical model in which only *the most important* Kekulé valence structures are considered, rather than considering contributions from conjugated circuits from *all* Kekulé valence. (3) Finally, we will see how, by extending Clar's model of π-aromatic sextet to biphenylene derivatives, by considering only the Kekulé valence structures of the "maximal innate degree of freedom", one can understand the relative stability of bent [*n*]phenylenes, which would be predicted to be unstable if the contributions from conjugated circuits from *all* Kekulé valence structures were considered.

II. Introduction

> *Es gibt keine Kunst, welche so schwerig ist wie die Kunst der Beobachtung.*
>
> Justus von Liebig (1803−1873)[88]

There is no doubt that the term "aromaticity" is one of the most widely used terms in chemistry. At the same time, "aromaticity" may well be one of the most widely misused terms in chemistry, not by being attributed to compounds that do not qualify as aromatic, but by becoming so unspecified that it is applied to too many compounds that show widely different physico-chemical properties. Labels that are so broad that they apply to a multitude of compounds are bound to cause confusion, just as confusion may arise when there are too many Smiths, Browns, and Jones in the same locality. To reduce the latter confusion, people have been given two and even three names; hence, it is understandable that similar attempts were made to discriminate among several types of aromaticity, like pseudo-aromaticity, homo-aromaticity, quasi-aromaticity, etc. (Table 2).

The root of the problem is not only that, from the very beginning, the term "aromaticity" was not rigorously defined, but also that, from the very beginning, opposing views on how to characterize aromatic compounds were advocated. Kekulé[89] in 1865 proposed that the concept of aromaticity be based on *structural features* of conjugated polycyclic compounds, but in the next year Erlenmeyer[90] advocated the use of *properties* of "aromatic" compounds to define aromaticity. If properties are to be taken as criteria, then the first question to be asked is which properties and why? But there is another serious problem with such an empirical approach that may imply a "circular argument".[91] In order to use such an approach, one has to decide *in advance* which molecules are aromatic so that their *properties* can be considered as *standard*. The standards selected in such an approach maintain a preferential treatment by being *assumed* to be aromatic prototypes, while they may in fact already be partially "contaminated" with some less than aromatic structural characteristics. For example, if we select as standards the well-established aromatic species, such as the benzenoid hydrocarbon compounds, then compounds that differ from benzenoids structurally may be found to be less aromatic. For example, azulene[92] and the [18]annulene discussed by Sondheimer and Wolovsky[93] may not qualify as aromatic compounds as much as benzenoids because they lack similarity to benzene. Yet benzene and azulene both, as well as [18]annulene, as we will see later, can be viewed as aromatic prototypes.

There are no such difficulties if we try to characterize aromaticity on the basis of some *structural features* of conjugated polycyclic compounds. If a compound has the feature considered essential for aromaticity, it is aromatic; if it lacks the critical feature, it is not. But, of course, the problem remains to find which *structural feature* of aromatic molecules is critical for aromaticity! There are a number of fallacies that have contributed to a misunderstanding of the notion of aromaticity. In order to illustrate just one of the common fallacies, consider a list of words in which each successive word differs only by one letter from the previous word, a "minor" change:

WHITE → *WHILE* → *WHALE* → *SHALE* →
SHAVE → *STAVE* → *STOVE* → *STORE* →
STORK → *STOCK* → *STACK* → *SLACK* →
BLACK

As we can see, an accumulation of minor changes may result in a major fallacy: *WHITE* = *BLACK*. The mathematician C. L. Dodgson (1832−1898) (better known as Lewis Carroll, the writer of the renowned book *Alice's Adventures in Wonderland*) is the author of numerous such illustrations, which he envisaged as the game of doublets. The English

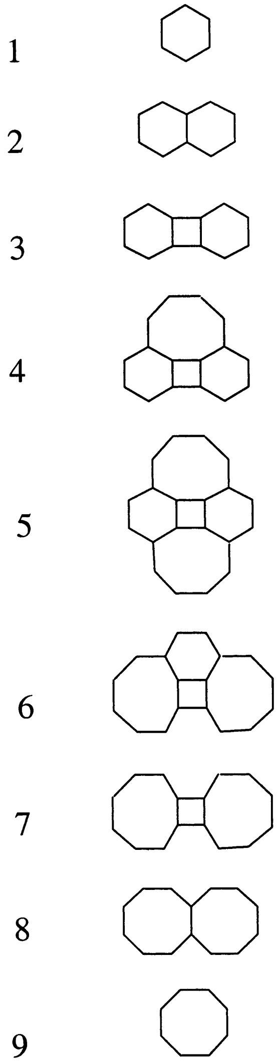


Figure 2. Sequence of compounds, starting with benzene and ending with cyclooctatetraene, which gradually change from aromatic into anti-aromatic.

magazine *Vanity Fair* runs contests challenging readers to come up with the shortest possible "transformation" of cases such as *WINTER* = *SUMMER*, *WOOD* = *TREE*, *FOUR* = *FIVE*, *OAT* = *RYE*, etc.[94,95]

It is not difficult to imagine how an accumulation of small changes in molecular properties could similarly result in the "doublet" *AROMATICITY* = *ANTI-AROMATICITY*. All that is needed is to find a sequence of compounds which differ little, starting with benzene and ending with cyclooctatetraene. In Figure 2 we show one such set of compounds, a sequence of similar compounds, in which compounds in adjacent positions in the list are expected to show only minor changes in their properties. However, an accumulation of these small changes results in a "proof" that *AROMATICITY* = *ANTI-AROMATICITY*. Figure 2 was constructed mainly to make the point that *properties* of molecules should not be used for their classification, because there are no clear-cut boundaries that would separate compounds in two or more classes.

III. Dilemmas

> (Aromaticity) *is a funny subject. The first time you go through the subject, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don't understand it, but by that time you are so used to the subject that it doesn't bother you any more.*
>
> See ref 96.

In trying to clarify the notion of aromaticity, one confronts several dilemmas. Should aromaticity be a qualitative concept or quantitative? Should aromaticity be characterized by structural attributes or by molecular properties? Is the valence bond approach or molecular orbital theory more suitable for definition of aromaticity? Could chemical graph theory offer better insights into aromaticity than the traditional quantum chemical approaches? We will address these dilemmas in the following sections.

A. Qualitative versus Quantitative Approaches

> *When you can measure what you are speaking about, and express it in numbers, you know something about it. But when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meager and unsatisfactory kind: It may be the beginning of knowledge, but you have scarcely, in your thoughts, advanced to the stage of science.*
>
> Lord Kelvin[97]

While some concepts in chemistry that serve us well are non-numerical and will remain qualitative, others have been from the start numerical and quantitative, even if not uniquely defined. For example, molecular shape and molecular similarity are qualitative, descriptive concepts that may not be characterized uniquely by a single number, or even by a sequence of numbers. Shape at best will require numerous descriptors that may not even be easy to order, while similarity may depend to a great extent on descriptors selected for the representation of objects considered. Thus, molecules that may be similar in one aspect are not necessarily similar when some other structural or experimental feature is considered.

As accumulation of data increases, some concepts that were initially qualitative may offer an opportunity for quantitative (numerical) characterization. This applies to several "ambiguous" concepts in chemistry, a selection of which is listed in Table 3. However, it is important to stress that characteriza-

Table 3. List of Somewhat Ambiguous but Common and Useful Concepts in Chemistry

ambiguous concepts
aromaticity
branching
complexity
resonance energy
reactivity
similarity
resonance
molecular shape
molecular size
molecular surface
molecular volume
flexibility
foldedness

tion of a structural property of a molecule by numerical descriptors ought to be preceded by first *defining* such quantities. When this is not the case, we may expect the use of alternative schemes for characterization of a single property. It may happen that, subsequently, one of the proposed schemes will be found better than the others and will prevail, and thus become "the definition" for the property considered. Often, the presence of alternative schemes for the same property or feature causes confusion rather than clarifying the concepts involved.

We may speak of a degree of aromaticity, a degree of branching, a degree of flexibility, a degree of foldedness, and a degree of chirality, but in each case we first have to define the branching, the flexibility, the foldedness, and the chirality, if these have not been well defined before. Similarly, we may attribute numerical magnitudes to molecular complexity, to molecular resonance energy, to molecular size, to molecular surface, and to molecular volume. It is conceivable that different authors may choose different numerical characterizations for the same structural aspects of molecules, which may, but need not, be the beginning of confusion. In such situations, it is essential that those who follow clearly indicate which particular definition they adopted in order not to cause confusion by overlooking the differences in the definitions for the same concepts as used by others.

It is not uncommon to see, in chemistry journals, research papers that use specific scientific terms *without* prior definition of such terms. Consider the widely used term "polycyclic aromatic hydrocarbon" (PAH), which is even the title of a well-known chemistry journal. Have you seen this term defined? What is a polycyclic aromatic hydrocarbon? Clearly, all polycyclic hydrocarbons formed by fusion of benzene rings would be recognized by most chemists as "polycyclic aromatic hydrocarbons", but these could also be called polycyclic benzenoid hydrocarbons. The term "polycyclic aromatic hydrocarbon" apparently applies to a wide class of compounds, which remain unspecified. Nevertheless, PAH is a useful term and is likely to survive because the term "aromatic" does not exclude variations in the level of the aromaticity that such compounds may have. Hence, although this vague label does not specify what it includes, it does suggests what it excludes. It is hoped that eventually the class of PAH compounds may allow for a finer sub-classification of the compounds grouped in this way that can range from "fully aromatic" to "empty" aromatic compounds, to borrow the terminology of Clar (which he used for individual rings and not molecules as a whole).

In contrast to the practice in chemistry, in which it is not uncommon to use terms without prior strict definition, the traditional practice in mathematical literature is to give, at the very beginning of a scientific paper, all the necessary definitions. This applies even to well-known concepts with which most readers may be familiar. It is then not surprising that, in the mathematical literature, there is little, if any, confusion regarding the concepts used. Mathematicians can trace this "good behavior" of clearly presenting the definitions of the terms used in their papers back to Euclid! The first books by Euclid on the elements of geometry started with definitions of a point, a line, a straight line, a plane, etc.[98] In contrast, chemistry has a humble beginning in mystic alchemy, which, as is known, was based more on wishful thinking than on rational thinking.

In order to keep pace with this noble tradition of mathematicians, we will try in this review to offer definitions for the most important concepts and ideas used. Since we will be using the language of discrete mathematics, and in particular will present applications of graph theory to chemistry, let us start with the definition of a graph, which is a mathematical object not to be confused with graph as a diagram or plot. The definition that we give is an "informal" definition that avoids notions of Descartes products among elements of sets—interested readers can search for an alternative rigorous definition in any textbook on graph theory.

Definition: *A graph is a mathematical object defined as a set of elements V, among which is defined a binary relation E.*

The elements in the set are called vertices and are, as a rule, graphically presented as small circles. A relation that either exists between two elements or not is called a binary relation (having only two possibilities, "yes" or "no", informally: any two elements are either connected or not). The relations, when depicted, are called edges and are drawn by connecting corresponding vertices, represented as small circles, by lines. Graphs, which can have multiple connections and even loops, in many ways resemble simple molecular diagrams. However, graph theory is concerned with *topological* and *combinatorial* properties of such objects, which can be represented pictorially in many different ways. Because graphs can well represent chemical molecules, many chemist may find graphs more familiar objects than they thought. However, one should keep in mind all the time that molecules do not represent graphs, but graphs may represent molecules. Graphs are abstract objects of no fixed geometrical form with a multitude of diverse graphical representations.

Concerning aromaticity, for some time it has been recognized and generally accepted that aromaticity is associated with the extra stability of cyclic conjugated systems relative to their acyclic counterparts. There are no disputes here, and such characterization may well continue to serve as a *qualitative* characterization of aromaticity. The problem with the above "definition" occurs when one considers *quantitative* aspects of aromaticity and tries to answer which of two or more molecules is more aromatic. The above description of aromaticity does not specify which "acyclic counterpart" is to be used as a standard when comparing different polycyclic systems. The *molecular resonance energy* (RE) is one such widely accepted measure of this "extra" stability, but again the calculation of the RE requires one to know what acyclic structure is to be assumed as the starting point. Additional difficulties may arise due to possible alternative computational definitions of the molecular RE. In the case of MO approaches, the following two definitions of RE have some merit:

(1) Dewar[43] defined RE as the difference between the total π-electron energy, E_π, and the energy of an acyclic polyene-like reference structure obtained by summing over all bonds (the corresponding bond types n_{ij}) their energies E_{ij}.

(2) Gutman, Milun, and Trinajstić,[99,100] and Aihara,[101] independently defined the "acyclic" standard, called the topological RE, through the eigenvalues of a polynomial related to the characteristic polynomial of the secular equation. In mathematical literature, such a polynomial is known as the matching polynomial of a graph.[102−104]

In the HMO model, the roots of the characteristic polynomial represent orbital energy levels and allow one to obtain molecular energy. Coulson pointed out in 1950 that the secular equation, which in the case of the HMO model is the characteristic polynomial of the graph adjacency matrix, can be constructed from a collection of contributions of various smaller cyclic and acyclic subgraphs.[105] Moreover, as shown by Sachs,[106] one can construct the characteristic polynomial by considering only certain combinations of *isolated edges* and *isolated cycles* of a molecular graph. For an introduction to the approach of Sachs for calculation of the characteristic polynomial, see ref 107. In the construction of the matching polynomial, one proceeds just as in the construction of the characteristic polynomial, except that one disregards all the contributions arising from components that involve *cyclic fragments*. Hence, the resulting polynomial bears a close relationship to the characteristic polynomial, but it lacks cyclic contributions. According to Trinajstić and Aihara, the roots of the matching polynomial serve to define the energy of the unique "acyclic" standard for the calculation of the molecular resonance energy. Such resonance energy has been referred to as topological resonance energy (TRE).

The matching polynomial, constructed by ignoring the contributions from cyclic fragments, is called the acyclic polynomial by Trinajstić et al. and the reference polynomial by Aihara. The approaches of Trinajstić and Aihara require that the roots of the matching polynomial for conjugated hydrocarbons are real numbers. Because the matching polynomial is not associated with a symmetric matrix, as is the case with the characteristic polynomial, there is no guarantee that its roots will be real numbers. However, Heilmann and Lieb[108,109] proved that, indeed, the roots of matching polynomials are always real. Godsil and Gutman have also shown the same.[110] For computation of the matching polynomial in benzenoid systems, see refs 107−118, while for computer evaluation of the matching and the characteristic polynomials, see refs 119 and 120.

Criticisms have been raised concerning the topological RE in that ambiguities may arise in calculation of RE in some situations due to alternative population of orbital levels with electrons.[121−124] To what extent such criticisms hold is not fully clear, particularly if one views the difference in the eigenvalues of the characteristic polynomial and the eigenvalues of the matching polynomials as a computational tool to extract the role of cyclic components in the characteristic polynomial and abandons the interpretation of the eigenvalues as one-electron orbital energies. While both Coulson's[105] and Sachs's[106] approaches to computation of the characteristic polynomial were directly applicable to the HMO model, both approaches can be extended to other MO models by introducing suitable weights for vertices and edges, as outlined by both Aihara[125,126] and by Mallion et al.[127]

Table 4. Non-observables of Chemistry

non-observables
aromaticity
hybridization
molecular orbitals
localized orbitals
natural orbitals
HOMO
LUMO
atomic charges
atom polarizabilities
Pauling bond orders
Coulson bond order
bond dipoles
bond polarizabilities
potential function
Kekulé valence structure
Clar's structure
Clar's π-sextet
Fries valence structure
anti-Fries valence structure
conjugated circuits
resonance energy
Rumer diagrams
partial ordering
substructure
topological indices
nucleus-independent chemical shift
ring currents

B. Observables versus Non-observables

> *The essential fact is simply that all the pictures which science now draws of nature, and which alone seem capable of according with observational facts, are mathematical pictures.*
>
> Sir James Jeans (1877−1946)[128]

Observables are defined, in the sense of Dirac's approach to quantum mechanics,[43] as quantities that can be experimentally measured and, in principle, computed from the first principles of quantum mechanics using the total molecular wave function. Hence, if one wants to compute an observable, one needs to know, and then use, the total molecular wave function of the molecule or, alternatively, the total electron density. Anything computed not using the total molecular wave function or the total electron density does not qualify as an observable. For example, in the calculation of Coulson's bond orders, one uses molecular orbitals rather than the total molecular wave function. Hence, Coulson's bond orders are non-physical, non-observable quantities. But that does not mean that they are not useful! They are useful as they allow comparison of CC bond lengths within the same molecule or in different molecules, and thus they allow one to predict unknown CC bond lengths.

"Aromaticity" is also a non-observable in the strict sense of Dirac's quantum theory. So are the resonance energy, the local aromaticity, the atomic charges, the bond polarizabilities, the bond dipoles, etc., including the HOMO−LUMO separations as typically calculated in simple MO theories. The same is again true of Kekulé valence structures, conjugated circuits,[51−53] Clar's π-sextets,[49] Pauling bond order,[48] valence structures of "the higher degrees of excitation",[129] Rumer diagrams,[130] sp, sp^2, and sp^3 hybrids

Table 5. Experimental and Theoretical Properties Used as Criteria of Aromaticity

physical properties
equalization of CC bond lengths (bond alternation)
deviation of peripheral bonds from those of benzene
ring currents
anisotropy of diamagnetic susceptibility
anisotropy of diamagnetic exaltation
Faraday effect (excess of magnetic rotation)
energy barrier to restricted rotation
calculated properties
first- and second-order bond fixation
π-electron delocalization
resonance energy

and hybridization in general,[48] etc., the quantities that are of interest in VB theory. Finally, the same can be said of various graph theoretical concepts, including topological RE, [9−101] various molecular descriptors (the so-called topological indices),[54−57] like the connectivity index $^1\chi$[61,62] and the variable connectivity indices $^1\chi^f$,[131−138] Hosoya's Z topological index,[60] Balaban's J index,[68,69] and the Wiener index W.[59] In Table 4 we have compiled a short list of a number of non-observables of interest in chemistry.

It is important to realize that a non-observable has a meaning and an interpretation that are mostly limited within the model for which it has been defined. Thus, typically a non-observable will not have a meaning outside the model for which it was constructed. For example, the Kekulé valence structures, which are fundamental to VB theory and chemical graph theory, have no simple meaning in MO theory. Analogously, the HOMO−LUMO separation, which has meaning in various MO models, has no simple interpretation in the VB model. Similarly, while there is a fair correlation between the Coulson bond orders and the Pauling bond orders for selection of smaller benzenoid hydrocarbons, as is to be expected for these two quantum chemistry models, one may find, somewhat unexpectedly, that there is an even better correlation between the Coulson bond orders and the graph theoretical connectivity indices,[139−141] which represent two totally unrelated molecular models. The connectivity index $^1\chi$ is defined as a bond-additive quantity in which bond (m,n), where m and n are the graph theoretical valences of vertices, makes a contribution $1/\sqrt{(mn)}$ to the molecular index.[61] Why should a graph theoretical construction like $^1\chi$ produce a good agreement with quantum chemically computed bond orders? Is it not possible that "totally unrelated models" have some unrecognized common ground?

C. Structural Criteria versus Properties as Criteria

There is no Royal road to Aromaticity.
See ref 142.

In Table 5 we have listed a selection of experimental properties of "aromatic" compounds that have been considered in the past for characterization of aromaticity. We have listed also the calculated (theoretical) properties used to characterize aromaticity. When comparing the two different approaches to aromaticity, we have to conclude that calculated properties have some advantages per se over the use of experimental properties. First, in principle, they can always be obtained. Second, they can be performed on non-existent structures, intermediates, and structures for which experimental data are missing. One should bear in mind that, today, about 20 million compounds are registered, but experimental properties of most molecules remain unknown. For example, "*The Toxic Substances Control Act (TSCA) Inventory has nearly 80,000 entries 50 % of which do not have data for even one physicochemical property and about 85 % of them have no data on any genotoxicity bioassay.*" [143]

What is wrong with using properties rather than structural features for classification of compounds? We have already mentioned the problem of selecting the "standard" property. That alone should be enough to reject properties as candidates for classification of compounds. But there are *additional* reasons for not following Erlenmeyer's suggestion that aromaticity be based on properties of aromatic compounds. Recollect that sugar, saccharin, and many other sweeteners would be classified in the same group if sweetness were the criterion for classification, yet they are structurally vastly different. Just because at the present we cannot recognize the *critical* structural features of aromatic compounds, this is not good enough reason for abandoning the aromaticity "ship" and lamenting the lack of merits of the notion of aromaticity. Suggestions to abandon the notion of "aromaticity" have been heard from time to time.[144−147]

We strongly advocate a "return to Kekulé" position that aromaticity should be characterized by the structural features of a molecule. We not only should reject the use of properties for classification of aromaticity, but should continue to *repudiate* approaches based on properties of molecules for characterization of aromaticity as being inherently prone to fallacious conclusions. If properties are used as criteria for classification of compounds, they will continue to blur the boundaries between fully aromatic, aromatic, non-aromatic, and anti-aromatic molecules because properties may vary continually between molecules. In contrast, structural components are either present or absent in a molecule, and thus a molecule either qualifies or does not qualify to belong to a particular class.

It needs to be recognized that Erlenmeyer's approach represents a *step back* and out of the prevailing attitude in chemistry, where the starting point is molecular structure. Consider in analogy, for example, a definition of n-alkanes not as compounds built by a regular increment of methylene groups, but as compounds showing some regularity in their properties. For instance, one could define n-alkanes as compounds characterized by regular increments of their boiling points (bp) with size. As one can find out, the bp of n-alkanes can be predicted with high precision (about 0.15 °C) over the range of several hundred degrees Celsius. Although such an "experimental" definition of n-alkanes would be legitimate, the approach would appear to most chemists as absurd. And, indeed, it appears as absurd because the *structural* features that define *n*-alkanes are so evident. Apparently, people are considering various *properties* for alternative “definitions” of aromaticity because we lack the *courage to admit* that we do not know what are the *critical structural features* that lead to aromaticity. Why should we define aromaticity using regularities of their properties, be it bond equalization, the magnitudes of ring currents, or any other property, and at the same time consider it ridiculous to define *n*-alkanes on the basis of the regular increments of their boiling points?

D. Valence Bond Theory versus Molecular Orbital Theory

> *The formulation is mathematically equivalent to the more usual formulation. There are therefore, no fundamentally new results. However, there is a pleasure in recognizing old things from a new point of view.*
>
> Richard P. Feynman (1918−1988)[148]

Quantum chemistry started with Heitler and London’s calculations on the H_2 molecule[32] that represent seminal valence bond calculations. Quantum chemistry was widely accepted among chemists through Pauling’s *The Nature of the Chemical Bond*,[48] in which the VB approach dominated. However, with Hückel’s work on the benzene MO model[149−151] and the relative ease of MO computations with overlapping $2p_z$ orbitals rather than interacting Kekulé valence structures, the MO method continually gained strength. The MO approach was popular in physics, from which Hückel adopted his (effectively binary) Hamiltonian, the so-called “hard-sphere” Hamiltonian that Felix Bloch used for calculations on metals.[22,23] Superficially browsing the literature may give an impression that VB is no longer a viable theoretical model. But that is not the case (for literature on VB, see refs 29−31). In our view, “valence bond versus molecular orbital theory” is, in fact, an ill-posed dilemma and should be replaced by the attitude, “valence bond *and* molecular orbital theory”.

One should not overlook the fact that both of these models represent just different starting points in quantum chemical calculations. It has been known for some time that if both methods were pushed to the limit by including the “higher order” contributions, they would both yield the same results. The situation is analogous to the relationship between Heisenberg’s “matrix mechanics” and Schrödinger’s “wave mechanics”, which are mathematically equivalent. For an account of *The History of Quantum Theory*, see the book by Hund (of Hund’s rules) with that title.[152]

The reason that MO theory has advanced so much is that it is relatively “easy” to compute corresponding matrix elements in MO models. For example, if the MO method is applied to a molecule like buckminsterfullerene,[153,154] one would consider overlapping among 60 π-electrons. In contrast, in the simple VB approach, the resonance theory, one has to consider the 12 500 Kekulé valence structures[155] that this spherical carbon allomer has. Hence, the choice is between considering a 60 × 60 matrix of a simple MO model and a 12 500 × 12 500 matrix of a simple VB model! But that is not all. There is available computer software (based on Gaussian functions) for considering more ambitious ab initio MO calculations, while more ambitious VB calculations would make an already bad situation much worse, because they would necessitate inclusion of an even larger number of Kekulé structures of higher “excitation”, and possibly structures involving charged carbon atoms. The number of valence structures for a system having *n* π-electrons to be considered in an accurate VB calculation is given by the Catalan numbers, which grow exponentially.[37−39] We ought to mention that there are also “hybrid” methods, which combine some aspects of MO and VB theories, like BORT, the approach developed by Živković.[155−162] BORT stands for “bond orbital resonance theory”, which conceptually follows the resonance pictures by interpreting chemical bonds in the MO rather than the VB sense. In the early development of quantum chemistry, Linnett proposed an approximate method of calculating wave functions that also differed from MO and VB methods. This approach was known as the “nonpaired spatial orbitals method”.[163]

Herndon,[164−168] who developed his “resonance theory”, has shown that simple VB approaches can lead to useful characterization of conjugated hydrocarbons. Herndon, in his approach, considers only the standard Kekulé valence structures of a molecule as the basis for his calculations. One starts by constructing the Hamiltonian matrix, the matrix elements of which are defined by interactions between pairs of Kekulé valence structures. Here Herndon introduces an important simplification, which makes his calculations even simpler than HMO calculations for the same benzenoid system. Herndon defines the interactions between Kekulé valence structures by quantum chemical integrals γ_1 and γ_2, the magnitude of which depends only on the number and the relative position of CC double bonds within various Kekulé valence structures. If two Kekulé structures, when superimposed, differ in locations of three CC double bonds within a single benzene ring only, their interaction is expressed by the integral γ_1. If two superimposed Kekulé structures differ in locations of five CC double bonds within two adjacent benzene rings, their interaction is given by the integral γ_2. One could continue and consider interactions between Kekulé valence structures that differ in locations of seven, nine, etc. CC double bonds, but Herndon decided that such interactions would be small. Hence, if two superimposed Kekulé valence structures differ in more than five locations of the CC bonds, it is assumed that their interaction is negligible. In Figure 3 we illustrate the interaction between the six Kekulé valence structures of pyrene graphically. Kekulé valence structures in Figure 3 connected by solid lines differ in locations of only three CC double bonds in a single benzene ring, while structures connected by dashed lines differ in locations of five CC double bonds in two adjacent benzene rings. The method of Herndon[164−168] is related to the approach outlined

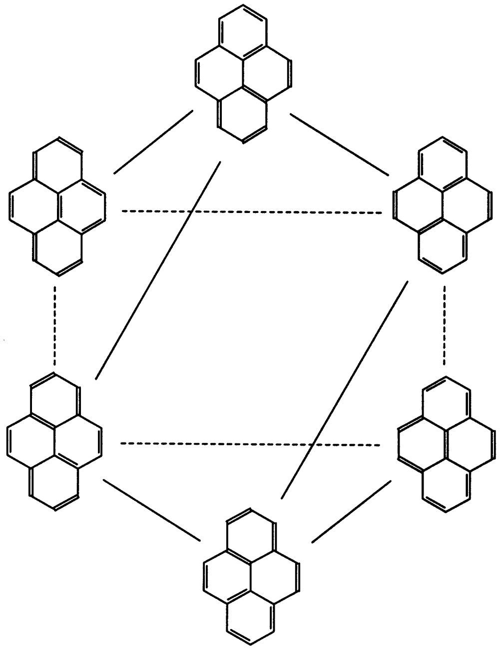


Figure 3. Herndon's graphical illustration of the interactions between the six Kekulé valence structures of pyrene.[164] The solid lines represent interactions given by the integral γ_1, and the dashed lines represent interactions given by the integral γ_2.

earlier by Simpson,[169] which although exposed in a textbook[170] was mostly undeservingly overlooked, never receiving due attention until Herndon rediscovered and resurrected the simple VB calculations 20 years later.

E. On Interlocking of the MO and the VB Methods

We should point out that there are several subtle connections between VB and MO approaches that tend to be overlooked and that clearly indicate that the two approaches are intimately related. Hence, the question is not MO or VB, but MO *and* VB. Let us mention some of these connections between the two major quantum chemical methodologies. Apparently, quite unexpectedly, Ham, Ruedenberg, and Platt[171–173] found a relation between the Coulson bond orders and the Pauling bond orders. As is known, the Coulson bond orders and Pauling bond orders offer somewhat different characterizations for CC bonds,[140,141] but as shown by Platt, Ham, and Ruedenberg, unexpectedly the two quantities are mathematically *closely* related. As is well known, the Coulson bond orders are obtained by summing for each bond the contributions made by the product of atomic coefficients over the occupied HMO.[46] However, if the same contributions from the molecular orbital Ψ_i are divided by the corresponding eigenvalue λ_i, one obtains, as Ham, Ruedenberg, and Platt found,[171,172] the Pauling bond order. Using this mathematical relationship between the Pauling bond orders and the Coulson bond orders, one can find the Pauling bond orders for CC bonds for molecules having very large numbers of Kekulé valence structures using the simple HMO approach! This would be particularly suitable for the giant benzenoids of Müllen[174–177] on one side and fullerenes on the other side.

Table 6. Block of the Inverse Adjacency Matrix of Naphthalene

	6	7	8	9	10
1	2/3	-2/3	1/3	-1/3	1/3
2	1/3	2/3	-1/3	1/3	-1/3
3	-1/3	1/3	1/3	-1/3	1/3
4	1/3	-1/3	2/3	1/3	-1/3
5	-1/3	1/3	-2/3	2/3	1/3

Another illustration of "hidden" connections between the simple MO and the simple VB methods was illustrated by Heilbronner,[178] who reported an intriguing connection between the graph theory and the HMO theory valid for bipartite graphs. Let us first define bipartite graphs:

Definition: *A graph is bipartite if its vertex set V can be partitioned into two subsets V* and V^0 such that each edge joins a vertex of V* with a vertex of V^0.*

All acyclic graphs and all graphs having only even-member rings are bipartite. Hence, graphs of benzenoid hydrocarbons are bipartite. Bipartite graphs have been known in chemical literature as *alternants*. The carbon atoms belonging to V^* and V^0 have been referred to as the "starred" and the "non-starred" carbon atoms. For bipartite graphs, Heilbronner came upon a graphical construction of $\mathbf{A}^{-1}$, the inverse of the adjacency matrix of a molecule (if the adjacency matrix has an inverse). We illustrate the approach of Heilbronner for naphthalene, which by being a bipartite graph allows one to write the adjacency matrix in the following form:

$$\mathbf{A} = \begin{bmatrix} \mathbf{0}_m & \mathbf{B}_{mn} \\ \mathbf{B}_{mn}{}^{\mathrm{T}} & \mathbf{0}_n \end{bmatrix}$$

Here, $\mathbf{B}_{mn}$ is a binary adjacency $m \times n$ matrix between vertices of V^0 and vertices of V^*, m and n are the numbers of elements in V^0 and V^*, respectively, $\mathbf{B}_{mn}{}^{\mathrm{T}}$ is the transpose of $\mathbf{B}_{mn}$, and $\mathbf{0}_m$ and $\mathbf{0}_n$ are $m \times m$ and $n \times n$ zero matrices, respectively. A submatrix $\mathbf{B}_{mn}$, which connects the "starred" and the "non-starred" carbon atoms in naphthalene, is shown in Table 6. In the mathematical literature, one refers to $\mathbf{B}_{mn}$ as a bi-adjacency matrix. We have numbered the "starred" atoms as 1−5, and the "non-starred" atoms as 6−10. Construction of the elements of the inverse matrix is illustrated in Figure 4. The elements of the inverse matrix are given by the quotient K_{mn}/K, where K is the number of Kekulé structures of a molecule and K_{mn} is the number of Kekulé structures for the residual of a molecule when vertices m and n (and all edges adjacent to them) are

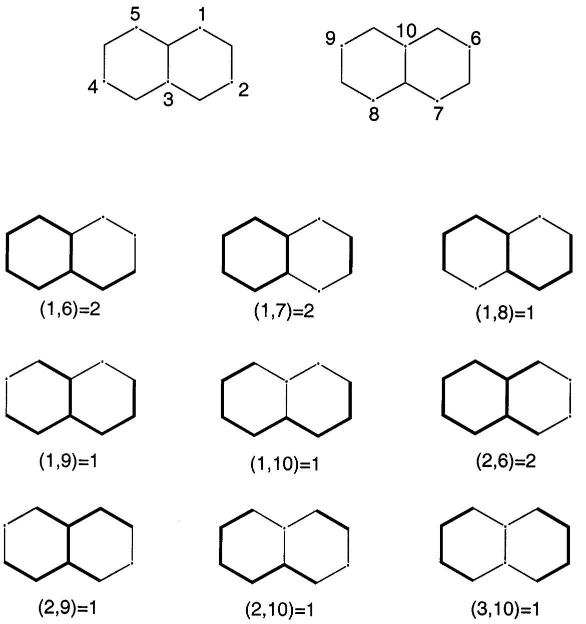


Figure 4. Graphical construction of $\mathbf{A}^{-1}$, the inverse of adjacency matrix **A**, of naphthalene as outlined by Heilbronner.[178] Only symmetry-non-equivalent matrix elements are illustrated.

erased. The signs of the elements of the matrix are determined by counting the number of CC double bonds between carbon atoms m and n. Elements are positive if there are an even number of CC double bonds between m and n or if m and n are adjacent. Elements are negative if there are an odd number of CC double bonds between m and n. Alternatively, as a footnote in the paper by Heilbronner[178] explains, the sign is given by the parity of the number $(Z - 1)$, where Z is the number of CC double bonds along any path from vertex m to vertex n. One could also determine the sign of the contributions in $\mathbf{A}^{-1}$ by considering only "conjugated chains" or "conjugated paths",[179,180] that is, the paths which start and end with CC double bonds along which there is a regular alternation of CC single and CC double bonds. Interestingly, this could have been an earlier discovery of paths within Kekulé valence structures having alternating CC bond types, but the significance of such paths has not been recognized at the time. As we will see later, circuits with alternating CC double and CC single bonds, which are the basis of the conjugated circuits method,[45-47] play a crucial role in determining the stability of polycyclic conjugated hydrocarbons and their aromaticity.

F. Chemical Graph Theory versus Quantum Chemistry

... give us insights, not numbers.

C. A. Coulson[181]

Again, this is an ill-posed dilemma that reflects much of the misconceptions and much of the misunderstandings of chemical graph theory. In Table 7 we have listed the kind of questions that are of interest in chemistry, the answers to which are not to be obtained from the standard quantum chemistry calculations, but for which chemical graph theory may offer answers. Observe that these questions do not belong to quantum chemistry, which at best may in some instances offer numerical values for a property considered. Many of the questions posed can be answered by using available algorithms of the chemical graph theory.[64] Typically, questions that involve the relative magnitudes of molecular properties belong to chemical graph theory. However, if one is interested in precise molecular geometry, molecular spectra, and such, the answers are to be sought using quantum theory. Because the molecular geometry and the molecular spectra are of considerable interest, it may appear that quantum chemistry may be concerned with more important questions and that therefore quantum chemistry is the more important methodology. That may be so, but it all depends on the questions one is asking and the problems one considers. If one is interested in problems beyond the reach of quantum chemical calculations, regardless of how important quantum chemistry is, clearly one has to consider other theoretical tools. Obviously, the two theoretical approaches, because they focus on different questions, are complementary to each other.

Despite being different and addressing different questions, nevertheless quantum chemistry and chemical graph theory (shortly GT, for graph theory) have much in common. In Figure 5 we have illustrated several overlapping regions and common topics between quantum chemistry on one side, that is, valence bond theory and molecular orbital theory, and chemical graph theory on the other side. As we see from Figure 5, the VB and MO methods have in common the Schrödinger equation, while MO and GT have in common the Hückel MO calculations. It is this aspect of the overlap of MO and GT that has been

Table 7. Questions To Which Chemical Graph Theory May Offer Answers

How many isomers has $C_{10}H_{22}$?
What is the number of alkanes having n carbon atoms and longest chain of length d?
How many Kekulé valence structures has C_{60}?
Why is the boiling point of 2,5-dimethylhexane greater than that of 2,2-dimethylhexane?
How many conformations has a normal alkane chain having N carbon centers?
Can the sum of carbon-13 chemical shifts be viewed as a molecular property?
Why do similar molecules sometimes display different properties?
How many degenerate rearrangement isomers are possible for P_7^{3-} ?
Why, within the HMO model, are 1,4-divinylbenzene and 2-phenylbutadiene isospectral?
Why, within the HMO model, do many structures show excessive degeneracy for certain eigenvalues?
Which isomer among cata-condensed benzenoids has the largest number of Kekulé structures?
How many benzenoid hydrocarbons have the same number K of Kekulé structures?
How large ought a finite system be to exhibit properties similar to those of the corresponding infinite system?
Which atoms (atomic groups) in a larger molecule having bioactivity constitute a pharmacophore?

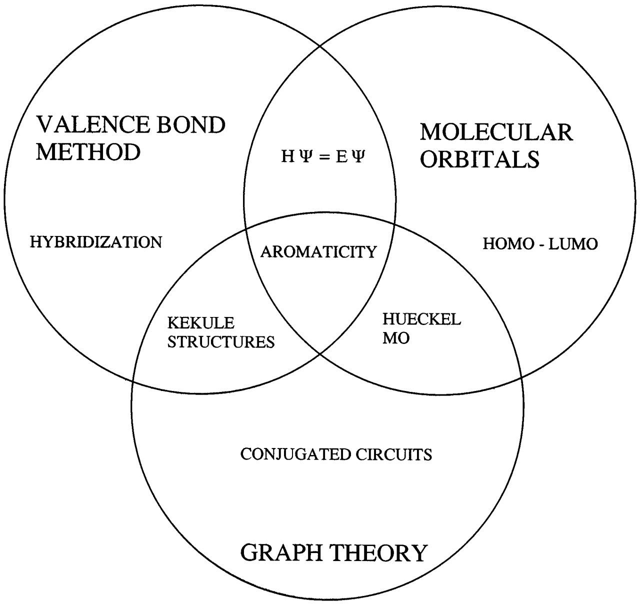


Figure 5. Schematic illustration of the overlapping of valence bond theory, molecular orbital theory, and chemical graph theory.

the cause for much of the misunderstanding of GT and identifying it with HMO theory. On the other hand, the common ground between VB and GT is Kekulé valence structures, which is known in the mathematical literature as the "complete 1-factor cover" of a graph. Of course, each of the three methodologies has concepts that are specific to it and which have no necessarily simple interpretation outside the particular methodology. In the case of VB this is the concept of hybrids, in the case of MO this is the notion of the HOMO−LUMO gap, and in the case of GT these are conjugated circuits. Finally, we find aromaticity, one of the central ideas in chemistry, which has meaning in VB, MO, and GT, and hence can be approached by all three methodologies. Observe that all subjects shown in Figure 5 are nonobservables in the strict sense of the quantum theory (excluding the Schrödinger equation, which represents a postulate).

Figure 5 offers an overview of the inter-relationship between the three methodologies of theoretical chemistry, VB, MO, and GT, but much more could be added. For example, molecular orbital theory and chemical graph theory, besides having in common one of the simplest calculations (the Hückel MO method), meet again at the other end of very complex ab initio calculations, the exact VB calculations known as graphical unitary group approach (GUGA), where graphs are used for book-keeping of the numerous configuration interaction contributions.[182−192] In Figure 6 we have illustrated one such graph from a paper by Duch and Karworski[192] on a graphical approach to the direct configuration interaction method which keeps track of the number of electrons and the number of orbitals involved in configurations. The graph that is shown corresponds to the case of six electrons and six orbitals, and it results in 141 orbital configurations. These graphical concepts have been introduced by Paldus,[182−185] Matsen,[186] and Shavitt,[187,188] and they allowed construction of algorithms for the direct configuration interaction (CI) methods.[189−192] For new developments in the Hückel theory, we direct readers to the work of N. Trinajstić.[70,193]

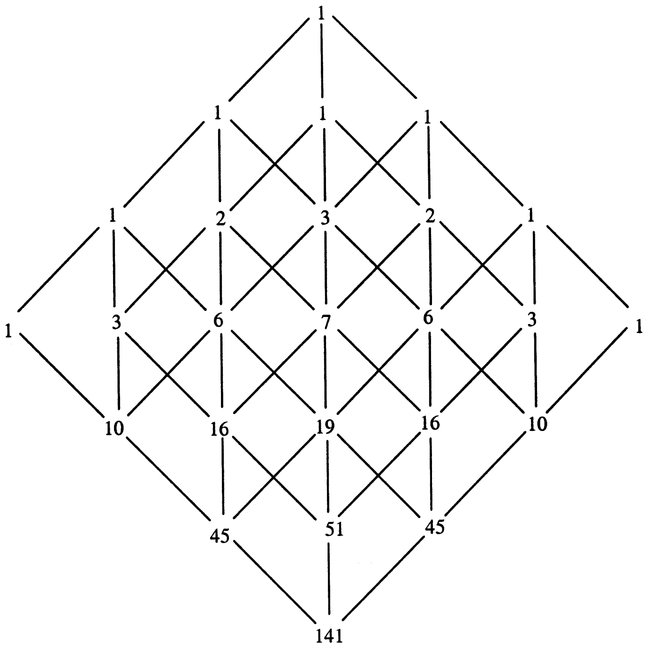


Figure 6. Graph of book-keeping of configuration interactions involving six electrons and six orbitals (as depicted in ref 192).

As shown in the center of Figure 5, the VB, MO, and GT methods have in common the quest for aromaticity. In this review, we will be concerned mostly with VB and GT approaches to aromaticity, but MO, although not given the same visibility in this review, plays an equally important role for clarification of aromaticity. On one side, it offers reliable SCF MO type calculations of the resonance energy, while on the other side, particularly with respect to GT, it opens avenues for extending the notion of aromaticity from hydrocarbons to heterocyclic compounds. We should mention in particular the route that Parr and Pearson[194] have pioneered by developing the notion of absolute hardness.

Before leaving this area where the three methodologies meet, one should recognize also the major differences between graph theory and quantum chemistry. Graph theory does not produce numbers, such as RE, on its own. Graph theory offers *expressions* for RE, but parameters that enter such expressions have to be either extracted from *experimental* data or *computed* using quantum chemistry. On the other hand, quantum chemistry gives numbers, such as RE, but does it give insights? Consider the benzenoids shown in Figure 7. Using quantum chemical calculations, we can obtain reliable RE values for many benzenoids, but we will have no idea why, for instance, benzo[*e*]pyrene **1/7** has a higher RE than benzo[*a*]pyrene **2/7**, or why the resonance energy per electron (REPE) is greater for triphenylene **3/7** than for coronene **4/7**. Quantum chemistry will supply us with RE numbers, but it is graph theory that has shown that these RE numbers are *additive*, and not bond-additive, or ring-additive, but additive in terms of conjugated circuits! Thus, in the case of the

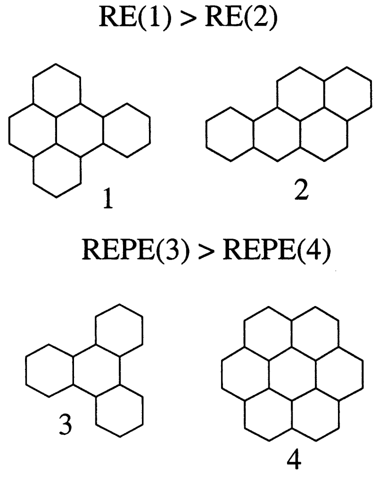


Figure 7. Benzenoids for which conjugated circuits point to different RE (top), and benzenoids for which conjugated circuits point to different REPE (bottom).

resonance energies, graph theory gives to quantum chemical calculations an *interpretation*, or in the words of the late Professor Coulson, an *insight*. It is regrettable that Coulson, who was quite optimistic about chemical graph theory (see Biographical Notes on Coulson), did not live to see its growth and successes.

In summary, this author very much agrees with a statement made by Paul Mezey at the meeting in Girona in 1995, during his presentation on molecular electron density calculations, that "*molecules have skeleton and molecules have body*".[195] Molecular *skeletons* are given by bond lines connecting atoms, and molecular *body* is given by electron density contours. However, in addition, as I stated in the closing remarks of that conference in Girona, besides having a *skeleton* and a *body*, molecules also have a *spirit*, which is reflected in the conceptual features associated with molecules as revealed by mathematical chemistry.

G. Clar 6*n* Rule versus Hückel 4*n* + 2 Rule

> *Finding useful information is an intelligent process requiring intelligent people because at the end of the day only the intelligent can recognize what is useful.*
>
> Tony Kent[196]

The Hückel $4n + 2$ rule represents an important success of early quantum chemistry, as it explains the stability of benzene and several annulenes and the lack of stability of cyclobutadiene, and the preference for alternation of CC single and CC double bonds in cyclooctatetraene. The rule predicts non-zero eigenvalues for monocyclic systems having $4n + 2$ carbon atoms and degenerate zero eigenvalues for monocyclic systems having $4n$ carbon atoms. Frost and Musulin[197] illustrated this rule elegantly by using the property of eigenvalues of cyclic systems given by cosine functions to design projections of vertices on energy coordinates (Figure 8). Zimmermann[198] modified the graphical diagram of Frost and Musulin for the case of Möbius systems (see Figure 9). Möbius π-systems are those in which, along a cycle of overlapping p-orbitals, by gradual twisting, eventually we have overlap of p-orbitals of opposite sign, for the pattern of π-orbital levels.

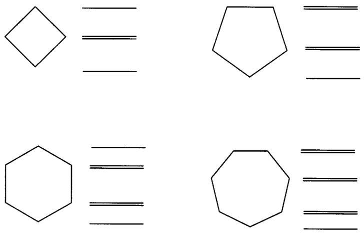


Figure 8. Eigenvalues of cyclic systems, depicted as a projection of vertices on a vertical axis, as illustrated by Frost and Musulin.[197]

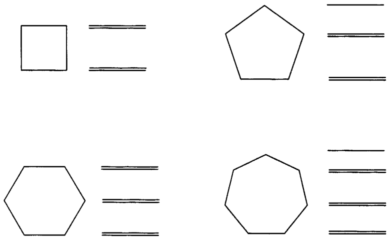


Figure 9. Modification of the projection diagram of Frost and Musulin for Möbius systems, as illustrated by Zimmermann.[198]

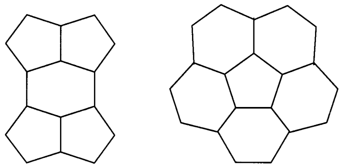


Figure 10. Failure of the perimeter rule: a "fully anti-aromatic" non-benzenoid system having 14 π-electrons on the periphery, and an aromatic corannulene having an odd number of electrons on the periphery.

The $4n + 2$ rule solved the "mystery" of the profound difference between benzene, [10]annulene, [14]-annulene, and [18]annulene on one side and the $4n$ monocyclic systems, like elusive cyclobutadiene and puckered cyclooctatetraene, on the other side. Attempts were made to extend the $4n + 2$ rule to polycyclic systems, for which it was not initially designed. Of numerous attempts in this direction, we will mention only that of Platt,[199] who proposed that the $4n + 2$ rule be applied to molecular periphery. It turns out that Platt's generalization of the Hückel $4n + 2$ rule is correct when one restricts attention to benzenoid hydrocarbons. For example, the perimeter rule correctly classifies pyrene (which has 16 π-electrons), perylene (which has 20 π-electrons), and coronene (which has 24 π-electrons) as aromatic as they have 14 or 18 π-electrons on the perimeter. But the perimeter rule does not give a correct answer for the non-benzenoid systems illustrated in Figure 10. The structure on the left, which has 14 π-electrons on the periphery, instead of being aromatic, as will be seen later, is in fact "fully anti-aromatic". On the other hand, the structure on the right (corannulene), which has 15 π-electrons on the periphery, is not

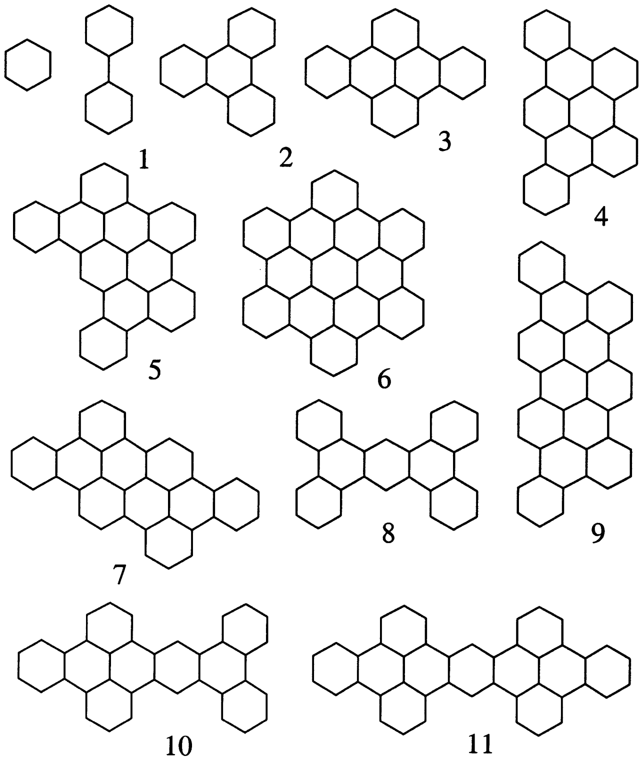


Figure 11. Unusually stable benzenoid hydrocarbons having 6*n* π-electrons, discussed by Clar.

covered by the rule, which deals only with even numbers, although, as will be seen later, bowl-shaped corannulene can be considered as "fully aromatic".

The Hückel $4n + 2$ rule received deserved attention, although the rule as proposed is of a very narrow scope. It has also received undeserved misuse. Its significance is not in its generality, but in that it offers an important insight into the difference between $4n + 2$ and $4n$ conjugated monocyclic systems like benzene and cycooctatetraene. It clarifies the aromaticity of the cyclopentadiene anion of Thiele[200] as well as the tropylium cation of Doering and Knox[201] and higher analogues. As is today well recognized, it strictly holds for monocyclic systems. In contrast, Clar's rule on the extra stability of $6n$ π-electron systems,[202] which has a wider applicability than the Hückel $4n + 2$ rule, neither has received due attention nor is widely known. Clar observed that benzenoid hydrocarbons which have $6n$ π-electrons (e.g., benzene, $n = 6$; diphenyl, $n = 12$; triphenylene, $n = 18$; dibenzopyrene, $n = 24$; and other benzenoid compounds shown in Figure 11) are unusually stable. This is how Clar described the unusual stability of these $6n$ π-electron systems:[202]

> *Dibenzopyrene (**3**) is colorless hydrocarbon and does not show the reactivity of pyrene. Tribenzoperylene (**4**) is also colorless and does not give benzogenic diene synthesis with maleic anhydride like perylene. Tetrabenzanthanthrene (**5**) and hexabenzocoronene (**6**) are pale yellow hydrocarbons of great stability...(hexabenzocoronene) melting point could not be determined because the melting-point tube melted long before the hydrocarbon.*

In view of these facts, it is puzzling that Clar's rule on the extra stability of $6n$ π-electrons, which is quite general, has been barely noticed, while the Hückel $4n + 2$ rule, with its known limited application, continues to be used and misused! We should add that all the unusually stable $6n$ hydrocarbons that have been synthesized recently by K. Müllen and coworkers,[174−177] known as "giant benzenoids", are systems having $6n$ π-electrons. Several giant benzenoids described by Müllen et al. are illustrated in Figure 12.

H. Hydrocarbons versus Heteroatomic Systems

> *When a man is tired of Hydrocarbons he is tired of Chemistry.*
>
> See ref 203.

In this review we have restricted our attention mostly to hydrocarbons. Why are we not to consider polycyclic conjugated hydrocarbons having heteroatoms? By omitting compounds with heteroatoms and by looking only to hydrocarbons, clearly we left out most of chemistry. First, we want to draw attention to chemists that there is a lot of interesting chemistry and chemical architecture, as well as unusual chemical properties, which involve hydrocarbons alone. In Figure 13 we illustrate several hydrocarbons that already show a great variation in geometry: spiropentane C_5H_8 (1), cubane C_8H_8 (3), bullvalene $C_{10}H_{10}$ (4), adamantane $C_{10}H_{16}$ (5), prizmane (6), diadamantane $C_{18}H_{24}$ (7), trypticene $C_{20}H_{14}$ (9), and others. In Figure 14 we show the skeletal forms of a selection of larger hydrocarbons that show a variety of different properties (listed in Table 8). To the compounds mentioned we should add the class of non-benzenoid hydrocarbons, which also show the considerable structural diversity that is the main topic of the present review. Hence, in defense of the chemistry of hydrocarbons, we started this section by paraphrasing Samuel Johnson's well-known statement,[182] "*When a man is tired of London he is tired of life*", because just as London is central to England, so are hydrocarbons central to chemistry.

The reason for limiting our attention to conjugated hydrocarbons when addressing the question of aromaticity is not our sole fascination with the chemistry of conjugated hydrocarbons or a lack of interest in non-hydrocarbons. The main reason that we have confined the analysis of aromaticity to conjugated hydrocarbon is to see if we can come to a consensus on what are the critical structural factors that define aromaticity. *If we cannot agree on what structural features are basic to the aromaticity of conjugated hydrocarbons, it is unlikely that we will ever agree on what structural elements are important for the aromaticity of non-hydrocarbons.* Therefore, at this stage in clarification of the concept of aromaticity, there is no sufficient justification to consider heteroconjugated systems in which *additional*, electronic factors will also play an important role in aromaticity. First, we have to resolve the problem of aromaticity of conjugated hydrocarbons. Hence, first we have to agree on the structural characterization of aromaticity of conjugated hydrocarbons and then, if such

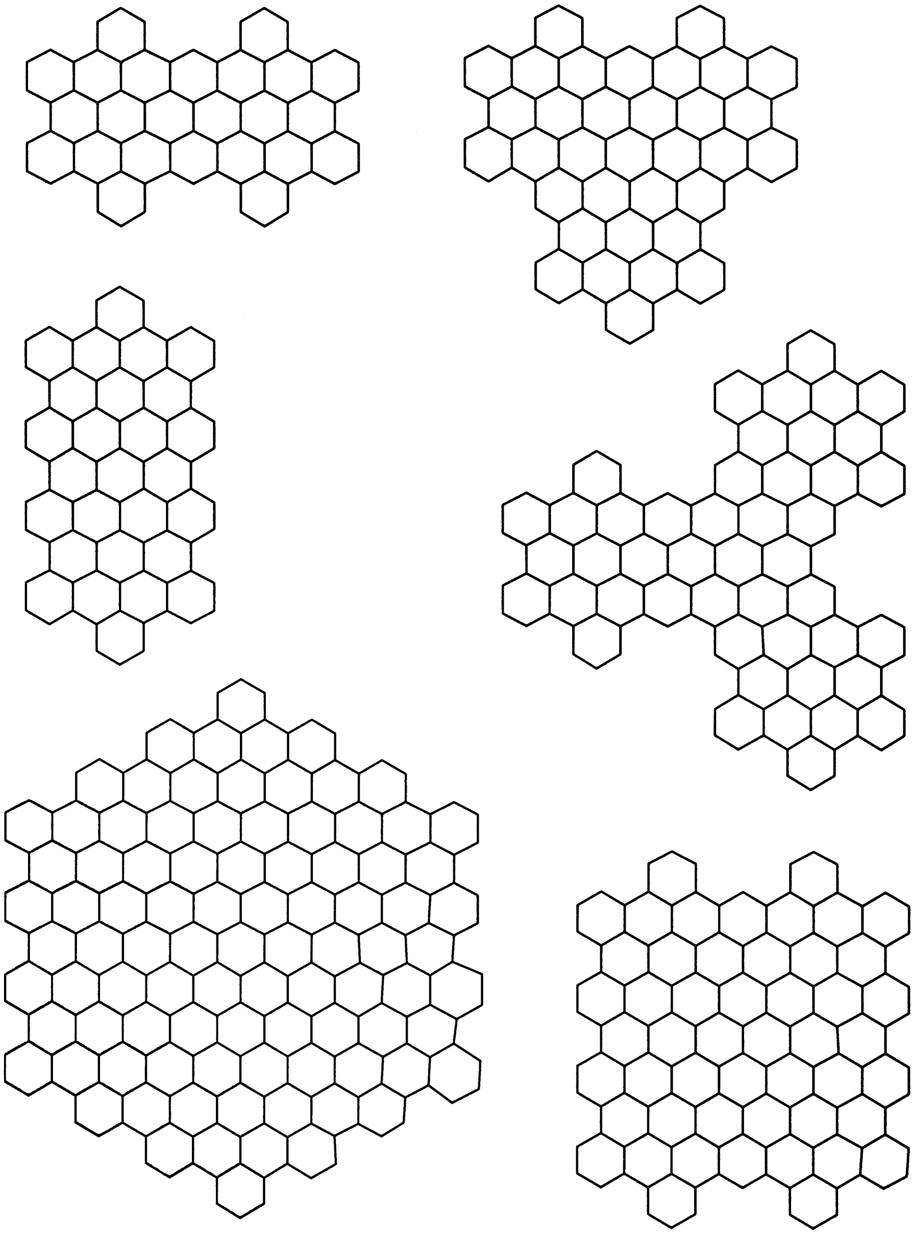


Figure 12. A selection of giant benzenoids described by Müllen and co-workers.[174−177]

characterization is accepted, we can proceed to consider how to extend the results previously restricted to conjugated hydrocarbons to heteroconjugated systems.

IV. Hidden Treasures of Kekulé Valence Structures

> *Science is to see what others have seen and to think what others have not thought.*
>
> Albert Szent-Gyorgi[204]

Kekulé valence structures have been around for over 135 years. They have received considerable attention, particularly in the early developments of the VB method from about 1935 to 1960, and yet conjugated circuits remained a "hidden treasure". It was only with the revival of chemical graph theory in the mid-1960s that topological and combinatorial features of chemical structure received a fresh attention.[205] This revival of chemical graph theory owes the most to Professor A. T. Balaban, who almost single-handedly stirred interest in the forgotten chemical graph theory of Cayley, Sylvester, and other early pioneers.[206] The revival of interest in Hückel MO and Kekulé valence structures eventually led to the discovery of conjugated circuits.

In Figure 15 we show all 14 Kekulé valence structures of benzo[*ghi*]perylene. A close look at the Kekulé valence structures of benzo[*ghi*]perylene shows that, while some are similar (and some are symmetry-related), others are visibly different. In particular, one can notice a difference between the first Kekulé structure, in which five rings out of six, when looked at in isolation, have the Kekulé valence structure of benzene, and the last structure, in which only one ring has the Kekulé valence structure of benzene. The first structure (structure A in Figure 15), which is the Kekulé valence structure with the maximal number of Kekulé benzene rings, is known as the Fries structure.[5,6] In the pre-quantum chem-

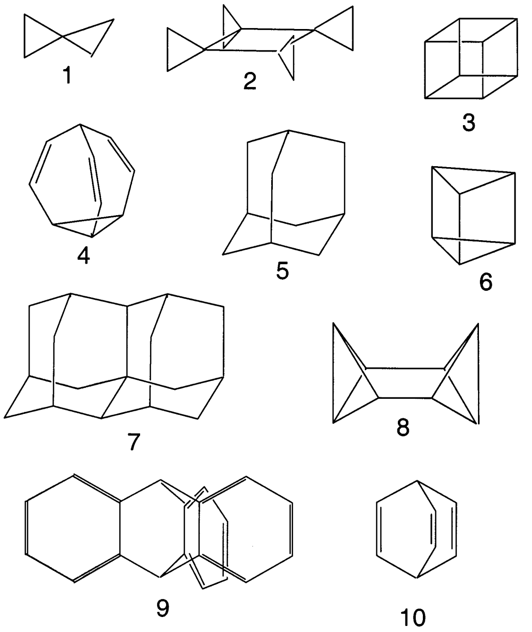


Figure 13. Hydrocarbons showing a great variation in geometry, including spiropentane C_5H_8 (1), cubane C_8H_8 (3), bullvalene $C_{10}H_{10}$ (4), adamantane $C_{10}H_{16}$ (5), prizmane C_6H_6 (6), diadamantane $C_{18}H_{24}$ (7), and trypticene $C_{20}H_{14}$ (9).

istry era, it was viewed by Fries as the most important Kekulé structure of a conjugated polycyclic compound. In analogy, one may refer to the last Kekulé structure of benzo[*ghi*]perylene (structure N in Figure 15), which has the smallest number of Kekulé benzene rings, as the anti-Fries structure.[207] We show in Figure 16, for a selection of benzenoid hydrocarbons, their anti-Fries valence structures.

A. Conjugated Circuits

> *It need be borne in mind that the nature is far too vast to hope to chart its expanse in complete detail. It is therefore important that every task undertaken should be selected because it is likely to tell something about a wide area, rather than merely the immediate neighborhood.*
>
> E. B. Wilson[208]

If different Kekulé structures carry different weights, then the question is how different are the three Kekulé structures of naphthalene? A close look at the three Kekulé valence structures of naphthalene (Figure 17) has led to the “discovery” of conjugated circuits. As one can see, the central Kekulé structure of naphthalene has two rings with Kekulé benzene formulas, while the other two structures (which are symmetry-related) have just one such ring. Rings with two CC double and four CC single bonds lack a regular alternation of CC single and CC double bonds, typical of benzene. However, if we combine the two CC double bonds of such rings with the three CC double bonds of the adjacent ring, we obtain a circuit along the periphery of naphthalene which has a *regular* alternation of CC single and CC double bonds. We refer to circuits with a *regular* alternation of CC single and CC double bonds as *conjugated circuits.* Hence,

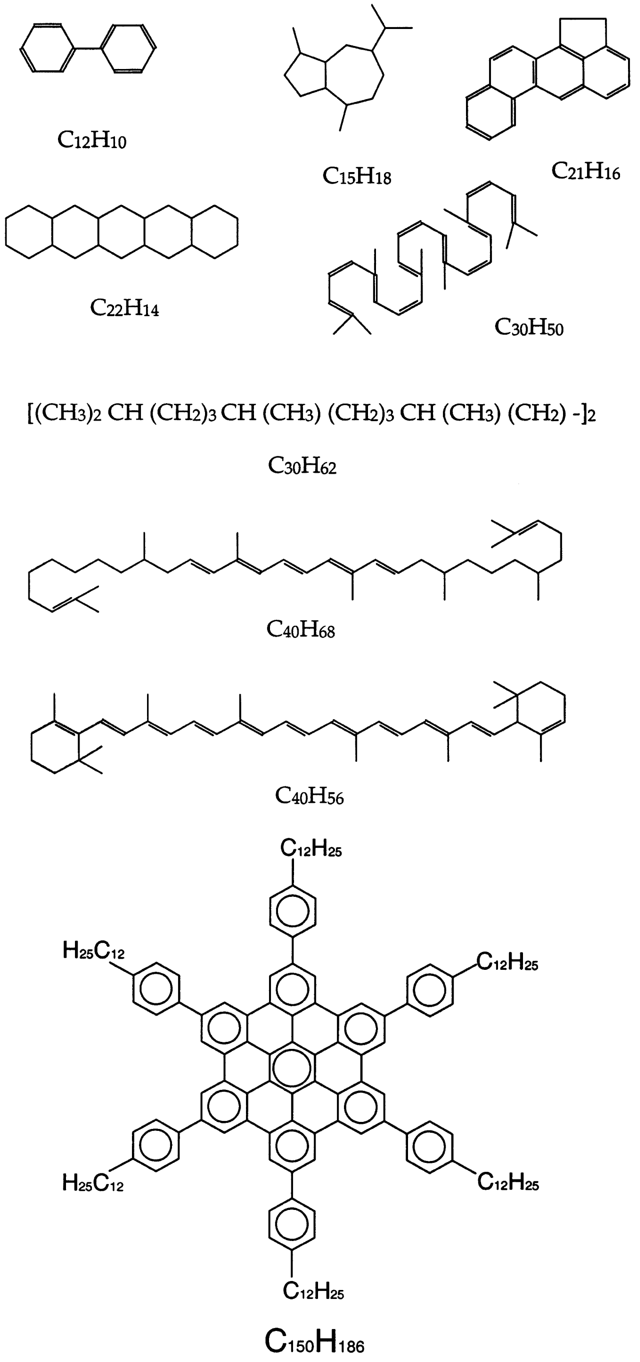


Figure 14. A selection of larger hydrocarbons that show a variety of physico-chemical properties.

Definition: *Conjugated circuits are those circuits within an individual Kekulé valence structure in which there is a regular alternation of CC double and CC single bonds.*

Conjugated circuits are necessarily even, having either $4n + 2$ or $4n$ carbon atoms. As we can see from Figure 17, the central Kekulé structure of naphthalene has two conjugated circuits having three CC double bonds (or involving six carbon atoms), and the other two Kekulé valence structures have one conjugated circuit having three CC double bonds and one conjugated circuit having five CC double bonds (or 10 carbon atoms).

Table 8. Selection of Hydrocarbons Having Interesting Properties

formula	name	property
(*S*)-$C_{10}H_{160}$	(*S*)-limonene	smells of lemons
(*R*)-$C_{10}H_{16}$	(*R*)-limonene	smells of oranges
$C_{12}H_{10}$	acenaphthene	dye intermediate; insecticide; fungicide
$C_{15}H_{18}$	guaiazulene	anti-inflammatory; anti-ulcerative
$C_{15}H_{24}$	(+)-(α)-copaene (sesquiterpene)	male medfly strong attractant
$C_{19}H_{32}$	tridecylbenzene	detergent; forms stable foam in the presence of fat
$C_{19}H_{40}$	pristane	lubricant; anti-corrosion agent
$C_{22}H_{14}$	pentacene	large crystal semiconductor
$C_{21}H_{16}$	3-methylcholanthrene	experimental use in cancer research
$C_{23}H_{46}$	muscalure	sex pheromone
$C_{30}H_{50}$	squalene	oil, agreeable odor; bactericide
$C_{30}H_{62}$	squalane	lubricant; transformer oil; perfume fixative; skin lubricant
$C_{40}H_{51}$	lycopene	carotenoid occurring in ripe fruit
$C_{40}H_{56}$	α-carotene	vitamin A precursor
$C_{40}H_{68}$	phytofluene	polyene hydrocarbon widespread in the vegetable kingdom
$C_{150}H_{186}$	hexabenzocoronene derivative	liquid crystal (component for photovoltaic films)
	polymantanes	new material: hydrocarbons built from fused adamantine units
	acenaphthofluoranthenes	conductive ladder polymer
	cis-polyisoprene $-[CH_2C(CH_3){=}CHCH_2]_n-$	natural rubber
	isoprene—isobutylene copolymer	synthetic rubber
	styrene—butadiene copolymer	
	ethylene—propylene copolymer	

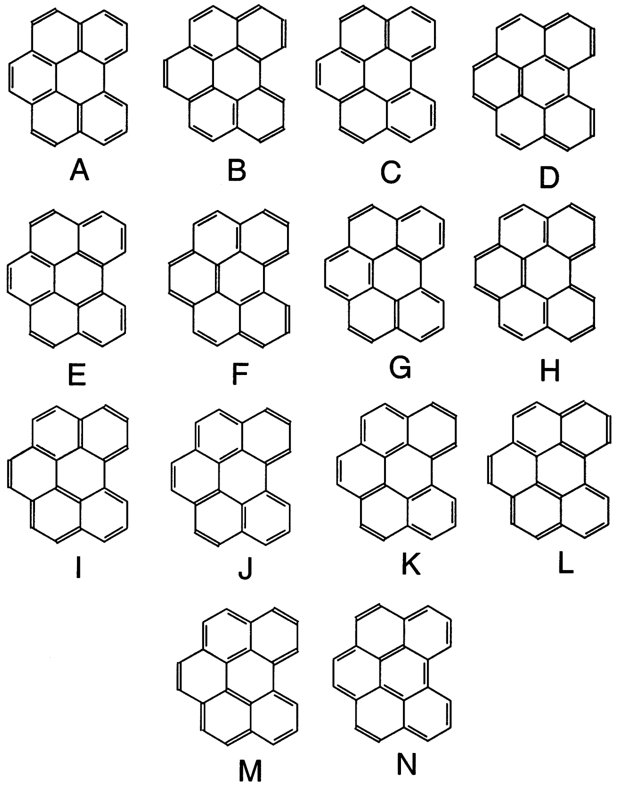


Figure 15. All 14 Kekulé valence structures of benzo[*ghi*]perylene.

In the first column of Figure 18 we show the five Kekulé valence structures of phenanthrene, and in each row we depict all its conjugated circuits, which include also combinations of *disjoint* conjugated circuits. The reason for considering disjoint conjugated circuits follows from an observation that otherwise some Kekulé valence structures would have more conjugated circuits than others. Thus, while the first four Kekulé structures of phenanthrene have three conjugated circuits each, if we do not count the disjoint combinations shown in the last column of the first four rows, the last Kekulé structure would have one conjugated circuit more. One can easily recognize that the fourth conjugated circuit of the last Kekulé structure of phenanthrene can be obtained as a *linear combination* of the other three conjugated circuits. If we use symbols R_1, R_2, and R_3 for the conjugated circuits of 6, 10, and 14 carbon atoms, we can express the last conjugated circuit as a superposition: $R_3 = 2R_2 - R_1$. If we allow this combination to be counted, then to be consistent we have to admit combinations of disjoint conjugated circuits, which are, from the mathematical point of view, similarly given as a linear combination of smaller conjugated circuits. Hence, one can differentiate *linearly independent* conjugated circuits, the number of which is given by the number of fused benzene rings, and *all* conjugated circuits, which include combinations of disjoint conjugated circuits. The number of all conjugated circuits is $K - 1$,[209] where K is the number of Kekulé valence structures for the molecule considered.

In Figure 19 we show all 13 conjugated circuits for one of the Kekulé structures of benzo[*ghi*]perylene. It is interesting to observe a fact that remained unknown until conjugated circuits were recognized as important components of Kekulé valence structures: one can construct the remaining 13 Kekulé valence structures of benzo[*ghi*]perylene, one by one, from this *single* Kekulé structure, and in general one can, after identifying all conjugated circuits, construct all the remaining Kekulé valence structures from any single Kekulé valence structure. To obtain the remaining 13 Kekulé valence structures of benzo[*ghi*]perylene, consider separately each of the 13 conjugated circuits. If within any of these conjugated circuits (or sets of disjoint conjugated circuits) one replaces all CC double bonds by CC single bonds and vice versa but leaves intact the bond type of all the remaining CC bonds which are outside the conjugated circuit (or circuits), one obtains a different, missing Kekulé valence structure.[209] Hence, *a single Kekulé valence structure contains information on all the Kekulé valence structures of a molecule!*

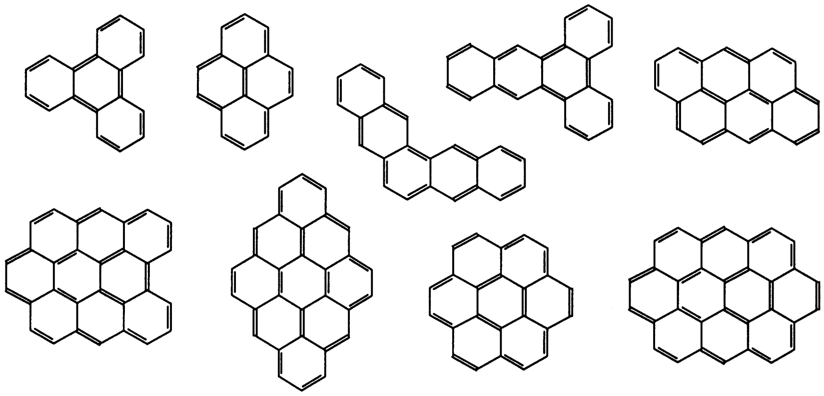


Figure 16. Anti-Fries valence structures for a selection of benzenoid hydrocarbons.

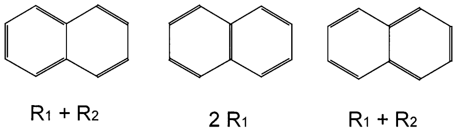


Figure 17. The three Kekulé valence structures of naphthalene and their decomposition in conjugated circuits.

The first paper on conjugated circuits appeared in *Chemical Physics Letters*, written by this author, followed by a paper in *Tetrahedron* in which a larger number of benzenoid conjugated hydrocarbons were considered, and a paper in the *Journal of the American Chemical Society* in which aromaticity was defined in terms of $4n + 2$ conjugated circuits. Gomes apparently made an independent discovery of conjugated circuits in his Ph.D. thesis, as has been pointed out in a paper on a quasi-topological method for the calculation of relative ring-current intensities in polycyclic conjugated hydrocarbons.[210] Gomes, in his thesis, used conjugated circuits and calculated their contributions to NMR chemical shifts, and later revisited the same topic, discussing the additivity of properties of polycyclic hydrocarbons over conjugated circuits.[211] However, in his thesis, Gomes cited the first paper on conjugated circuits already published in *Chemical Physics Let*ters, which of course means that conjugated circuits were not discovered independently by him. In an article on "Graph Theory and Theoretical Chemistry", Balaban added a note: "*The importance of conjugated circuits was recognized, simultaneously with, and independently from, Randić, by Gomes and Mallion*."[212] In another paper Gutman and El-Basil have a note, "*The Theory of conjugated circuits has been independently developed by Gomes*",[213] and then they cite three papers by Gomes from 1979, 1980, and 1981 (underline in quotation added by M.R.).

To the best of my knowledge, Mallion never made any claims about the discovery of conjugated circuits. Also to the best of my knowledge, Gomes used conjugated circuits (for calculation of ring currents) but made no claims about *development* of the model.

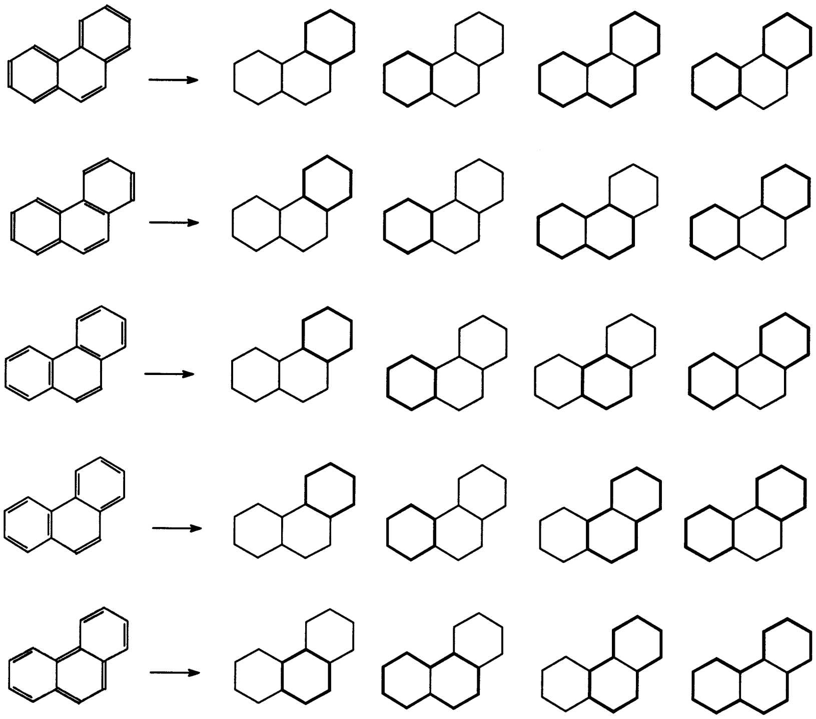


Figure 18. Decomposition of the five Kekulé valence structures of phenanthrene into conjugated circuits (including combinations of *disjoint* conjugated circuits).

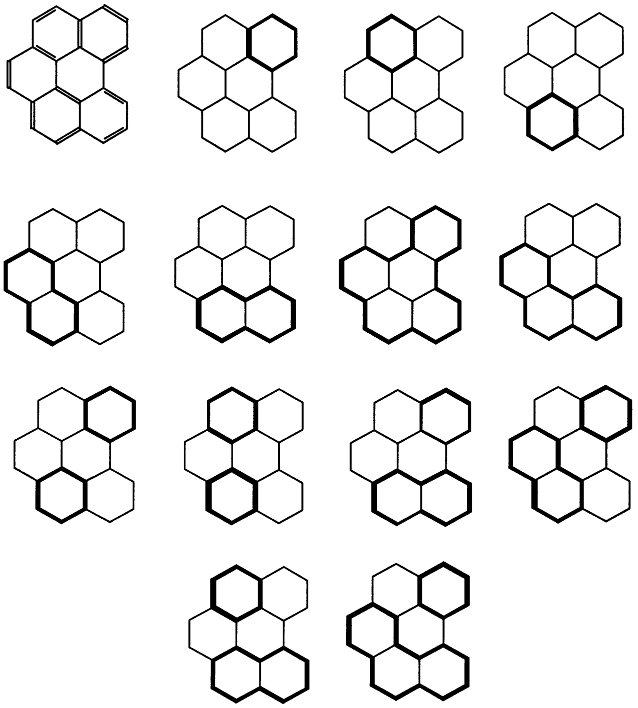


Figure 19. All conjugated circuits for one of the Kekulé structures of benzo[*ghi*]perylene.

This does not negate that he may have come across conjugated circuits independently, as it is also conceivable that, besides Gomes, others may have come close to the idea of conjugated circuits. In this context, it is interesting to mention that Linus Pauling found conjugated circuits bearing semblance to his work on susceptibility of benzenoid hydrocarbons, as he wrote in a private letter of 24 March 1976 to this author:

> *Dear Professor Randic:*
>
> *I was pleased to receive your letter and your papers, which I have examined with interest. I agree with you that it is better to make rather simple calculations, such as yours, than the very complicated ones.*
>
> *Your work on conjugated circuits reminds me of a paper that I wrote on the diamagnetic anisotropy of aromatic molecules, Journal of Chemical Physics 4, 673 (1936). You might want to look at this paper, which was the first theoretical discussion of anisotropy of diamagnetic susceptibility of aromatic molecules.*
>
> *Again let me thank you for writing to me.*
>
> *Sincerely,*
>
> *Linus Pauling*

Gutman and Cyvin have pointed out that the idea of *symmetric difference* known to mathematicians is closely related to conjugated circuits (vide infra).[214] The questions of priority have always been painful and controversial in the sciences, as we have seen from the disputes over the invention of calculus between followers of Newton and Leibniz (see the biographical note on Cayley). Sometimes it is not even so important who first *introduced* a novel idea, but who *developed* the idea to a stage of maturation. For instance, the notion of the aromatic π-sextet is originally attributed to Armitt and Robinson,[215] but it was Clar who developed the model and deserves the credit for the idea of describing local variations in benzenoid hydrocarbons by aromatic π-sextet and migrating π-sextets. Moreover, it appears that Robinson was not very enthusiastic about the "aromatic sextets" described by Clar, although Clar refers to them in his booklet, *The Aromatic Sextet*, as Robinson's aromatic sextet.[216] It also appears that Robinson completely abandoned the notion of aromatic π-sextet. For some comments on the aromatic π-sextet, see the biographical note on Clar at the end of this article.

According to the statement made by Gutman and Cyvin in their book, *Introduction to the Theory of Benzenoid Hydrocarbons*, on p 80 in a section entitled "The Conjugated Circuit Model": "*The Theory outlined in this chapter has to be associated with the name of Milan Randić who discovered it and eventually elaborated it and applied it to numerous classes of conjugated molecules.*"[452]

In mathematics, conjugated circuits appeared as a result of an operation called *symmetric difference* between a pair of 1-factors, that is, a pair of Kekulé valence structures in the case of benzenoid graphs. Symmetric difference is a collection of edges in a graph that is common to two 1-factors. As discussed by Gutman and Cyvin, cycles in symmetric difference are known as *alternating cycles*. In mathematics in general, one considers all sorts of graphs, non-planar graphs included, and the concept of alternating cycles has never emerged as being of particular importance or interest.

B. Innate Degree of Freedom

> *... it is almost always worthwhile to explore a region which is really new. Unexpected results can generally be relied upon under these circumstances.*
>
> E. Bright Wilson[208]

There is an additional "hidden treasure" in Kekulé valence structures worthy of the attention of chemists. Consider again the 14 Kekulé valence structures of benzo[*ghi*]perylene, and let us focus attention on the last Kekulé valence structure shown in Figure 15. Organic chemists immediately recognize this particular Kekulé valence structure as "unimportant" and not very representative of the molecule. What typifies this particular Kekulé structure is not only that many of its rings have only two CC double bonds but that, in this particular case, by selecting a *single* CC bond, the location of *all* other CC double bonds may be determined. It is easy to verify that, if we assign the CC double bond type to the central CC bond of the "bay" region of benzo[*ghi*]perylene, the locations of all the other CC double bonds follow. In the other 13 Kekulé valence structures there is no such unique CC bond that determines the bond type for all the remaining CC bonds, but there may be two or more bonds which, when assigned CC double bond type, allow the bond types for the remaining CC bonds to be determined. This observation has led to the concept of the "innate degree of freedom", or shortly, "degree of freedom" (*df*) of a Kekulé valence structure.[217−221]

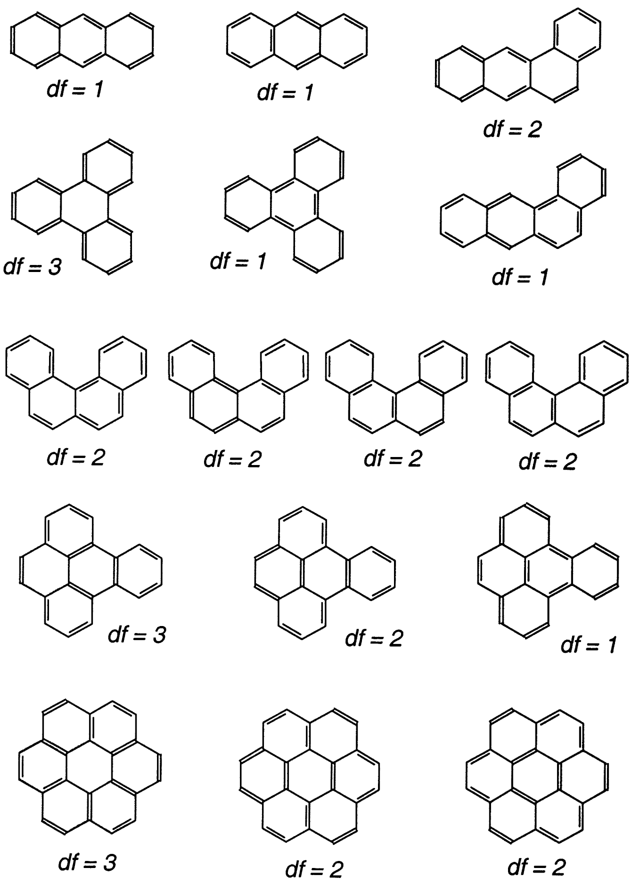


Figure 20. A selection of Kekulé valence structures of several small benzenoid hydrocarbons and the corresponding innate degree of freedom, *df*.

Definition: *The degree of freedom of a Kekulé valence structure is given by the smallest number of CC bonds which, when assigned C=C type, determine the CC bond types for all the remaining CC bonds.*

Hence, in the case of benzo[*ghi*]perylene, the last (the anti-Fries) Kekulé valence structure of has $df = 1$. The reader may try to determine the *df* for the other Kekulé valence structures of benzo[*ghi*]perylene and will immediately see that this may not be an easy task. In the next paragraph, we have listed *df* values for the remaining Kekulé structures of benzo[*ghi*]-perylene to assist those who tried to find them on their own to verify their findings.

In some cases finding the *df* is simple. It is not difficult to see that *all* Kekulé structures of linearly fused benzenoid hydrocarbons — naphthalene, anthracene, tetracene, pentacene, etc. — have $df = 1$. It suffices to assign C=C type to any of the “vertical” CC bonds in such molecules, and the bond types of all other CC bonds will be determined. Of the five Kekulé valence structures in phenanthrene shown in Figure 18, only the last (anti-Fries) structure has $df = 1$. The remaining four Kekulé structures of phenanthrene have $df = 2$, because a selection of C=C bond in one of the terminal benzene rings can in no way influence the selection of C=C bonds in the other terminal ring. In Figure 20 we have illustrated some Kekulé valence structures having different *df* values for a selection of small benzenoid hydrocarbons.

To determine the *df* for a Kekulé valence structure of a benzenoid hydrocarbon in general could be quite tedious and error-prone. For example, in ref 219, where only relatively small benzenoids were considered, an erroneous *df* value for one of the Kekulé structures of pyrenopyrene was reported (for the correct value, see Appendix 3 at the end of this review). Of the 14 Kekulé valence structures of benzo[*ghi*]perylene shown in Figure 15, the first 8 (structures A−H) have $df = 3$, the next five (structures I−M) have $df = 2$, and the last structure (N), as already mentioned, has $df = 1$. To find the *df* requires a rather careful examination of the Kekulé valence structure. The innate degree of freedom *df* is not simply related to the number of different conjugated circuits, although, as will be seen later, there is an intimate relationship between the two concepts. Observe that the first eight Kekulé structures have different numbers of R_1 conjugated circuits, and the same is true for the next five Kekulé structures. Moreover, structures I and J, which have $df = 2$, have three R_1 conjugated circuits, just as the structures E−H, which have $df = 3$. Hence, the *df* cannot be determined from the count of conjugated circuits R_1.

However, if we pay attention only to disjoint conjugated circuits, a close look at the Kekulé valence structures of benzo[*ghi*]perylene shows that structures A−H have *three disjoint* R_1 conjugated circuits, while valence structures I−M have *two disjoint* R_1 conjugated circuits. At the same time, structures A−H have $df = 3$, and structures I−M have $df = 2$. It is tempting, then, to expect that the number of *disjoint* R_1 conjugated circuits in a Kekulé valence structure determines its degree of freedom.[87] This can be immediately understood, because if one selects a distribution of C=C and C−C bonds in one such ring, then by virtue of the fact that the other R_1 rings are *disjoint*, the selection of CC bond type in other rings cannot be influenced. This would agree with the findings of Hansen and Zheng,[222] who have proved for *cata-condensed benzenoids* a theorem which states that the degree of freedom for such structures is given by the number of disjoint Kekulé benzene rings that one can write for the structure.

If one wants to generalize such findings for *peri-condensed benzenoids*, one has to observe that, in peri-condensed systems, disjoint conjugated circuits of *different* size may occur. Hence, the formulation based on “disjoint Kekulé benzene rings” need not apply because the number of disjoint Kekulé benzene ring structures can be lower than the number of disjoint conjugated circuits. This is illustrated on one the Kekulé valence structures of both coronene and benzo[*a*]coronene in Figure 21. In both cases, there is only *one* R_1 conjugated circuit. Hence, there is only *one* “disjoint Kekulé benzene ring”, but the two Kekulé valence structure have $df = 2$. The choice of two CC bonds that determined the positions of all the remaining CC double bonds need not be unique. For example, one can select as CC double bonds the two “vertical” C=C bonds in the leftmost benzene ring, after which the bond type for all remaining CC bonds is determined, but equally one can select C=C in the central ring, an adjacent benzene ring.

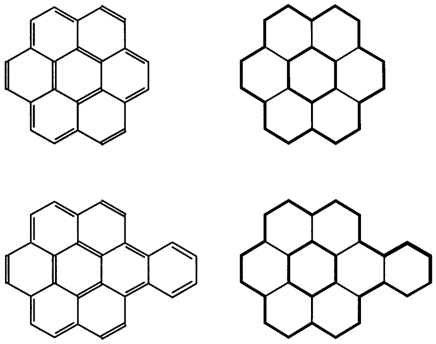


Figure 21. Disjoint conjugated circuits of different size, illustrated on one of the Kekulé valence structures of coronene and benzo[*a*]coronene.

Clearly, the location of CC double bonds in the central ring cannot determine the locations of CC double bonds on the molecular periphery, or in general the location of CC bonds in one conjugated circuit cannot determine the location of C═C bonds in any other disjoint conjugated circuit. It remains to be proved that the number of disjoint conjugated circuits (which need not be of the same size) equals the number of degrees of freedom of a Kekulé valence structure. Before the proof is offered, we have to formulate our expectations as a conjecture:

Conjecture: *The maximal number of disjoint conjugated circuits equals the innate degree of freedom, df, of a Kekulé valence structure.*

Hence, the count of disjoint R_1 circuits does not necessary give the correct answer for *df*. The maximal number of disjoint (independent) conjugated circuits, which could be of different sizes, determines the innate degree of freedom of the Kekulé valence structure of a benzenoid hydrocarbon.[87] We will see later that the innate degree of freedom, or more correctly the maximal number of disjoint conjugated circuits, was the "missing link" that leads to mathematical characterization of Clar's valence structures and contributes to solving the "inverse problem" for Clar structures.

C. Clar Structures

We can view Clar structures formally also as a "hidden treasure" of Kekulé valence structures, because each Clar structure can be viewed as a superposition of a subset of Kekulé valence structures. For a given Clar structure, it is not difficult to derive the subset of Kekulé valence structures that, upon superposition, make the Clar structure. This is illustrated in Figure 22 for the first Clar structure of chrysene shown in Figure 1, which has two π-aromatic sextets. Each π-sextet can be decomposed into two Kekulé valence structures of the benzene ring. Thus, a Clar structure having two sextets is built from four Kekulé valence structures, and in general a Clar structure having k π-sextets is built from 2^k Kekulé valence structures. The opposite process, that of finding in advance which k Kekulé valence structures among all K structures of a benzenoid hydrocarbon participate in superposition to yield a Clar structure, represents the "inverse problem". The inverse problem, as is typical for inverse problems in general, is more difficult to solve. In the case of benzo[*ghi*]perylene, the inverse problem consists of finding structural criteria, or a criterion, which will enable one to select 8 out of the 14 Kekulé valence structures shown in Figure 15 as those needed for construction of the Clar structure of benzo[*ghi*]perylene.

The importance of the inverse problem of the Clar structures lies not only in the possibility of fully mathematically characterizing Clar structures, which are essentially introduced through geometrical considerations; even more significantly, solving this problem may allow us, for the first time, to extend the notion of Clar structures to non-benzenoid com-

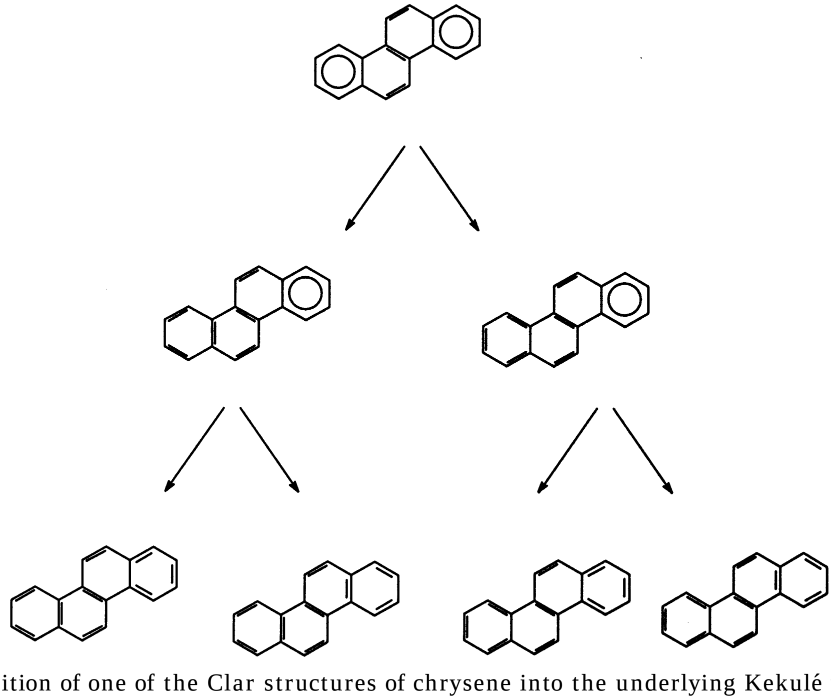


Figure 22. Decomposition of one of the Clar structures of chrysene into the underlying Kekulé valence structures.

pounds beyond biphenylene for which already Clar depicted structures with π-aromatic sextets, including fullerenes!

V. Graph Theoretical Approach to Chemical Structure

> *It may not be wholly without interest to some of the readers ... to be made acquainted with an analogy that has recently forcibly impressed me between branches of human knowledge apparently so dissimilar as modern chemistry and modern algebra ... I hardly ever take up exceedingly valuable ... Notes for Chemical Students, which are drawn up exclusively on the basis of Kekulé's exquisite conception of valence, without deriving suggestions for new research in the theory of algebraic forms.*
>
> James J. Sylvester (1814−1897)[223]

As noted in the biographical notes at the end of this review, J. J. Sylvester was a mathematician who was particularly interested in the connection between algebra and chemistry. This adds some weight and significance to the above quotation and his fascination with Kekulé valence structures. His work was published in mathematical journals, and he was addressing as "readers" mathematicians, of course. Graph theory is a branch of discrete mathematics which considers discrete objects and studies combined topological and combinatorial properties of such objects. (For introductory books, see refs 224 and 225; for textbooks, see refs 102, 226, and 227; for an advanced monograph, see ref 228; for graph theoretical terminology, see ref 229; for historical development, see ref 230). Although the origin of graph theory has been traced to Euler[231] and the year 1736, the first mathematical book on graph theory appeared 200 years later, just before the World War II, in 1936. It was written in German by D. König,[232] a professor at the University of Budapest (Hungary). Graph theory should not be viewed as a branch of topology (which is concerned with the properties of neighborhoods and has no metrics) or as a branch of combinatorics (which is concerned with the properties of permutations and combinations). Graph theory is a part of discrete mathematics, known before 1920 by the clumsy label of "topological and combinatorial mathematics", which is concerned with the topological and combinatorial properties of discrete objects. As already said, the main novelty of graph theory, in distinction to topology and combinatorics, is that for graphs one can define a *metric*, of which we take advantage in applications to chemistry.

A. Metric

A graph is mathematically defined as a set of elements (called vertices) and a set of binary relations (called edges) which supports metrics; hence, the concept of distance holds. The following are the axioms that define the distance:

$D(x,y) > 0$

Distance is positive ($D(x,y) = 0$ only if $x = y$).

$D(x,y) = D(y,x)$

Distance does not depend on direction.

$D(x,y) + D(y,z) \geq D(x,z)$

Triangular inequality: direct connection is the shortest distance.

Most often, the number of edges between the vertices defines the distance between two vertices in a graph. However, whenever the axioms on metric are satisfied, one can speak of distance. Hence, there are alternative distance measures that have been considered for graphs. For example, if one considers the edges of a polycyclic graph to be unit resistors, then because the Kirchhoff laws satisfy the axioms on distance, one can speak of the "resistance distance".[233] For additional illustrations of the use of metrics on graphs, see works by Klein and collaborators,[234−241] Skorobogatov and Dobrynin,[242] and others.[243−246]

B. Chemical Graphs

The most common graphs in chemical graph theory are molecular graphs with atoms as vertices and edges as bonds. However, there are other types of graphs, including other types of molecular graphs, that are of interest in chemistry, and these are listed in Table 9. If as vertices we consider bonds and as edges we consider incidence of bonds, we obtain the so-called *line graphs*. E. Estrada and co-workers[247−251] found that the connectivity indices of line graphs might offer better correlation between molecules and some of their physico-chemical properties than would regressions based on similar descriptors derived directly from molecular graphs in which atoms are vertices and bonds are edges. Related to line graphs are factor graphs, in which CC double bonds in the Kekulé valence structure are assumed as vertices and adjacent CC bonds are those separated by CC single bonds.[252−258] Vertices in chemical graphs can represent molecules, isomers, or Kekulé structures, while edges may represent paths of chemical reactions, degenerate rearrangements, or the "resonance" between Kekulé valence structures, respectively. Clearly, neither are graphs just simplified molecular diagrams nor is "chemical graph theory" just a synonym for HMO theory!

C. Isospectral Graphs

Apparently, much of the early misunderstanding about and hostility toward chemical graph theory was caused by erroneous identification of chemical graph theory with the Hückel molecular orbital method. Although part of graph theory, the so-called spectral theory,[259−261] has substantial overlap with HMO theory if one restricts attention to eigenvalues of the adjacency matrix, even in this area there were many novel results of chemical graph theory which were unknown in HMO theory. For example, Balaban and Harary pointed out that the characteristic polynomial does not uniquely determine the connectivity of a molecule;[262] that is, there are molecular graphs

Table 9. Graphs of Interest in Chemistry: The First Column Shows What the Vertices Represent, and the Second Column Shows the Relationship

vertices	edges	author(s)	comment
Intramolecular Graphs			
atoms	bonds	Cayley Silvester	
edges	incidence		line graphs
C=C bonds	adjacency	Joella El-Basil	factor graphs
carbons and hydrogens	CC adjacency and HH gauche sites	Randić	
polygonal faces	adjacency		duals
Intermolecular Graphs			
molecule	degenerate isomerization	Balaban	vertex and edge transitive graphs
Kekulé structures	interactions	Herndon	
Kekulé structure	resonance	Gründler Randić	median graphs
benzene rings	resonance	Gutman	
isomers	path length adjacency	Randić	
Embedded Graphs			
atoms	bonds		part of diamond lattice
carbon atoms	CC bonds		part of graphite lattice
benzene rings	fusion	Smith Balaban	
benzene rings center	common CC bond	Balaban	dualist graph
DNA bases	sequence adjacency	Nandy	
proteins in a gel	abundance adjacency	Randić	zigzag curve
proteins in a gel	mass and charge dominance	Randić	partial ordering
structures/molecules	clustering		hierarchical clustering graphs
Special Graphs			
caterpillar trees			branches of length one
Fibonacci graphs			families of benzenoids
Sachs graphs		Sachs	disjoint edges and cyclic subgraphs
rooted trees			single vertex emphasized
Book-Keeping			
graph	symmetry operations	Cayley	
configurations	interaction	Paldus Matsen Shavitt	

that will have all eigenvalues equal. This was first found by Sinogowitz and was published by Collatz in 1957[263] (as Collatz reported, this discovery remained unpublished but was found earlier by Sinogowitz, who perished during World War II). Fisher and others[264−266] reported on several graphs that have all eigenvalues equal, but this interesting mathematical aspect that has bearing on the HMO theory was totally unknown to chemists while HMO was the theory of the day. It was only in 1973 that Živković[267] found, by browsing through the *Dictionary of π-Electron Calculations*, by Coulson and Streitwieser,[268] that 1,4-divinylbenzene and 2-phenylbutadiene (separated by only few pages in the book!) have *all* 10 eigenvalues identical. The corresponding molecular graphs (with hydrogen atoms suppressed, as is customary in presenting graphs in organic chemistry) are illustrated in Figure 23. Numerous additional isospectral graphs have since been constructed.[262−286]

Isospectral graphs are important in connection with the “inverse problem” that emerges in various branches of science. Kac,[287] in an article, “Can You Hear the Shape of a Drum?”, was among the first to show that, in classical physics, simply knowing the vibrational spectra associated with an instrument does not allow one to reconstruct the shape of the source instrument, that is, the precise shape of the vibrating drum. In other words, drums of different shapes may produce the same sound. The occurrence of isospectral graphs has shown that the inverse problem for graphs cannot be solved knowing just the spectra, or in the case of π-electron systems knowing just the HMO energy levels. At least this is the case for a simplified Hamiltonian such as is used in the HMO method. Fisher,[288] in an article, “On Hearing the Shape of a Drum”, extended the considerations of Kac to discrete “drums” (i.e., polycyclic graphs).

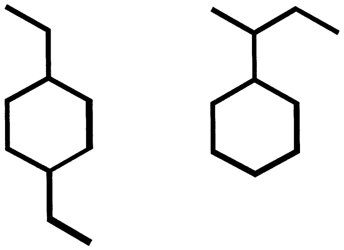


Figure 23. Isospectral pair 1,4-divinylbenzene and 2-phenylbutadiene, which have *all* their HMO eigenvalues identical.[267]

That different graphs can have identical spectra (i.e., eigenvalues) has been known for some time in mathematical literature[263,266] and in physics.[264,265] Moreover, it was shown that such graphs are not as rare as initially thought. Schwenk[289] has shown for trees (acyclic graphs) that as the size of the graphs increases, the number of isospectral graphs increases, and in the limit of infinitely large graphs, almost all graphs have isospectral partners. In Figure 24 are

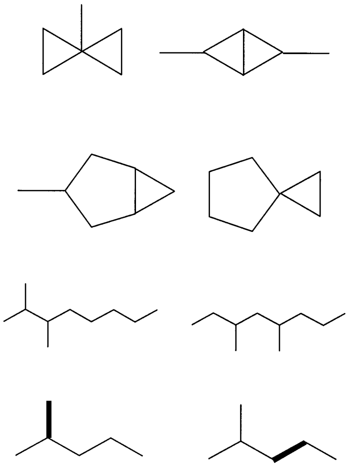


Figure 24. Additional isospectral graphs, including the smallest isospectral multi-trees.[269−286]

shown a few additional isospectral graphs to illustrate that this may occur even for small systems. The last pair of graphs in Figure 24 represents the smallest isospectral multi-trees, i.e., acyclic graphs with one edge having a different weight (simulating, for instance, a CC double bond). Unfortunately, these results were found at the time when the HMO method was, for the most part, already only of historical and mostly educational interest, and no longer a viable research tool. Nevertheless, one should give due credit to this part of chemical graph theory for leading to the discovery of a number of interesting aspects of the HMO model that were overlooked at the time when the HMO approach was widely used.

There is yet another caveat concerning isospectral graphs that is worth mentioning. Some "noise" has been made by Heilbronner and Jones[290] to demonstrate that, while isospectral graphs may be of some mathematical interest, they are not relevant for chemistry. In other words, the HMO model is no longer a viable model for chemistry. They displayed the ionization potentials of the isospectral pair 1,4-divinylbenzene and 2-phenylbutadiene that show no similarity with each other. If the concept of isospectrality were relevant, and HMO theory correct, then such molecules should show identical spectra. However, if the objective of Heilbronner and Jones was to show that the HMO model is not a useful model to discuss molecular spectra and ionization potential, it would suffice to show HMO computations just for a *single* molecule, almost *any* single molecule! As Hermann[291] described, when it comes to characterization of molecules, the isospectrality is an artifact of the neglect of hydrogen atoms. More realistic descriptions of chemical structure have led, in all cases considered, to different spectra for different molecules. Hermann concludes that, "*Hence using an appropriate translation of the chemical structure into topological matrix, the isospectral artifacts are of no relevance any longer and the topological matrices and their invariants can be meaningful tools for investigating chemical structures in physicochemistry.*"[291]

It is interesting to point out, as first observed by Balasubramanian[292] for fullerenes having 90 carbon atoms or less, and later reported by Balaban et al.[293] for all 1812 fullerene isomers of C_{60}, that none of them are isospectral. Hence, while isospectral graphs are common among acyclic structures,[289] apparently they are not so common among highly cyclic cages representing possible carbon skeletons of fullerenes.

D. Embedded Graphs

In chemical applications of graph theory, besides "ordinary" graphs that have no fixed geometry, one may also consider graphs that are rigidly *embedded* in either 2-D space or 3-D space. As a consequence, rigidly embedded graphs have fixed geometry. For a list of topics in which embedded graphs have played an important role in chemistry, see Table 10. Balaban and Harary[294] in 1968 considered enumeration of cata-condensed benzenoid hydrocarbons and introduced the so-called "dualist" graphs, which are constructed by considering as the vertices the centers of individual benzene ring and as the edges the lines connecting vertices that belong to rings having a common CC bond. The fixed geometry of dualist graphs is determined by the geometry of the underlying benzenoid hydrocarbons. The term "dualist" was used to make a distinction with the concept of a *dual* of a graph, or a *dual* of a polyhedron, terminology already known and used in mathematics, which is obtained by representing each face of a planar graph or polyhedron by a vertex and connecting vertices belonging to a face with a common edge.[102] Dualist graphs represent one of the simplest embedded graphs having fixed bond lengths of equal length and fixed angles. As early as 1961, Smith had constructed such graphs but merely used them as a simplified notation for polycyclic benzenoid hydrocarbons.[295] In Figure 25 we show all dualist trees (with fixed angles of 120° and 180°) for cata-condensed benzenoids with five fused benzene rings. For additional illustrations on the use of dualist graphs, see refs 296−299. The dualist graphs in which vertices have two "colors" have been used for construction of graph polynomials that count either conjugated circuits or the aromatic π-sextets of Clar.[300]

In other applications, embedded graphs have been found useful for numerical characterization of folded proteins,[301,302] for characterization of DNA sequences,[303−312] and for characterization of proteomics maps.[313−321] On the other hand, the diagrams that pictorially represent partial ordering (vide infra), which arise when one compares objects that are characterized by two or more variables, can also be embedded. Such an embedding of partial ordering over the proteomics map offers an alternative numerical characterization of cell proteomes.[319,320] In a similar way, by constructing partial ordering of isomers, one arrives at the "Periodic Table of Isomers".[322−326] In such a table, isomers are ordered with respect to the number of paths of length two and paths of length three (isomers necessarily have the same paths of length one, that is, the number of bonds).

Other structural invariants, besides paths, can be used for construction of embedded graphs, which may allow one to recognize regularities in physico-chemical data among isomers. Thus, for example, Diudea and co-workers[327] used the higher order walks, rather

Table 10. Embedded Graphs (in 2-D or 3-D Space) Arising in Applications of Graph Theory to Chemistry and Biochemistry

topic	author(s)	year	ref
simplified representation of benzenoids	Smith	1961	*a*
enumeration of conformers	Balaban and Harary	1968	*b*
partial ordering of isomer	Randić and Wilkins	1979	*c*
reduced graphs	Jerman-Blažič and Trinajstić	1982	*d*
2-D graphical representation of DNA	Hamory	1989	*e*
	Nandy	1994	*f*
	Leong and Mogenthaler	1995	*g*
chain conformations on graphite lattice	Randić, DeAlba, and Kleiner	1995	*h*
protein modeling	Li, Helling, Tang, and Wingreen	1996	*i*
folded proteins	Randić and Krilov	1996	*j*
line-adjacency graphs	Randić, Vračko, Novič, and Basak	2000	*k*
3-D graphical representation of DNA	Randić, Vračko, Nandy, and Basak	2000	*l*
2-D non-overlapping graphical DNA	Guo, Randić, and Basak	2001	*m*
3-D proteomics	Randić, Zupan, and Novič	2001	*n*
2-D graphical	Randić, Vračko, Lerš, and Plavšić	2003	*o*
partial ordering of protein gel spots	Randić	2002	*p*
4-D representation of DNA	Randić and Balaban	2003	*q*
DNA cluster graph	Bajzer, Randić, Plavšić, and Basak	2003	*r*
2-D compact representation of DNA	Randić, Vračko, Zupan, and Novič	2003	*s*

[a] Smith, F. T. *J. Chem. Phys.* **1961**, *34*, 793. [b] Balaban, A. T.; Harary, F. *Tetrahedron* **1968**, *24*, 2505. [c] Randić, M.; Wilkins, C. L. *Chem. Phys. Lett.* **1979**, *63*, 332. [d] Džonova-Jerman-Blažič, B.; Trinajstić, N. *Comput. Chem.* **1982**, *6*, 121. [e] Hamory, E. *BioTechniques* **1989**, *7*, 710. [f] Nandy, A. *Curr. Sci.* **1994**, *66*, 309. [g] Leong, P. M.; Mogenthaler, S. *CABIOS (Comput. Appl. Biosci.)* **1995**, *12*, 503. [h] Randić, M.; DeAlba, L. M.; Kleiner, A. F. *J. Chem. Inf. Comput. Sci.* **1995**, *12*, 503. [i] Li, H.; Helling, R.; Tang, C.; Wingreen, N. *Science* **1996**, *273*, 666. [j] Randić, M.; Krilov, G. *Chem. Phys. Lett.* **1996**, *272*, 115. [k] Randić, M.; Vračko, M.; Novič, M.; Basak, S. C. *MATCH* **2000**, *42*, 181. [l] Randić, M.; Vračko, M.; Nandy, A.; Basak, S. C. *J. Chem. Inf. Comput. Sci.* **2000**, *40*, 1235. [m] Guo, X.; Randić, M.; Basak, S. C. *Chem. Phys. Lett.* **2001**, *350*, 106. [n] Randić, M. Zupan, J.; Novič, M. *J. Chem. Inf. Comput. Sci.* **2001**, *41*, 1339. [o] Randić, M.; Vračko, M.; Lerš, N.; Plavšić, D. *Chem. Phys. Lett.* **2003**, *368*, 1. [p] Randic, M. *Int. J. Quantum Chem.* **2002**, *90*, 848. [q] Randić, M.; Balaban, A. T. *J. Chem. Inf. Comput. Sci.* (in press). [r] Bajzer, Ž.; Randić, M.; Plavšić, D.; Basak, S. C. *J. Mol. Graphics Modell.* (in press). [s] Randić, M.; Vračko, M.; Zupan, J.; Novič, M. *Chem. Phys. Lett.* (in press).

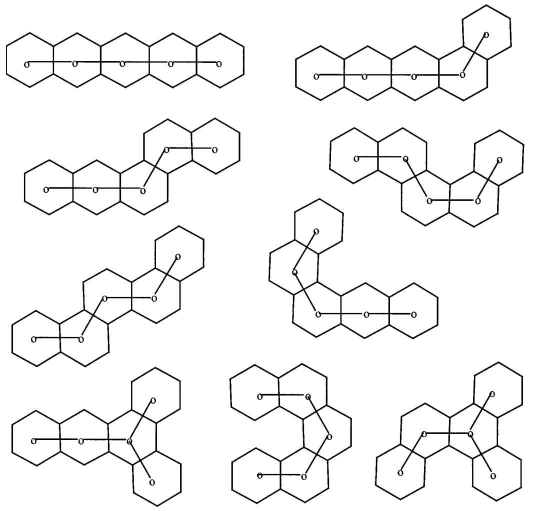


Figure 25. Dualist trees (with fixed angles of 120° and 180°) representing non-branched cata-condensed benzenoids having five fused benzene rings.

than paths, and obtained a regular pattern showing variations in the boiling points for octanes. Dias constructed the "Table of Conjugated Hydrocarbons" based on variations of critical structural elements for fused benzenoid hydrocarbons.[328−336] Finally, embedded "resonance" graphs, in which vertices correspond to various Kekulé valence structures of a benzenoid hydrocarbon and edges connect those valence structures which differ in sites of three CC double bonds within a single benzene ring only, offer an alternative graphical representation of benzenoids.[337−339]

E. Partial Ordering

We ought to say more about partial ordering as theoretical tool, because partial ordering apparently is not so well known among chemists. As already mentioned, when objects to be compared are characterized by two (or more) properties, as a rule they cannot be simply ordered. Consider a set of objects X_k characterized by two properties, a_k and b_k. Two objects X_i and X_j can be ordered only if $a_i > a_j$ and $b_i > b_j$, in which case we say that X_i dominates X_j, or X_j is dominated by X_i. For example, in proteomics, map proteins from cells of the same kind or a tissue are separated by the charge and by the mass (electrophoretically and chromatographically, respectively). While there are many proteins that have greater charge and greater mass than others, there are even more cases in which a protein having a greater charge has a smaller mass than another protein, and vice versa. Partial ordering[340−345] seeks all possible sequences of subsets of objects for which simple ordering holds, that is, all subsets for which $a_i > a_j$ and $b_i > b_j$. The mathematical foundation for partial ordering can be traced to the Scottish mathematician Muirhead, who 100 years ago was interested in comparing arithmetic and geometric sequences.[346−348] His work was later generalized by Karamata.[349] The result of an analysis of partial ordering can be presented pictorially as a hierarchical diagram (or directed graph) in which only the relative positioning of objects that preserve hierarchy is relevant.

Partial ordering, particularly the order relation between sets of non-negative numbers with a constant sum, has found significant applications in mathematics, physics, and chemistry.[350−355] It has also been used in quantitative structure−activity relationship (QSAR) studies for identification of pharmacophores.[356−359] The reason for mentioning partial ordering in an article on aromaticity is that a view was expressed that the concept of aromaticity belongs to those to which partial ordering can be applied.[360] The same may be true of some of the ambiguous concepts of Table 3, like molecular branching. In fact, Ruch and Gutman[361] specifically mentioned molecular branching as one such concept, although at least half a dozen various topological and structural indices were proposed to characterize molecular branching.[325,362−368]

In order to illustrate the point and, in the end, to bring a link to characterization of aromaticity, consider the following question: Which is more branched: 2,2-dimethylhexane or 2,5-dimethylhexane? The first has one branching center with four branches, and the second has two branching centers but each having three branches. The view of those who consider branching as a concept belonging to partial ordering would argue that such questions have no meaning, that is, that the two structures are not *comparable*. This view may have obtained some support because of disagreements between the relative magnitudes of different indices of branching assigned to the same structure. However, it is possible, just like with aromaticity, that branching can be mathematically rigorously defined and numerically well characterized, but that we have not yet come upon such well defined characterization of molecular branching! Indeed, the most recent work[369] on molecular branching seems to support this view (see also ref 317 for an application). It appears possible to justify a particular numerical characterization of molecular branching in terms of the departure of a structure from the extreme structures, that of the linear structure and that of the "star" structure (i.e., a structure without any branches and a structure with a single center having the maximal number of branches, respectively).

It is our view that the same is true for the concept of aromaticity, viewed as partial ordering or a vectorial quantity, having many (equally valued) components. Such views, while legitimate, in our opinion only indicate that we have not yet found the *critical structural characteristics* that define aromaticity. As long as this is the case, the multivalued aspects (and associated confusion about aromaticity) will continue. But, as we will see in this article, aromaticity can be rigorously defined, at least in the case of conjugated hydrocarbons, by using the important but mostly overlooked structural concept of conjugated circuits. This will be elaborated later in the article.

VI. On Enumeration of Benzenoid Hydrocarbons

The first contributions to chemical graph theory were concerned with enumeration of isomers. That enumeration of isomers, and in general chemical structures of a particular form, is difficult can be appreciated indirectly from the fact that Cayley reported 357 and 799 as the numbers of C_{12} and C_{13} isomers, respectively,[370] but the correct numbers are 355 and 802, respectively. Henze and Blair[371] in 1931 made a significant contribution to isomer enumeration by developing recursion formulas for enumeration of acyclic structures. An important step in the development of graph theoretical enumerations, often overlooked, is the work of Wheland,[129] who attempted to enumerate "excited" valence bond structures for benzenoid hydrocarbons as early as 1935. Wheland was the first to introduce a counting polynomial for book-keeping of the count of valence structures of different degrees of excitation. Finally, in 1937, Polya[372] outlined the most powerful tool, the cycle index, for enumeration of isomers. The cycle index takes into consideration the symmetry of objects to be enumerated by using properties of the permutation groups.

The problem of enumeration of structures (isomers included) is closely tied with the problem of ordering of structures,[373] the problem of orderly construction of graphs (structures) of prescribed form,[374−376] the problem of graph isomorphism[377−379] (in order to recognize and eliminate duplicates in construction of graphs), and of course, the problem of graph automorphism (symmetry).[283,380−385] Enumeration of graphs and structures is quite a wide field in applied mathematics, on which several reviews,[386−391] including books,[392,393] have been written. Here we will only briefly comment on enumeration and construction of benzenoid hydrocarbons, which is a subset of graphs that can be superimposed on a graphite lattice. The fact that molecular graphs of benzenoids can be viewed as rigid structures superimposed on a graphite lattice allows the use of *unique* boundary codes[394] for the construction of such graphs. Thus, it is possible to construct, from the boundary code, the adjacency matrix of a benzenoid.[395] In this way, construction of benzenoid graphs is transformed into construction of acceptable peripheral codes, which by being unique allow reconstruction of the benzenoid hydrocarbon. Enumeration and construction of peri-condensed benzenoid has been known to be more difficult.[392,396,397]

In order to illustrate the growth of benzenoids with the increase of the number of fused benzene rings (n), we list below the number of cata-condensed benzenoids (N) up to n = 11 benzene rings, as reported by Balaban et al.:[398]

n	1	2	3	4	5	6	7	8	9	10	11
N	1	1	2	5	12	36	118	411	1489	5572	21,115

This count includes benzenoid hydrocarbons that would be unstable by having eight or more linearly fused benzene rings. For comparison, the total number of peri-condensed benzenoids with n = 11 benzene rings is about twice the number of cata-condensed benzenoids (N = 41 764), to which one should add 78 350 non-Kekuléan structures (systems for which one cannot write Kekulé valence structures), giving a total of just over 120 000 possible structures for analysis.

Since the first enumeration of benzenoid hydrocarbons by computer by Balasubramanian, Kaufman, Koski, and Balaban,[397] several methods for computer-oriented coding and enumeration of benzenoids have been reported.[399−406] With improvements of the computer programs, enumeration of benzenoid hydrocarbons has been extended to ever larger and larger systems. For example, Müller and collaborators

Table 11. Formula Periodic Table of Dias,[328] Illustrated for the Case of Benzenoid Hydrocarbons

					$C_{14}H_{10}$	$C_{18}H_{12}$	$C_{22}H_{14}$
					$C_{20}H_{12}$	$C_{24}H_{14}$	$C_{28}H_{16}$
					$C_{26}H_{14}$	$C_{30}H_{16}$	$C_{34}H_{18}$
				$C_{24}H_{12}$	$C_{32}H_{16}$	$C_{36}H_{18}$	$C_{40}H_{20}$
				$C_{30}H_{14}$	$C_{38}H_{18}$	$C_{42}H_{20}$	$C_{46}H_{22}$
			$C_{32}H_{14}$	$C_{36}H_{16}$	$C_{44}H_{20}$	$C_{48}H_{22}$	$C_{52}H_{24}$
			$C_{38}H_{16}$	$C_{42}H_{18}$	$C_{50}H_{22}$	$C_{54}H_{24}$	$C_{58}H_{26}$
		$C_{40}H_{16}$	$C_{44}H_{18}$	$C_{48}H_{20}$	$C_{56}H_{24}$	$C_{60}H_{26}$	$C_{64}H_{28}$
	$C_{42}H_{16}$	$C_{46}H_{18}$	$C_{50}H_{20}$	$C_{54}H_{22}$	$C_{62}H_{26}$	$C_{66}H_{28}$	. . .
	$C_{48}H_{18}$	$C_{52}H_{20}$	$C_{56}H_{22}$	$C_{60}H_{24}$	$C_{68}H_{28}$	. . .	. . .
$C_{50}H_{18}$	$C_{54}H_{20}$	$C_{58}H_{22}$	. . .	. . .	. . .	. . .	. . .
$C_{56}H_{20}$	$C_{60}H_{22}$	$C_{58}H_{22}$	. . .	. . .	. . .	. . .	. . .
$C_{62}H_{22}$	. . .	. . .	. . .	. . .	. . .	. . .	. . .
. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .

extended their initial count of benzenoids having $n = 11$ "hexagons" to those having $n = 14$ hexagons (approximately 1.5×10^7), and then to $n = 16$ hexagons (approximately 3.6×10^9). This, as quoted in ref 407, consumed about three months of uninterrupted central processing unit (CPU) time made available at the Computer Center of the University of Düsseldorf. These computer enumerations, however, do not discriminate fused systems having the Kekulé structures from those for which no Kekulé valence structure can be written. Thus, if these numbers are to be of interest in chemistry, they ought to be further filtered, and that is the reason that we prefer to refer to such results as enumeration of "fused hexagonal systems", rather than condensed benzenoids. By 1998, Caprossi and Hansen[407] reported the number of "fused hexagonal systems" with 21 fused rings (approximately 1.0×10^{12}), and two years later Brinkmann, Caprossi, and Hansen[408] reported the number of "fused hexagonal systems" with 24 fused rings (approximately 1.2×10^{14}). Most recently, Guttmann and co-workers[409] presented a new algorithm that allows a radical increase in the computer enumeration of "benzenoid hydrocarbons". They reported the number of "benzenoids" built from up to 35 fused benzene rings (approximately 5.8×10^{21}). This "race" in enumeration of "fused hexagonal systems" may continue, with mathematicians apparently winning over chemists. However, although it is clear that such computations, which are rather intricate, can be made, as the number of fused rings increases, they appear to be becoming less and less relevant for chemistry. The topic of enumeration of benzenoid hydrocarbons has been extended to include coronoid hydrocarbons, which include structures built from fused benzene rings but which allow, in the interior part, faces that cover the area of two and more benzene rings, which are usually referred to as "holes".[410]

A question can be raised: When does a chemical formula C_nH_m represent a benzenoid hydrocarbon? J. R. Dias developed an algorithm for deciding when the formula C_nH_m is compatible with a benzenoid hydrocarbon. He then arranged the possible entries in a table called the "Formula Periodic Table", that we have already mentioned,[328−336] which is illustrated in Table 11 for the case of benzenoid hydrocarbons. Similar tables have been constructed for non-benzenoid polycyclic hydrocarbons,[411−414] for coronoid hydrocarbons,[415] etc. It should not be overlooked that the entries in the Formula Periodic Table are all compatible empirical formulas of polycyclc hydrocarbons; hence, an entry represents the totality of isomers that have the same formula, but which among themselves may have considerably different properties. In that respect, the Formula Periodic Table does not relate to individual benzenoids but to classes of benzenoids having the same formula. Bytautas and Klein have constructed similar Formula Periodic Tables for different classes of compounds, such as alkanes,[416,417] but also benzenoid hydrocarbons.[418] They considered various properties of respective molecular graphs (i.e., graph invariants) and calculated the average values for each group of isomers having the same empirical formulas. In this way, the Formula Periodic Table becomes a "Table of Properties", analogous in some respect to the Periodic Table of Elements and the Periodic Table of

Isomers, but instead of each entry corresponding to a single element or isomer, it belongs to a class of compounds.

A topic closely related to enumeration and construction of benzenoid hydrocarbons is enumeration and construction constrained by specific structural requirements. An example is enumeration of benzenoid hydrocarbons having a bay region. According to Jerina and co-workers,[419−421] the presence of a bay region is critical for the carcinogenic activity of benzenoid hydrocarbons. Let us first define a bay region, following Balasubramanian et al.:[397]

Definition: *A bay region is a local structural element in benzenoid hydrocarbons which involves three benzene rings arranged as in phenanthrene, of which one has to be a terminal* C_6H_4 *ring.*

Balasubramanian et al.[397] and Knop and co-workers[422,423] developed a computer program that identify benzenoids having bay regions. A nice feature of these programs is that the output is presented graphically by listing benzenoid structures so that one can visually inspect the results. An inspection of the results for benzenoids having six or less fused rings shows that the number of bay regions is the same for *isoconjugated* structures, like benzo[*c*]phenanthrene and chrysene, or dibenzo[*aj*]tetracene and dibenzo[*al*]tetracene. Apparently, this has not been incorporated in the computer programs, which list all benzenoids having bay regions, whether isoconjugate or not.

Definition: *Two or more conjugated hydrocarbons are isoconjugated if there is a one-to-one correspondence between their Kekulé valence structures which fully agree in the count of all their conjugated circuits.*

Relationships between carcinogenity and theoretical reactivity indices in polycyclic conjugated hydrocarbons are outside the scope of this review, but interested readers can find some introductory material in refs 424−427. A recent review on enumerations in chemistry, which includes historical material, an outline of enumerative methods, and reports on the current results, can be found in *A Specialist Periodical Report: Chemical Modelling: Application and Theory*.[428]

VII. Kekulé Valence Structures Count

> *Ist es nicht eine ebenso wurdige Aufgabe der Mathematik richtig zu zeihnem, wie die, richtig zu rechnen.*
>
> Felix Klein (1849−1925)[429]

Because Kekulé valence structures are central to the concept of conjugate circuits, we will follow with a discussion of the properties of Kekulé valence structures, their construction, and their enumerations. We will be relatively brief and would like to direct the attention of readers to the book by Cyvin and Gutman[79] on Kekulé structures in benzenoid hydrocarbons, where the enumeration and properties of benzenoid structures are discussed on over 300 pages. Kekulé valence structures have been around for quite a while. They offer qualitative descriptions of conjugated cyclic hydrocarbons, suggesting delocalization of CC single and CC double bonds. Let us start with a mathematical definition of Kekulé valence structure:

Definition: *A Kekulé structure is a valence structure covered by the maximal number of disjoint (double) edges so that all vertices are incident to one of the disjoint edges.*

In the mathematical literature, a Kekulé structure of a graph is known as 1-factor. The necessary and sufficient conditions for a graph to have 1-factor are known in the mathematical literature, in the case of bipartite graphs, as a theorem of P. Hall,[430] also known as the “marriage theorem”. The necessary and sufficient conditions for a general graph to have 1-factor are known as a theorem of W. Tutte.[431] The mathematical works of P. Hall and W. Tutte for the most part passed unnoticed in the chemical literature, with the exception of Hosoya, who drew the attention of chemists to them.[60] However, the use of the theorem of Tutte implies an exhaustive examination of various components of a graph, which makes it not practical. As we will see, there are numerous efficient algorithms not only for determining if a molecular graph has 1-factor, but also for determining the number of 1-factors, that is, the number of Kekulé valence structures for a molecule.

The number of Kekulé valence structures, K, is of interest as a simple index of molecular stability. It was Clar[49] who was first to recognize that if one cannot draw Kekulé valence structures for a polycyclic system, that is, if $K = 0$, then such structures are non-existent. On the other hand, the relative stability of benzenoids appears to grow with K; more precisely, it is proportional to the logarithm of K.[432] Thus, phenanthrene with *five* Kekulé structures is more stable than anthracene, which has *four* Kekulé structures. The logarithm of K was shown to offer a fair quantitative correlation with molecular RE. However, there are benzenoids that have the same number of Kekulé valence structures that would be predicted to have the same RE (for their construction, see ref 433). Such compounds (illustrated in Figure 26) nevertheless show some variation in their RE, as reflected in more sophisticated expressions for RE (to be discussed later), and thus point to the limitations of the simple empirical formula $\mathrm{RE} = \log K$. Clearly, among benzenoid hydrocarbons having the same number of fused benzene rings, those having the largest K are expected to be the most stable. Construction of benzenoids with the maximal number of Kekulé valence structures for a given number of hexagons has been reported.[434,435] In Figure 27 we have illustrated benzenoids with the maximal number of Kekulé valence structures for a given number of fused benzene rings. Among smaller benzenoid hydrocarbons, these include phenanthrene and triphenylene.

For smaller benzenoid and non-benzenoid hydrocarbons, it is not difficult to construct all the Kekulé valence structures. Pauling himself describes the brute force approach as follows:[436]

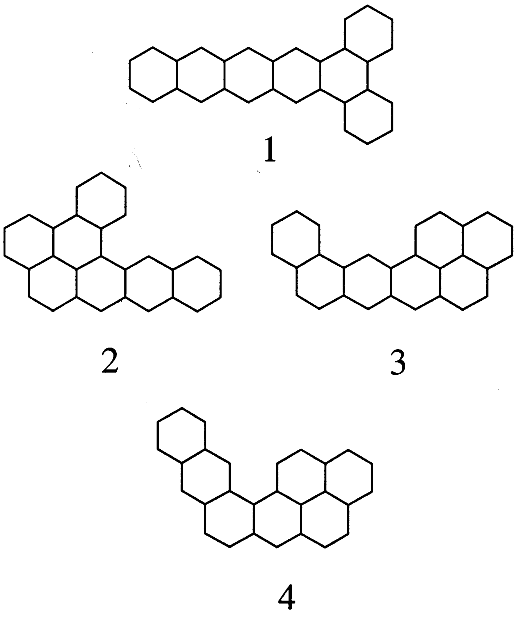


Figure 26. Illustration of benzenoid hydrocarbons having the same number of Kekulé valence structures.[433]

> *A few minutes suffice to draw the four unexcited structures for anthracene, the five for phenanthrene or the six for pyrene ... an hour or two might be needed for the 110 structures of tetrabenzoheptacene.*

Finding K for benzenoid hydrocarbons having a dozen fused rings requires more efficient schemes. A simple graph theoretical algorithm for construction of Kekulé valence structures is as follows:[437]

(1) Construct two copies of the molecular diagram.
(2) Select a CC bond and assign to it CC double and CC single bond type in each of the copies, respectively.
(3) Complete the assignment of bond types for neighboring bonds, if possible.
(4) Continue by constructing two copies of each not completed molecular diagram.
(5) Go to step (2).

The slow part in enumerating Kekulé structures by drawing Kekulé valence structures is the very drawing of numerous copies of molecular skeletons. This process can be accelerated by preparing blank copies of molecular structure to which CC double bonds are later assigned. By using such templates of molecular skeletal forms, one can obtain all the Kekulé valence structures of tetrabenzo[*de*,*no*,*st*,c_1,d_1]heptacene that Pauling mentioned in less than five minutes, rather than an hour or longer. Incidentally, tetrabenzo[*de*,*no*,*st*,c_1,d_1]heptacene is one of the many benzenoid hydrocarbons prepared by Clar.[438]

In Figure 28 we show the initial steps of the above algorithm, which already gave 3 of the 14 Kekulé valence structures of benzo[*ghi*]perylene. If one is interested only in K, one need not continue the above process to exhaustion. It suffices to reduce the original structure to smaller ones for which K values are known. For example, in Figure 28, besides the three Kekulé valence structures shown on the right-hand side of the figure, we have two unfinished fragments on the left-hand side. One of these involves disjoint fragments of benzene ($K = 2$) and naphthalene ($K = 3$), which results in 2×3, or 6, Kekulé valence structures, and the other, the fragmentary structure, contains phenanthrene ($K = 5$). Thus, the left-hand side of Figure 28 would generate 11 Kekulé valence structures. This, with the already found 3 Kekulé valence structures shown on the right-hand side of the figure, makes 14 Kekulé structures of benzo[*ghi*]perylene. Chapter 8 of the book by Trinajstić,[70] *Chemical Graph Theory*, gives a good review of various schemes for obtaining K. In the book by Trinajstić, the above approach is referred to as "the method of fragmentation", which appears to have been already known to Wheland.[129]

We continue with outlining selected algorithms for counting Kekulé valence structures separately for cata-condensed and peri-condensed benzenoids.

Definition: *A cata-condensed benzenoid hydrocarbon is a system built from fused benzene rings such that two adjacent rings have no other common adjacent rings.*

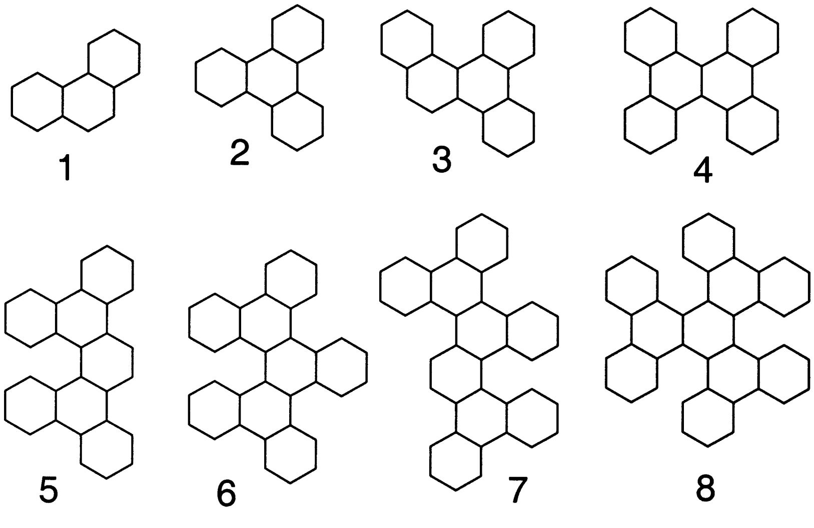


Figure 27. Cata-condensed benzenoid hydrocarbons with the maximal number of Kekulé valence structures for a given number of fused benzene rings.[434,435]

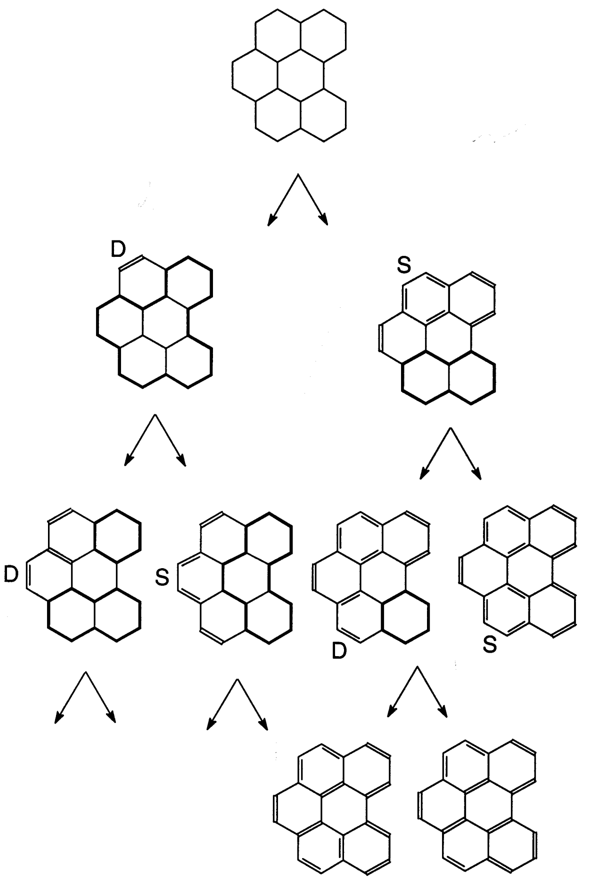


Figure 28. Initial steps for a systematic construction of Kekulé valence structures, illustrated on benzo[*ghi*]-perylene, that already yield 3 of the 14 Kekulé valence structures.[437]

Definition: *A peri-condensed benzenoid hydrocarbon is a system built from fused benzene rings such that at least two adjacent rings have a single common adjacent ring.*

A. Non-branched Cata-condensed Benzenoids

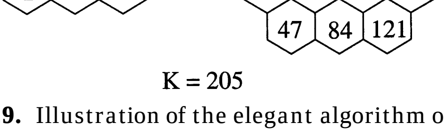


Figure 29. Illustration of the elegant algorithm of Gordon and Davison[439] for the count of Kekulé valence structures in non-branched cata-condensed benzenoids.

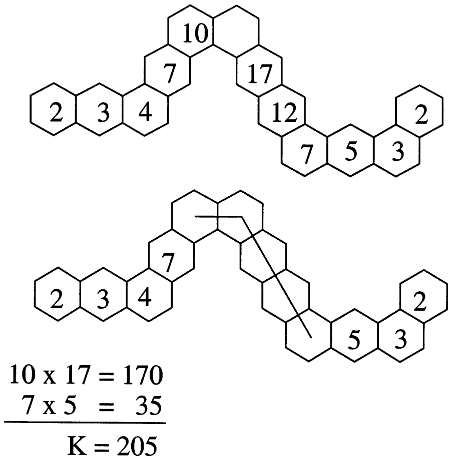


Figure 30. Modification of the algorithm of Gordon and Davison for cata-condensed benzenoids.

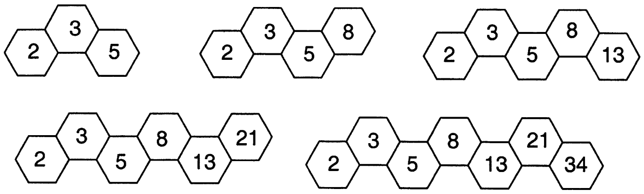


Figure 31. Fibonacci numbers as the count of Kekulé valence structures for families of cata-condensed benzenoids in which every benzene ring is a “kink” ring.

Gordon and Davison[439] outlined an elegant algorithm for counting K in non-branched cata-condensed benzenoids, illustrated in Figure 29: To obtain K, insert in the first ring the number 2, since benzene has two Kekulé structures. Add +1 to each successive ring if it is linearly fused, giving 3, 4, etc., respectively, for anthracene, tetracene, etc. When arriving at a “kink”, that is, a ring at which the direction of fusion of benzene rings changes, add the number in the preceding ring. Thus, for the cata-condensed benzenoid shown in Figure 29, we have to add 3 + 4 to get 7 (which is K for benzanthracene). Continue to add that number until another “kink” arises. The inscribed number gives K for benzenoids ending at a particular ring, the last number giving K for the benzenoid depicted.

For long cata-condensed benzenoids, the algorithm of Gordon and Davison (GD) can be modified is illustrated in Figure 30. First, select a “kink” ring (somewhere in the middle of the structure). Apply the GD algorithm to the two fragments obtained when the selected ring is erased, which will yield K_1 and K_2 for their respective number of Kekulé valence structures. For the benzenoid shown in Figure 30, we obtain $K_1 = 10$ and $K_2 = 17$. Now erase all rings linearly fused to the “kink” ring and apply the GD algorithm to these smaller two fragments, which will yield k_1 and k_2 for their respective number of Kekulé valence structures. For the benzenoid shown in Figure 30, we obtain $k_1 = 7$ and $k_2 = 5$. The number of Kekulé structures for the molecule is given by $K = K_1K_2 + k_1k_2$, which for the benzenoid shown in Figure 30 gives 170 + 35 = 205. If all rings of a fragment are erased or crossed, then the corresponding $k_i = 1$.

For families of cata-condensed benzenoids in which every benzene ring is a “kink” ring (illustrated in Figure 31), the GD algorithm immediately yields Fibonacci numbers 2, 3, 5, 8, 13, 21, 34, ... as the number of Kekulé valence structures for the corresponding cata-condensed benzenoids. Fibonacci numbers first appeared in a book on algebra written by Fibonacci (in the 13 century!) to illustrate the fast growth of a population of rabbits.[440]

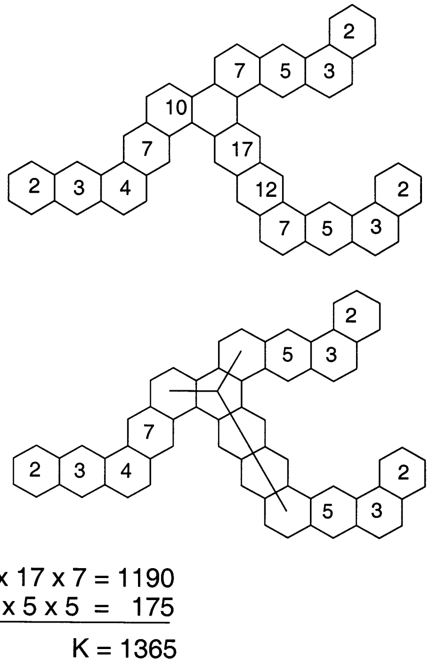


Figure 32. Modification of the Gordon−Davison algorithm to yield K for cata-condensed benzenoid having three branches.

B. Branched Cata-condensed Benzenoids

The GD algorithm can be modified to obtain K for a branched benzenoid having three branches (see Figure 32). If the central ring is erased, one obtains three branches having K_1, K_2, and K_3 Kekulé valence structures. By erasing, in addition to the central ring, all rings that are linearly fused to the central ring, we obtain three smaller fragments with k_1, k_2, and k_3 Kekulé valence structures. The number of Kekulé structures for the molecule is then $K = K_1K_2K_3 + k_1k_2k_3$.[441] A variation of this procedure considers, instead of individual benzene rings, smaller fragments of linearly fused benzene rings adjacent to a branching ring.[442]

C. Benzenoid Lattices

The term “lattice” in chemistry (crystallography) may refer to any regular arrangements of atoms in crystals. In contrast, “lattice” in mathematics[443] is used in a very restrictive sense as follows:

Definition: *A lattice is a hierarchical arrangement of elements in which there is only one element at the top, which dominates all other elements, and only one element at the bottom, which is dominated by all other elements. The other elements of a lattice can both dominate and be dominated by other elements.*

In the United States in the mathematical literature, it is customary to refer to the top element of a lattice as the “master” and the bottom element as the “slave”. In chemical literature, where already we have seen such geographic labels as “fjord”, “cove”, “bay”, and even “beach”[444] for fragments of the periphery of benzenoid hydrocarbons in the case of oriented benzenoid molecules, the terms “peak” and “valley” have been used to describe vertices on the periphery which dominate or are dominated by immediate neighbors. In many European countries one uses socially less “disturbing” terms: “supremum” and “infinum”, words of Latin origin, to replace the terms “master” and “slave”, respectively. Observe that a benzene ring, if oriented so that one carbon is at the top and one at the bottom, already represents a lattice. In Figure 33 we illustrate several smaller benzenoids that can be viewed as a lattice when oriented as shown. However, a given benzenoid, e.g., pyrene, can be oriented so that it no longer represents a lattice, in which case the algorithm for latticed does not apply. The number K for lattices is obtained by a generalization of the GD algorithm, in which first one considers in isolation the benzene rings at the molecular periphery. The GD algorithm is then applied to the peripheral benzene rings that are linearly fused to the bottom (slave) ring. In these one inscribes the numbers 2, 3, 4, etc., as far as possible on both sides of the lattice. From the numbers inscribed at the periphery, one gets the numbers to be inscribed in the interior rings that are directly above them. The numbers to be inscribed in the interior rings are given by the sum of the numbers just below each ring. Upon completing calculation of the numbers in the interior, one can extend the assignment of ring numbers to the remaining part of the periphery using the rule for the “kink” rings of the GD algorithm at the sites where before assignment was interrupted. The process continues until all the benzene rings have inscribed a number; then, the largest number at the top of the lattice is K for the lattice.[445]

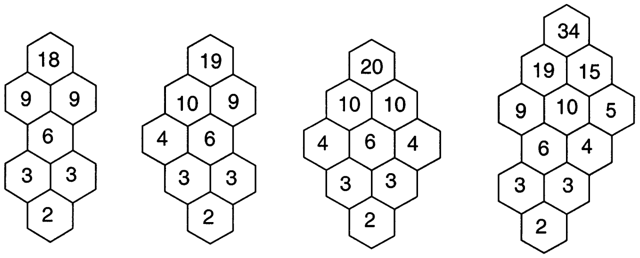


Figure 33. Several smaller benzenoids depicted as lattices. The inscribed numbers at the top indicate K for the corresponding lattice.[445]

We will describe in more detail this modified GD algorithm for the last lattice shown in Figure 33. To obtain K, start at the bottom benzene ring of the lattice, in which one inserts 2. Apply the GD algorithm to the linearly fused peripheral rings above the lowest ring having the label 2. This will give K for the corresponding fragments of the molecular periphery: at the left we have $k = 3$ for the naphthalene fragment, and at the right we have $k = 5$ for the tetracene fragment. In the next step, consider the interior rings just above the rings that have inscribed numbers. Assign to these rings the sum of the two numbers below. In this way we obtain $k = 6$, $k = 10$, and $k = 15$, which are the K numbers for pyrene, anthanthene, and its higher homologue. At this stage we are “stuck”: we cannot make further assignments. To continue the process, consider the central ring of the phenanthrene moiety, for which two rings have

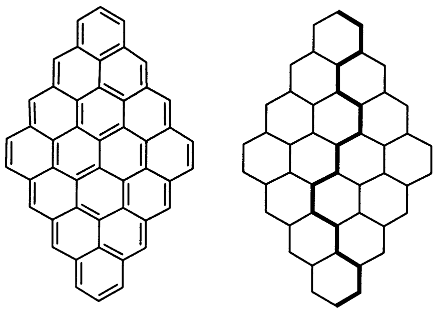


Figure 34. One-to-one correspondence between the Kekulé valence structures and the paths illustrated on one of the Kekulé structures of $C_{48}H_{18}$. At the right: the unique path connecting slanted C=C bonds.[446]

values $k = 3$ and $k = 6$ already assigned. Use the rule for the "kink" rings of the GD algorithm and assign to the top ring the sum $3 + 6$. This gives $k = 9$ for the benz[*a*]pyrene fragment of the lattice. Now we can continue to complete the assignment for the remaining rings using again the sum rule (that is, by adding the k values for the two rings just below a ring for which a k value has not yet been obtained). When the process is completed we find $k = 34$ for the top benzene rings, which is K for this lattice. The process ends when all rings have been assigned numerical values. In summary, the algorithm for finding K in benzenoid lattices represents a combination of the Gordon and Davison algorithm for cata-condensed benzenoids (which is applied to the lattice periphery) and the rules of the Pascal triangle (which apply to the interior benzene rings).

We can illustrate on a benzenoid lattice an important one-to-one correspondence between the count of Kekulé valence structures and the count of monotone paths.

Definition: *A monotone path is a path connecting a peak and a valley such that each move goes from a higher position in a hexagon to a lower position.*

In Figure 34 we show one of the 70 Kekulé valence structures of $C_{48}H_{18}$. The CC double bonds are shown as thick edges and CC single bonds as thin edges. We will follow Lewinter et al.[446] and refer to the CC bonds of the benzenoid shown in Figure 34 as "vertical" or "slanted" edges. Lewinter et al. observed that, in every row of the benzenoid lattice, there is but one "slanted" CC bond. If one connects the "slanted" edges by the adjacent vertical edges, one obtains a *single* path that connects the "master" and "slave" carbon atoms, as illustrated on the right side of Figure 34. Hence, each Kekulé structure is associated with a unique path from the top to the bottom of a lattice; thus, counting the paths is tantamount to counting Kekulé valence structures.

We also take this opportunity to point out how apparently different geometrical problems are mathematically equivalent. In Figure 35 on the left we have depicted the same Kekulé structure shown in Figure 34, but we have shortened the "vertical" CC bonds considerably. As one can see, the "vertical" CC bonds do not play an important role in determining the shape of a path from the top to the bottom of the lattice. When the "vertical" CC bonds are further reduced and approach zero length, we obtain in the limit the diagram shown on the right in Figure 35. This diagram can be viewed as a fragment of a 5 × 5 coordinate grid, which is referred to in graph theory as a mesh of a graph G, or shortly $M(G)$:

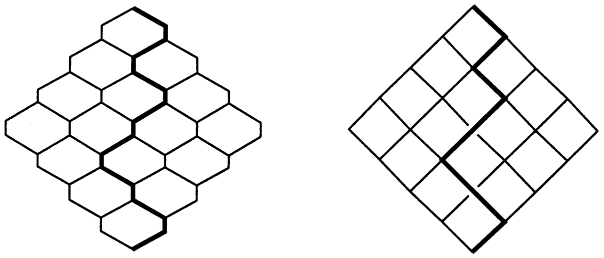


Figure 35. Benzenoid of Figure 34, viewed as a 5 × 5 coordinate grid on which the corresponding path is shown.[446]

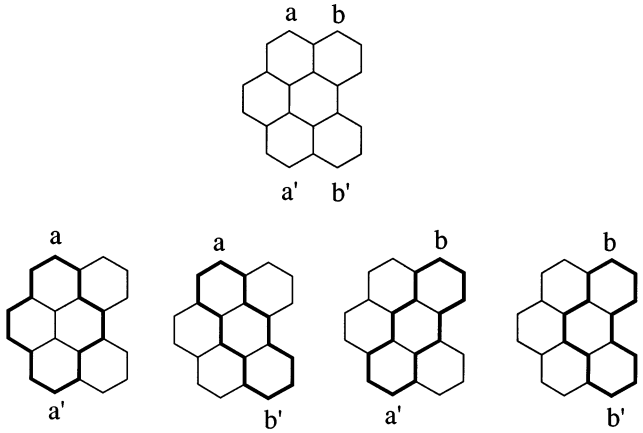


Figure 36. The approach of John and Sachs,[447] illustrated on benzo[*ghi*]perylene.

Definition: *The vertices (x,y), such that x and y are integers satisfying $1 \leq x \leq a$ and $1 \leq y \leq b$, represent mesh $M(a,b)$. Two vertices (x,y) and (x',y') are adjacent if either $x = x'$ and $|y - y'| = 1$, or $y = y'$ and $|x - x'| = 1$.*

Observe that mesh $M(a,b)$ represents an equitable bipartite graph for which one can construct a $k \times k$ bi-adjacency matrix, where k is the number of starred and non-starred vertices. Thus, the count of paths in a $k \times k$ mesh is the same as the count of Kekulé structures for a complete benzenoid lattice having k^2 benzene rings, and in the case of an $a \times b$ mesh, for a corresponding benzenoid parallelogram having $a \times b$ benzene rings. As discussed by Lewinter et al.,[446] this approach can be extended to non-parallelogram-like lattice benzenoids having fewer benzene rings than complete parallelogram-like lattices.

D. Peri-condensed Benzenoids

To find K in peri-condensed benzenoid systems that do not represent a lattice is more involved. However, John and Sachs[447,448] described an algorithm to obtain K values that can be linked to the GD algorithm and its generalization to lattices. The approach of John and Sachs is illustrated in Figure 36 for benzo[*ghi*]perylene, having two "master" and two "slave" rings, which are labeled by a,b and a',b', respectively. Benzo[*ghi*]perylene is not a lattice but can be viewed

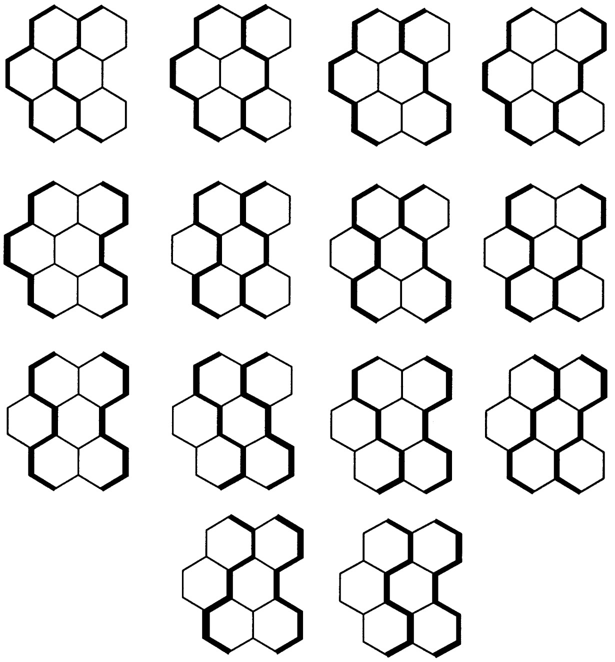


Figure 37. One-to-one correspondence between paths and the Kekulé valence structure illustrated for benzo[*ghi*]perylene.

as a combination of two overlapping lattices. Hence, we will use informally the terms "master" and "slave" for carbon atoms of the corresponding sub-lattices. Observe that any two pairs of labels, like (a,a'), (a,b'), (b,a'), and (b,b'), and interconnecting hexagons considered in isolation correspond to a lattice. Using the algorithm already outlined for finding K for lattices, we can easily obtain $K_{aa'}$, $K_{ab'}$, $K_{ba'}$, and $K_{bb'}$. To obtain K for the molecule, we construct in this case a $|2 \times 2|$ determinant with $K_{aa'}$ and $K_{ab'}$ as the elements of the first row (or column) and $K_{ba'}$ and $K_{bb'}$ as the elements of the second row (or column, respectively). K is given by the value of this determinant. In a case of a benzenoid having n "masters" and n "slaves", one constructs an $|n \times n|$ determinant in which columns are labeled a, b, c, ... and rows are labeled a', b', c', ... (or vice versa). The corresponding elements (x,y) of the determinant are given by the value k for the corresponding lattices having x and y on the top and the bottom ($x = a, b, c, ...$ and $y = a', b', c', ...$). K is given by the value of the $|n \times n|$ determinant.

The approach of John and Sachs is particularly suitable for calculation of the K values of the giant benzenoids described by Müllen and co-workers (Figure 12). The smallest of these giant benzenoids, "super-naphthalene", "super-phenalene", and "super-triphenylene", already have $K = 16\,100$, $K = 540\,000$, and $K = 66\,998\,000$, respectively. However, calculation of these large numbers follows from relatively small $|5 \times 5|$ and $|6 \times 6|$ determinants. For a numerical illustration of such calculations, consult ref 449.

It has been pointed out by Gordon and Davison that their algorithm was based on *enumeration* of distinct monotone paths in a benzenoid system. In the case of lattices, K indicates the count of distinct paths from the top of a lattice to the bottom carbon atom. In Figure 37 we illustrate this one-to-one correspondence between paths and the Kekulé valence structure for benzo[*ghi*]perylene. Sachs[450] rigorously proved the one-to-one correspondence between paths and the count of Kekulé valence structures. Observe that, once all the paths have been identified, one can draw Kekulé valence structures by replacing each path with a conjugated chain that starts and ends with a CC double bond. Such assignment of CC double bonds determines the bond type for CC bonds that are not part of any conjugated chain.

E. Miscellaneous Benzenoids

Gutman, Cyvin, and co-workers[79,451] have considered, in a number of publications, enumeration of the Kekulé valence structures for numerous benzenoids that belongs to different classes, characterized by an overall identical shape. We direct the reader to the book by Cyvin and Gutman, *Kekulé Structures in Benzenoid Hydrocarbons*,[79] where the results of such enumerations are collected for many classes of different benzenoids. A shorter account of enumeration of Kekulé valence structures can be found in another book by Gutman and Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons*,[214] and a review article by Klein, Babić, and Trinajstić, "Enumeration in Chemistry".[428] Among these various systems, of particular interest are the so-called "fully benzenoid" hydrocarbons described by Clar, having $6n$ π-electron and being unusually stable. Polansky and Gutman[453] were the first to consider this class and arrived at a combinatorial expression for the number of Kekulé structures for fully benzenoid hydrocarbons. Their formula, however, has little practical value, except perhaps to show that there are such formulas, because among other drawbacks it requires summations over all possible combinations of mutually disjoint ring. It is thus reminiscent of the elegant theorem of Tutte on the existence of a Kekulé structure, which may be easy to understand but difficult to apply in practice. That the "analytic" formula of Polansky and Gutman has little use has been indirectly acknowledged by Gutman and others,[454] who in another paper on enumeration and classification of "fully benzenoid" systems and enumeration of their Kekulé valence structures structure did not use their analytic formula but instead used a special computer program for actual computation of K, based on a technique proposed by Brown.[455]

A brief review of various methods used for enumeration of Kekulé structures for rectangle-shaped benzenoids has appeared in *Topics in Current Chemistry*, volume 153.[451] Enumeration of Kekulé valence structures has also been extended to a class of *generalized* benzenoid hydrocarbons, the so-called coronoid hydrocarbons, which are built from fused benzene rings, but permitting in the interior one or more larger "holes". For some coronoids it was possible to get an adequate mathematical formulation,[456] or a practical and relatively simple algorithm.[457] We should add that Yen[458] in 1971 presented equations for the determination of the number of Kekulé valence structures for several families of peri-condensed benzenoids, including the square (parallelogram) model, symmetric circular systems, the rectangular model, and a skew strip model.

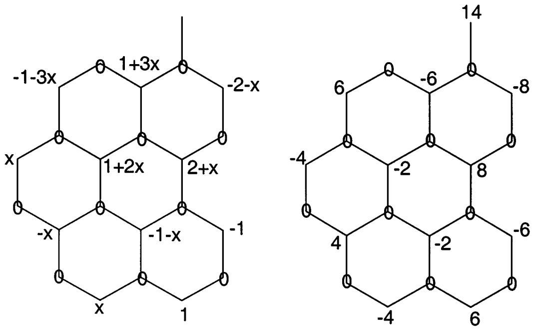


Figure 38. Illustration of the method of Plat[199] that determined K from properties of the coefficients of NBMO.

Sheng[459] outlined an economical two-vertex elimination method for deciding whether a polycyclic benzenoid hydrocarbon has Kekulé valence structure, and brothers He Wenjie (mathematician) and He Wenchen (chemist) discuss enumeration of Kekulé structures using a matrix corresponding to “peak” and “valley” carbon atoms.[460] We should also mention the quick and robust method of Kearsley[461] for assigning CC double bonds in a Kekulé valence structure on the basis of an ordered fragmentation of the molecular skeleton.

F. The Approach of Platt

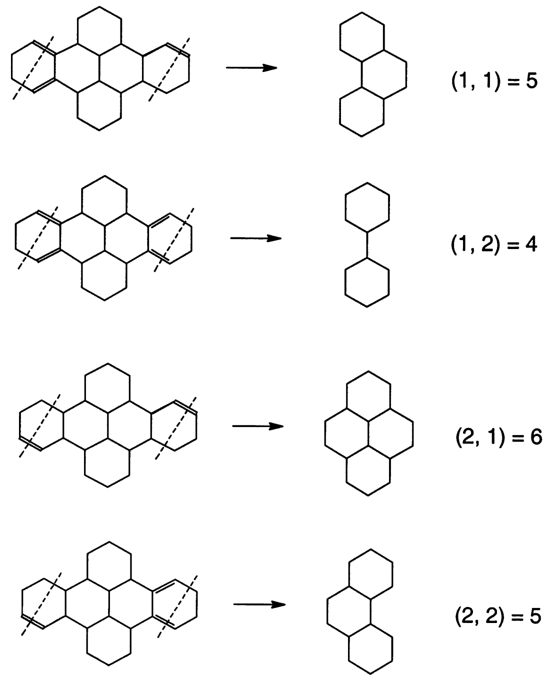
We will mention here Platt’s[199] method for finding K in larger benzenoids because it is based on totally different concepts. His approach, which apparently it is not well known, is intriguing as it reveals another elusive link between VB and MO theories. For instance, neither the book by Cyvin and Gutman, *Kekulé Structures in Benzenoid Hydrocarbons*,[79] with over 200 references, which on over 300 pages discusses calculation of K, nor the follow-up book by Gutman and Cyvin on the theory of benzenoid hydrocarbons,[214] mentions Platt and his approach. Platt based the calculation of K on the properties of non-bonding molecular orbitals (NBMO’s). It is well known from HMO theory that for benzenoid hydrocarbons NBMO’s have zero amplitudes on alternating carbon centers (see Figure 38). At the same time, non-zero amplitudes of NBMO’s on adjacent carbon centers satisfy the zero sum rule: The coefficients of NBMO’s on adjacent atoms add to zero for each carbon atom. In the case of radicals, Platt has shown that the coefficient at the terminal carbon gives K for the underlying benzenoid hydrocarbon. This is illustrated in Figure 38 for benzo[*ghi*]perylene. One starts by assigning zero amplitudes to alternate carbon atoms. One then assigns “1” as the amplitude to a starting carbon atom (shown in the bottom row of carbons of benzo[*ghi*]perylene). By applying the zero sum rule, one can determine the amplitude of one or more neighboring carbon atoms. If a carbon atom cannot be assigned a coefficient, one assigns to it a variable x as the amplitude and continues using the sum rule to find the coefficients of neighboring non-zero carbon atoms. The process continues until all non-zero carbon atoms have been assigned non-zero NBMO coefficients. The value for the unknown variable x can be subsequently determined from the sum rule applied to the carbon atom involving undetermined contributions expressed with variables x, y, etc. There are always enough sites to allow solving for undetermined variables x, y, etc., the solutions of which are constrained to integers. K is given as the sum of coefficients adjacent to the site of radical substitution.

On the left side of Figure 38, we started by assigning 1 and x to the two bottom carbon atoms. By following the sum rules, we can assign values for all non-zero carbon atoms, ending with the atomic coefficients $1 + 3x$, $1 + 2x$, and $2 + x$, which have to add to zero. This gives $4 + 6x = 0$, or $6x = -4$. Because x has to be an integer, we have to multiply the initial coefficients 1 and x by 6, getting 6 and $6x$ or -4, respectively. Once all non-zero entries have been assigned with the initial steps revised in this way, we find at the top that $K = 14$. Benzo[*ghi*]perylene is too a small structure to illustrate the power of the Platt algorithm, which can be applied with similar ease to the giant benzenoids shown in Figure 12.

Herndon has drawn attention to the above almost forgotten approach of Platt in several publications.[462−464] Coefficients of NBMO’s were also discussed by Longuet-Higgins[465] and others.[466,467] NBMO’s have been of interest in various problems of chemistry. First, they play an important role in HMO theory. The zero sum rule, which states that the sum of the coefficients in the NBMO’s around each atom is equal to zero, was first used by Longuet-Higgins.[468] The enumeration of bonding (N_+), non-bonding (N_0), and antibonding (N_-) orbitals in HMO models by the graph theoretical approach, which takes advantages of graph theoretical transformations that leave the numbers N_+, N_0, and N_- unchanged, was outlined by Cvetković, Gutman, and Trinajstić.[469,470] Gutman and Trinajstić offered a graph theoretical classification of conjugated hydrocarbons based on two parameters: the difference $N_+ - N_-$ and N_0.[471] Although this classification relates to Hückel molecular orbitals, it can be extended to more elaborate MO approaches; thus, it has some validity beyond HMO theory. More recently it was shown that the non-bonding orbitals of many graphite-derived carbon frameworks can be understood in terms of the non-bonding orbitals of the infinite graphite sheet.[444,472] For additional developments of the HMO method, consult ref 193.

G. Computer Programs for Calculating *K*

There are several computer programs that calculate K.[392,455] When one is considering benzenoid hydrocarbons, one can take advantage of the fact that the absolute value of the constant term in the characteristic polynomial is the square of K.[474,475] For bipartite graphs (benzenoids systems and other polycyclic systems having only even-member rings), as G. G. Hall[476] pointed out, one can obtain K as the value of the determinant of one of the blocks of the adjacency matrix. Torrens[473] constructed a fast computer algorithm for permanents of sparse matrices of alternant hydrocarbons, and such are the adjacency matrix of molecular graphs of benzenoid hydrocarbons.



$$T = \begin{bmatrix} 5 & 4 \\ 6 & 5 \end{bmatrix}$$

Figure 39. Construction of the 2 × 2 transfer matrix for a tetrabenzanthracene polymer.

H. Transfer-Matrix Method

Finally let us mention the approach known as the transfer-matrix method, which is particularly useful for systems that have repeating sub-units, e.g., systems with high symmetry and polymers. Besides applications to benzenoid and non-benzenoid polymers, the transfer-matrix method is suitable for systems with rotational symmetry, such as buckminsterfullerene, C_{60}. In fact, the first reported value for the number of Kekulé valence structures in buckminsterfullerene C_{60}, which is 12 500, was obtained using the transfer-matrix method.[477] The transfer-matrix method has been used for some time in statistical mechanics.[477−479] Klein and co-workers[480−485] pioneered the application of the transfer-matrix method for chemical enumerations.

In Figure 39 we illustrate construction of the 2 × 2 transfer matrix for a tetrabenzanthracene polymer. In this polymer, two CC bonds connect the neighboring monomer units, each of which can be either a CC double or a CC single bond. If both connecting bonds were either single or double, then all the remaining CC bonds in the polymer would have fixed CC bond type. A transfer matrix is constructed by considering the four possible assignments for the connecting bonds: DS,DS, DS,SD, SD,DS, and SD,SD, where S and D designate CC single and CC double bonds, respectively. The corresponding matrix elements are given by the number of Kekulé valence structures for the monomer unit when the two connecting bonds take any of the four possible assignments. This is illustrated for dibenzopyrene on the right side of the Figure 39. For example, when we assign DS,DS bond types to connecting CC bonds (top of Figure 39), the K for the monomer unit is that of a phenanthrene fragment with $K = 5$, but with DS,SD assignment the monomer unit becomes a diphenylene fragment with $K = 4$, etc. In this way we obtain the transfer matrix shown at the bottom of Figure 39.

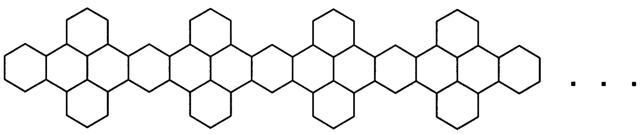


Figure 40. Benzenoid polymer.

For any finite molecule which is a member of a family that is based on the same repeating monomer unit, the number of Kekulé valence structures is given by the formula

$$K_N = A(\lambda_1)^N + B(\lambda_2)^N$$

where A and B depend on the end groups, which may be equal or different. The end groups may differ from polymer to polymer, even when polymers have the same repeating unit. λ_1 and λ_2 are the roots of the equation $\det|\, T - \lambda I \,| = 0$, where I is the 2 × 2 identity matrix. In the case of the transfer matrix shown in Figure 39, the secular equation is a quadratic equation, $x^2 - 10x + 1 = 0$ with roots $\lambda_{1,2} = 5 \pm \sqrt{24}$. Using known values for K_A and K_B, one can calculate the "end" constants A and B and then derive K_N for a polymer having N units. For more details, consult refs 480−485.

I. Use of Recursion Relations

To find K for a family of structurally related compounds, such as polymers of different lengths having conjugated polycyclic units (i.e., benzenoid polymers), it is useful to develop recursion formulas.[486−489] In such situations, the Kekulé structure counts follow a recursion,

$$K_{N+1} = AK_N + BK_{N-1}$$

from which one can quickly find K_{N+1} once the constants A and B (which depend on the "end" group for the polymers considered) are known. For example, for the benzenoid polymer shown in Figure 40, with $K_1 = 20$, $K_2 = 198$, $K_3 = 1960$, and $K_4 = 19\ 402$, one obtains a set of linear equations,[483]

$$198A + 20B = 1960$$
$$1960A + 198B = 19\ \ 402$$

which gives $A = 10$ and $B = -1$ and leads to the recursion

$$K_{N+1} = 10K_N - K_{N-1}$$

The coefficients A and B differ only in sign from the coefficients of the secular equation $\det|\, T - \lambda I \,| = 0$ given earlier.

The recursive approach is suitable for rigorous evaluation of the expression for resonance energies within the model of conjugated circuits for structurally related benzenoid hydrocarbons of increasing

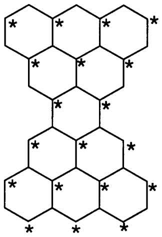


Figure 41. Graph of a non-existent benzenoid (having $K = 0$) having an equal number of "starred" and "unstarred" carbon atoms.

size. Using the algebra of large numbers, Živković et al.[485] developed the exact formulas for contributions from individual benzene rings of polymers with up to 25 000 repeating units (close to half a million carbon atoms). All arithmetic procedures were carried out in terms of whole numbers retaining all digits, of which there were sometimes more than 10^5. The particular program was developed and implemented for computer by Živković.[489]

J. Use of Signed Matrices

Before we outline Kasteleyn's[490,491] ingenious method for counting the number of Kekulé structures that is based on the signed matrix of a graph, that is, matrices of graphs which may have positive and negative entries, we have to introduce a few basic definitions of graph theory. We have already defined a bipartite graph as a graph in which one can partition the vertex set into two subsets, V^* and V^0, so that only vertices belonging to different sets are connected. We can now consider *equitable* bipartite graphs, defined as follows:

Definition: *A bipartite graph is equitable if the number of vertices in the two subsets* V^* *and* V^0 *is equal, that is,* $n^* = n^0$.

If a molecular graph has Kekulé valence structure then it is equitable, because each C=C bond joins a starred and non-starred carbon atom. The opposite need not be true, as is illustrated with the graph of a non-existing hydrocarbon Figure 41, for which $K = 0$. Clar[49] speculated that the hydrocarbon shown in Figure 41 could possibly exist by having weak *para* bonds between two condensed triangulene systems, but attempts to synthesize the compound failed. For bipartite molecules, the ground-state spin is simply given as the difference between the numbers n^* and n^0 of starred and non-starred sites:

$$S = |n^* - n^0|/2$$

In fact, this is a theorem of Lieb and Mattis.[492] Hence, for equitable bipartite graphs, like that shown in Figure 41, we have $S = 0$. As pointed out by Klein,[10] in all cases investigated so far, the VB predictions of ground-state spin appear correct when compared with the full configuration interaction calculations or the Pariser–Parr–Pople model,[493,494] with accurate ab initio calculations,[494–496] or with experiment.[497–500]

The signed matrix is related to the adjacency matrix of a graph, with the distinction that some of its entries may be negative. In order to construct the signed matrix, one first considers an embedded planar graph and assigns alternating directions (or signs) to individual bonds of even-member rings. If an edge is directed from i to j, then the matrix element $S_{i,j} = -1$. Consequently, the matrix element $S_{j,i} = +1$, and the signed matrix is necessarily antisymmetric. The absolute value of the determinant of the **S** matrix gives K^2, analogous to the relationship between the absolute value of the determinant of an adjacency matrix and K^2, already known to Dewar and Longuet-Higgins,[474] and Günthard and Primas.[475] "Signed" matrices can be constructed for planar polycyclic graphs only. We may add that most graphs representing the molecular skeletons of cyclic compounds met in chemistry are planar, although very large and complex structures may have a nonplanar graph. Planar and non-planar graphs are differentiated in graph theory as follows:

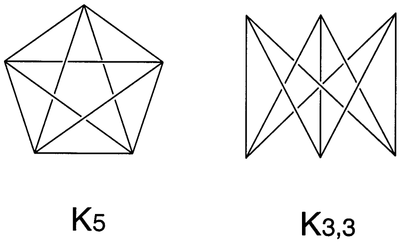


Figure 42. The smallest non-planar graphs of Kuratowski:[502] the complete graph on five vertices K_5, and the complete bipartite graph $K_{3,3}$ having six vertices.

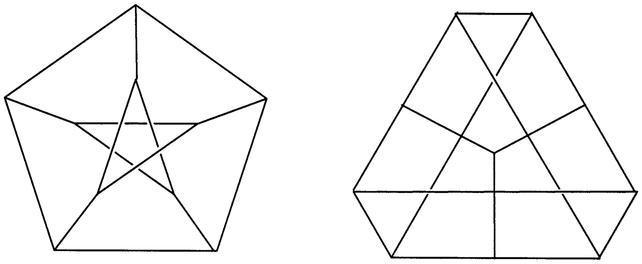


Figure 43. Two different representations of the Petersen graph.

Definition: *Planar graphs can always be drawn so that no crossing of edges occurs. Moreover, according to a theorem of Fary, planar graphs can be drawn always with edges as straight lines.*[501]

Definition: *Non-planar graphs cannot be drawn without at least one crossing of edges.*

The Polish mathematician Kazimier Kuratowski[502] proved in 1930 that the smallest non-planar graphs are the complete graph on five vertices K_5, the complete bipartite graph $K_{3,3}$ having six vertices (Figure 42). Although the molecular skeletons of most molecules can be represented as planar graphs, nonplanar graphs are also of considerable interest in chemistry. In Figure 43 we show the Petersen graph[503] that Prelog and Dunitz[504] used to illustrate the relationship between isomers in the rearrangements of trigonal bipyramidal complexes under the mechanism in which an exchange of the axial and the equatorial ligands occurs. It is illustrated in two pictorial forms of different symmetry in order to emphasize that graphs are defined by the *connectiv-*

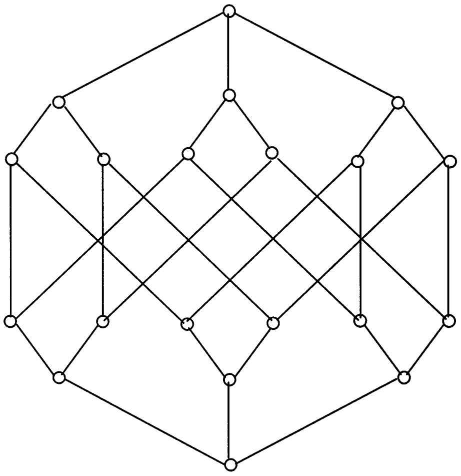


Figure 44. The first "reaction" graph introduced in chemistry in 1966 by Balaban et al.[505] to represent degenerate rearrangement of $C_2H_5^+$, known as the Desargues–Levi graph.

ity, which can be pictured in different geometrical ways. Planarity of a graph and planarity of a molecule are therefore different things. For example, all Platonic polyhedra are 3-D objects; hence, in a geometrical sense they are non-planar, but their graphs (which can be depicted also as Schlegel projections) are planar. The first non-planar graph of interest in chemistry was introduced in 1966 by Balaban et al.[505] It is known as the Desargues–Levi graph (Figure 44) and represents degenerate rearrangements of the $C_2H_5^+$ carbonium ion via multiple 1,2-shifts. For alternative geometrical representations of the Desargues–Levi graph, see ref 506.

VIII. Enumeration of Conjugated Circuits

Enumeration of conjugated circuits within individual Kekulé valence structures is, as we will see, very important, as it yields expressions for molecular resonance energy (RE). We have already pointed out that one can differentiate between *linearly independent conjugated* circuits and *linearly dependent and disjoint combinations of conjugated circuits*. In the following we will restrict attention to linearly independent conjugated circuits only. In the case of benzenoid hydrocarbons, the number of linearly independent conjugated circuits equals the number of condensed benzene rings, except in cases involving structures having essentially single and essentially double CC bonds (e.g., the central CC bonds in perylene, zethrene, and floranthene; Figure 45). Rings with CC bonds that have the same bond type in all Kekulé valence structures do not participate in formation of conjugated circuits.

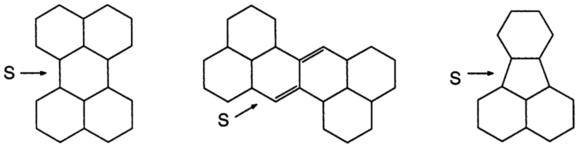


Figure 45. Benzenoids with essentially single and essentially double CC bonds illustrated on perylene, zethrene, and fluoranthene

For smaller molecules, conjugated circuits can be enumerated directly by inspecting all Kekulé valence structures of a molecule. If one is interested in linearly independent conjugated circuits, which will be the case in this review unless otherwise stated, it is convenient to inscribe numbers 1, 2, 3, ... directly into benzene rings involving R_1, R_2, R_3, ..., conjugated circuits, respectively. This is illustrated in Figure 46 for the 10 symmetry-non-equivalent Kekulé valence structures of benzo[*ghi*]perylene.[507,508] We inscribe "1" in all rings having three alternating CC double bonds. The number "2" is inscribed in rings that are adjacent to rings already having the label "1" *iff* (that is, if and only if) they are part of an R_2 conjugated circuit having five CC double bonds. Hence, combined adjacent rings "1" and "2" represent the Kekulé valence structure of a naphthalene fragment with alternating CC double bonds on the periphery of the fragment. The number "3" is inscribed similarly in rings that are either adjacent to R_2 rings or adjacent to two R_1 rings forming conjugated circuits having seven CC double bonds on their periphery, and so on. Under each Kekulé valence structure shown in Figure 46, we have summarized the count of conjugated circuits R_1, R_2, R_3, and R_4 by a four-digit code, the digits of which give the number of conjugated circuits of different size. The count of the conjugated circuits for a molecule as a whole is obtained by adding the contributions from individual Kekulé valence structures.

A more efficient algorithm for counting conjugated circuits R_1, R_2, R_3, and R_4 is based on enumeration of conjugated circuits for individual symmetry-unrelated benzene rings, rather than considering individual Kekulé valence structures. This approach, which has been outlined in ref 507, is particularly suited for large systems which may have very many Kekulé valence structures but a relatively small number of symmetry-non-equivalent fused benzene rings. For example, "super-phenalene" has $K = 540\,000$,[509] but only 34 fused benzene rings, of which only eight are symmetry-non-equivalent. The algorithm is as follows:

Algorithm

(1) Consider one ring at a time and outline all conjugated circuits R_1, R_2, R_3, ... possible for that ring.
(2) Complete the assignment of CC double bond for adjacent bonds when possible.
(3) The number of Kekulé structures of the fragment having unassigned CC bonds gives the occurrence of $R_1/2$, R_2, R_3, ... The number of R_1 is twice the number of the Kekulé structures of the fragment because the benzene ring has two Kekulé valence structures.

In Figure 47 we illustrate this ring-based algorithm on one of the four symmetry non-equivalent rings of benzo[*ghi*]perylene. In the first row of Figure 47 we consider R_1 conjugated circuits for the first ring (A) of benzo[*ghi*]perylene. In the second row we show all possible R_2 conjugated circuits of benzo[*ghi*]perylene which involve ring A. The last row of Figure 47 shows all conceivable R_3 conjugated circuits involving ring A (defined by alternating CC single and CC double bonds on the periphery of phenanthrene, anthracene,

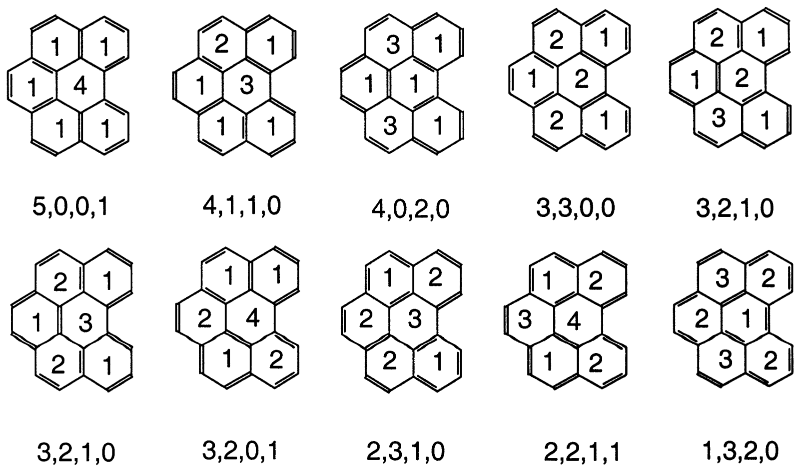


Figure 46. Enumeration of linearly independent conjugated circuits for 10 symmetry-non-equivalent Kekulé valence structures of benzo[*ghi*]perylene by inscribing integers that indicate the size of conjugated circuits involving individual rings. Under each structure is given the number of R_1, R_2, R_3, and R_4 conjugated circuits.

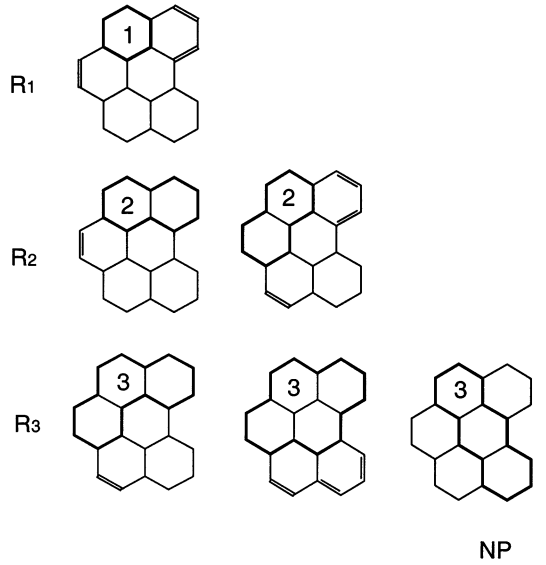


Figure 47. An alternative route for enumeration of contributing conjugated circuits, illustrated for a single ring of benzo[*ghi*]perylene.

and pyrene). However, the last possibility shown has to be ignored because it does not allow completion of a Kekulé valence structure for the CC bonds not involved in construction of the conjugated circuits.

We have designated the four non-equivalent rings as A, B, C, and D. For each ring separately we count its participation in conjugated circuits of different sizes. For example, ring A appears as R_1 in six Kekulé structures, because the fragment left unassigned is that of naphthalene with $K = 3$, but R_1 can have two Kekulé structures, which gives as the answer 6. The same ring can appear in five Kekulé structures as part of the R_2 conjugated circuit, which follows from examination of the two structures in the second row of Figure 47. When all the structures have been examined and contributions added from symmetry-equivalent structures, we obtain the expression for RE for the molecule. In the case of benzo[*ghi*]perylene, symmetry-non-equivalent fragments include benzene, naphthalene, and phenanthrene having two, three, and five Kekulé valence structures, respectively. For the case considered, we have the following ring participation in different conjugated circuits: A = (6, 5, 3, 0); B = (10, 4, 0, 0); C = (8, 5, 1, 0); and D = (2, 3, 5, 4). As a result, the sum (2A + 2B + C + D), which gives for the total (42, 26, 12, 4), represents the expression for molecular RE. In the case of cata-condensed benzenoids, Balaban and Tomescu[510,511] derived analytical expressions for the enumeration of conjugated circuits.

For a recent description of efficient algorithms for calculating the contributions of conjugated circuits to the resonance energy expressions of benzenoid hydrocarbons, see the paper by Lin.[512] In this work, Lin considers larger fragments of several fused benzene rings for which one enumerates conjugated circuits. The search for conjugated circuits in a large molecule was then reduced to a search for a selection of characteristic fragments. Such an approach has been previously used by this author,[139] Herndon,[164] Klein and co-workers,[513,514] and Trinajstić and co-workers[515] on smaller benzenoids, while Lin was able to extend the approach to giant benzenoids.

Use of Signed Matrices. The transfer-matrix method, the approaches using recursive relations, and the method based on signed matrices all can be suitably modified to yield the count of conjugated circuits. We will mention only the use of signed matrices for enumeration of conjugated circuits.

Klein and Liu[516] have shown how the method of Kasteleyn, based on signed matrices, can be modified to give the count of conjugated circuits in polymeric systems. The approach has an important advantage in that it gives directly the quotient K_{RN}/K which enters the expression for RE, without the necessity to calculate K_{RN} and K separately. Here, K is the number of Kekulé valence structures and K_{RN} is the number of conjugated circuits of size N ($N = 1$ for conjugated circuits R_1, $N = 2$ for conjugated circuits R_2, etc.). To obtain the count of conjugated circuits, one first inverts the signed matrix $\mathbf{S}$ to obtain $\mathbf{S}^{-1}$. One then selects any circuit in a molecule and calculates the determinant of the minor of the submatrix obtained by considering only the matrix elements between the vertices forming the circuit considered. Klein and co-workers applied this approach to numerous planar carbon networks, most having five- and seven-member rings,[517] and to several thousands of fullerenes (many of which had more than a million Kekulé valence structures).[518]

IX. Approximate Approaches versus Ambitious Computations

> *If, then, the problem of mathematical determination of the properties of simple molecules is in effect solved, the problem of the understanding of the regularities of molecular structure is just opening up.*
>
> Robert G. Parr[519]

We will briefly review various VB approximate methods here and show that the conjugated circuits method can be related to VB approaches and that, therefore, it has a sound quantum chemistry basis. This is needed because later we will relate Clar's π-sextet model to the conjugated circuits model and will show that, therefore, one can justify Clar's empirical approach by quantum chemical arguments.

Pauling and Wheland initiated semi-empirical valence bond (VB) approaches to benzenoid hydrocarbons in 1933.[36] It was soon recognized that solving the problem for large structures is difficult and clearly some simplification was needed. This agrees with the well-known and often cited quotation of Dirac:[47]

> *The underlying physical laws necessary for mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.*

Often, however, the continuation of the quotation is not transmitted, which says:[47]

> *It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex systems without too much computations.*

We underlined the word "explanation" to emphasize that, besides *computations*, there is a part of modeling that necessitates *interpretation* of computations. In 1929, when Dirac wrote his paper on "Quantum Mechanics of Many-Electron Systems" (from which the above quotations were taken), he could not have anticipated the emergence of fast computers that would made it possible to get involved in heavy computations. But "heavy" computations do not eliminate the need for an "*explanation of the main features of complex systems*". True, what was complex in 1929 need not be equally complex a hundred years later, but a hundred years later other complex systems will emerge, to which the above Dirac quotation will apply as it did in 1929. Development of fast computers tends to give an impression or illusion that there are no limits to computational capabilities. In this age of euphoria of computerization, some may have overlooked the fact that, as computers may have no limitations, there is also no limit to the complexity of molecular systems, particularly as we drift into molecular biology and cell biology, not to mention the ultimate complexity of the human brain. This illusion or perception of computers as a tool of unlimited power prompted me to present the following quotation in the format of a question and answer, as a reminder that there are inherent limitations in extending computations to systems of ever increasing complexity.

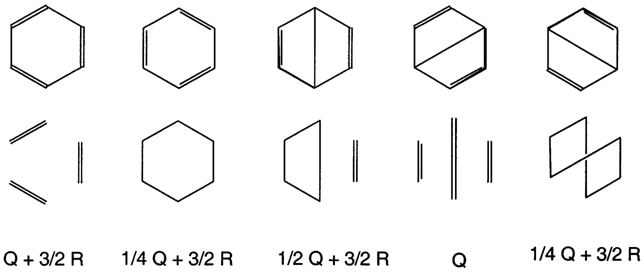


Figure 48. Calculation of VB matrix elements between different canonical structures using the method of "islands" of Pauling.

> *Question: Who can and who cannot tell the difference between Zinfandel and Pinot Noir?*
>
> *Answer: Schrödinger can and Schrödinger Equation cannot.*[520,521]

The above quotation was inspired by a quotation attributed to Joan Gussow,[522,523] "*As for butter versus margarine, I trust cows more than chemists*", which in an elegant way reminds us that there may be some inherent limitations in technical imitations of nature.

A. Semi-empirical Valence Bond Approaches for Benzenoid Hydrocarbons

1. Pauling–Wheland Valence Bond Approach

The Pauling–Wheland valence bond approach is based on considering a set of canonical valence structures for a molecule, known also as Rumer diagrams,[130] in which no crossing of valence lines representing pairing of π-electrons occurs. In the case of benzene, Rumer diagrams are, in fact, the two Kekulé structures and three Dewar structures (Figure 48). The calculation of matrix elements between different canonical structures is carried out by using the method of "islands" described by Pauling.[524] Matrix elements between different canonical structures then reduce to the form

$$1/2^n(qQ + rR)$$

where Q and R are Coulomb and exchange integrals, respectively, and q and r count the occurrence of Q and R terms. In the lower part of Figure 48, we show matrix elements for symmetry-unrelated combinations occurring for benzene canonical forms. For additional introductory details, consult, for example, the textbook by Sandorfy.[525]

The main disadvantage of the Pauling–Wheland valence bond approach is the fast growth of the number of canonical structures to be considered as the sizes of molecules increase. For example, benzocyclobutadiene, which has just two more π-electrons than benzene, has 14 canonical structures, compared to only 5 canonical structures for benzene, while

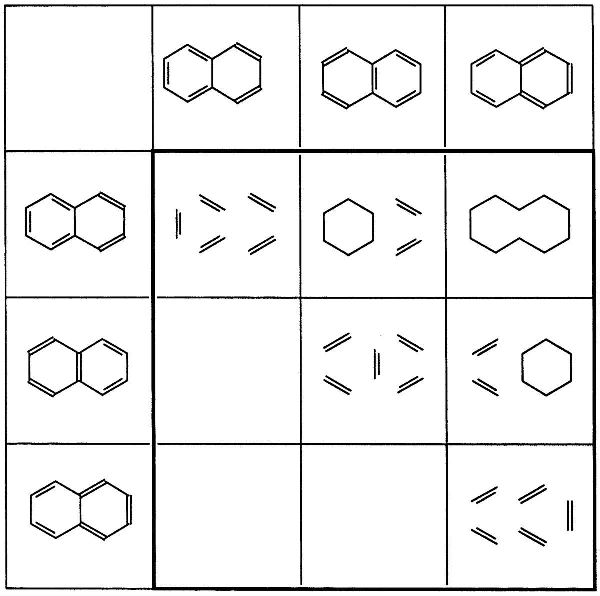


Figure 49. Superposition diagrams for the three Kekulé valence structures of naphthalene.

naphthalene has 42 canonical structures by having only two more π-electrons than pentalene. The numbers 1, 2, 5, 14, 42, 132, 429, 1430, ... are the Catalan numbers, characterized by very fast growth and given by

$$C_n = (2n)!/\{n!(n + 1)!\}$$

They occur in several problems of interest in chemistry,[526−530] particularly in enumeration of so-called "excited" valence structures. They are named after the Belgian mathematician Eugene Charles Catalan (1814−1894), but the 18th century Mongolian scientist Ming Antu had already known these numbers.[531]

2. Pauling–Wheland Resonance Theory

The Pauling−Wheland resonance theory is based on considering Kekulé valence structures only as a basis for quantum chemical computations on benzenoid hydrocarbons. Arguments were outlined which support, at least for the case of benzenoid hydrocarbons,[7,482] the idea of using only Kekulé valence structures as a basis for VB computations. One can speak of Kekulé space, based on Kekulé valence structures of benzenoids, and develop appropriate Kekulé space algebra.[494] Formally, the Pauling−Wheland resonance theory differs from the Pauling−Wheland valence bond approach in that now one is restricting the Rumer diagrams to involve only structures with the nearest-neighbor spin-pairing. As Pauling[524] has shown, the overlap and Hamiltonian matrix elements between different Kekulé structures are conveniently expressed in terms of superposition diagrams obtained by superimposing the π-bonds of a pair of Kekulé structures. In Figure 49 we show superposition diagrams for the three Kekulé valence structures of naphthalene merely to illustrate some distant similarity of such diagrams with both the conjugated circuits and Clar's structures. The superposition matrix is symmetric, and only the elements on and above the main diagonal are shown.

The matrix elements of the Pauling−Wheland resonance theory between Kekulé structures K and K' are given as[7−10]

$$\langle K \mid H \mid K' \rangle = -(3/2)\, J \,\langle K \mid K' \rangle$$

where J is an exchange parameter and $\langle K \mid K' \rangle$ is the overlap integral:

$$\langle K \mid K' \rangle = (1/2)^{N-n-nn}$$

Here, N designates the number of π pairs, n is the number of "small" islands, and nn is the number of "large" islands. Small islands involve a pair of adjacent carbon atoms, and large islands involve cyclic contributions having six or more carbon atoms. For more details, readers should consult relevant publications by Klein and collaborators.[533−537]

3. Herndon–Simpson Model

The Herndon−Simpson model may be viewed as a version of the Pauling−Wheland resonance theory in which overlap between Kekulé structures is ignored (assumed to be zero; alternatively, Kekulé valence structures are viewed as orthogonal). Simpson[169] noticed that the combinations of the ground and excited states of benzene resemble conventional Kekulé valence structures. This led him to interpret such combinations as exact orthogonal Kekulé structures, which led to a simplified version of the VB approach, referred to often as the Herndon−Simpson model. Simpson's model was not recognized at the time as a viable approach to characterization of the stability and aromaticity of benzenoids and most likely would have been totally forgotten. However, Herndon[164−168] developed his resonance theory (which was later found to have formal similarities to Simpson's approach) and was able to show that it gives molecular resonance energies that are as good as one gets from the Dewar and de Llano[45] SCF MO type calculations. The success of Herndon's resonance theory resurrected Simpson's approach and showed that a simple theory, if it involves the crucial structural elements, can sometimes work as well as quite sophisticated models. The validity of such a philosophy has been recognized and much expounded upon by the late Professor C. A. Coulson, as is evident from quotations given in ref 538.

4. Hierarchical VB Schemes

Hierarchical VB schemes are illustrated in Figure 50 on the left. The diagram represents a modification of a similar diagram representing the hierarchical relationship between different VB models considered by Klein et al.[7,534] At each successive step, a model with additional computational simplifications is introduced, but not necessarily at the expense of precision. We have listed as the last variant of the parametrized VB model the Herndon and Hosoya[539] model, which considers as the basis not Kekulé valence structures but Clar-type valence structures (that will be outlined later in greater length). Is it

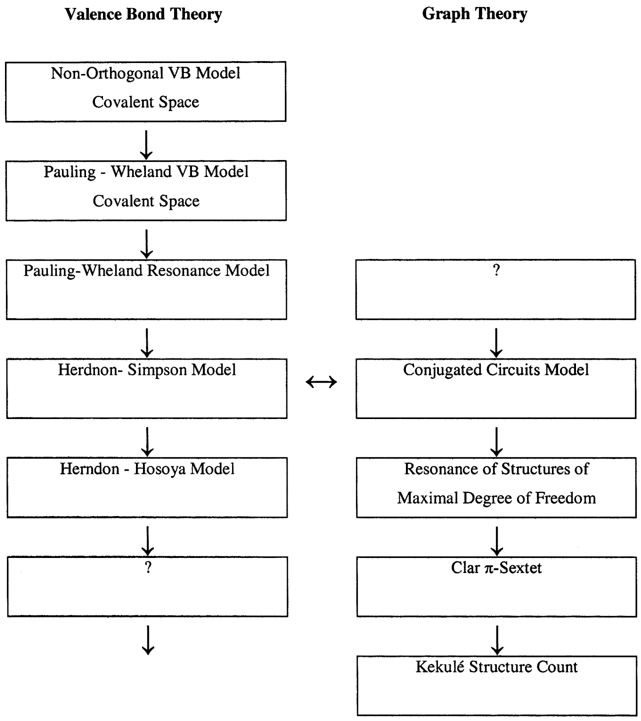


Figure 50. Diagram representing the hierarchical relationship between different VB models (based on the work of Klein et al.[7,534]).

possible to have a still simpler, essentially VB approach than that of Herndon and Hosoya?

In parallel to the VB hierarchical relationship of different models shown on the right-hand side of Figure 50, we depicted a similar hierarchical relationship for several graph theoretical approaches, starting with the conjugated circuits model as the central and historically the first VB-type graph theoretical model. The conjugated circuits model, as has been recognized by Herndon,[540] and Schaad and Hess,[541,542] can be cast in a format that is mathematically equivalent to the Simpson–Herndon VB approach. We have also pointed out in several publications that the mathematical formulations of the structure–resonance theory put forth by Herndon and the conjugated circuits approach are practically identical, "*since resonance integrals are enumerated by a procedure that involves a sequential deletion of each conjugated circuit from the molecular π graph of the molecule under consideration.*[164]"[540] Herndon also pointed out the apparent relationship between both methods and the "island" procedure described by Eyring and Kimball,[543,544] and Pauling.[524] In the middle of Figure 50, we have indicated with a horizontal bi-directional arrow the close relationship between the two approaches. The mathematical equivalence between two models, however, does not mean that the approaches are conceptually equivalent. The Herndon–Simpson model is a variant of the VB method, hence a quantum chemical method, while the conjugated circuits method is of combinatorial and graph theoretical origin. We end this section by quoting a brief summery by D. J. Klein concerning the hierarchical scheme for valence bond theoretical models, illustrated in Figure 50:[545]

> *There are other motivational derivations, including the elegant existential quantum-mechanical motivation of Simpson*[169] *and Herndon,*[164] *and the independent lucid chemical graph-theoretical motivation of Milan Randić.*[51] *But as we believe is pedagogically important there is a more traditional quantum-chemical derivation*[9,546,547] *via the Pauling–Wheland*[36,548] *valence bond model, which in turn derives from the usual Schrödinger equation in a sequence of steps, as indicated in Figure 45 with details elsewhere.*[7,9] *The scheme is seen to exhibit proper many-body size-extensivity for energies, with the present conjugated-circuit formulas being obtained as Hamiltonian expectation (for a reasonable wavefunction ansatz).* (Reference numbers have been changed to correspond to the numbering in the current review.)

X. Conjugated Circuits Model

> *Conjugated circuit theory shares with Hückel theory the feature that it can be completely evaluated from the graph of a molecule. Starting from Kasteleyn's result that the determinant of an appropriately signed adjacency matrix gives the square of the number of Kekulé structures, it is possible to show that counting conjugated circuits just involves evaluating appropriate small minors of the inverse of the adjacency matrix. Conjugated circuit computations are thus not significantly more time consuming than ordinary Hückel calculations. We have found that they are much more sensitive than Hückel calculations ...*
>
> T. G. Schmalz and D. J. Klein[549]

Conjugated circuits are structural invariant and, as such, can serve for characterization of individual Kekulé valence structures, for characterization of local aromaticity, as well as for characterization of conjugated compounds as a whole. For example, for the 10 symmetry-non-equivalent Kekulé valence structures of benzo[*ghi*]perylene, we obtain the characterization shown in the column labeled "Kekulé structure code" in Table 12, already depicted in Figure 46. Hence, the Kekulé structure code is simply an enumeration of conjugated circuits within a Kekulé valence structure. The overall molecular characterization is obtained by summing the contributions from individual Kekulé valence structures. In the next column of Table 12, we give the expressions for the contributions to molecular RE for individual Kekulé valence structures. By adding the contributions of all Kekulé structures, we obtain the expression for molecular RE for the molecule, as shown in the last row of Table 12. The numerical values for molecular RE as well as contributions of individual Kekulé valence structures were obtained by using a parametrization of the contributing R_1, R_2, and R_3 based on SCF MO calculation (expressed in electronvolts) (vide infra).

We see from Table 12 that, although initially all Kekulé valence structures were assumed to have the same weight, they make visibly different contribu-

Table 12. Contributions of Various Kekulé Valence Structures of Benzo[*ghi*]perylene (Shown in Figure 46) to Molecular Resonance Energy (RE)

structure	(R_1, R_2, R_3, R_4)	contribution to RE	numerical value
A	5, 0, 0, 1	$(5R_1 + R_4)/14$	0.291
B, C	4, 1, 1, 0	$(4R_1 + R_2 + R_3)/14$	0.263
D	4, 0, 2, 0	$(4R_1 + 2R_3)/14$	0.250
E	3, 3, 0, 0	$(3R_1 + 3R_2)/14$	0.239
F, G	3, 2, 1, 0	$(3R_1 + 2R_2 + R_3)/14$	0.226
H	3, 2, 1, 0	$(3R_1 + 2R_2 + R_3)/14$	0.226
I, J	3, 2, 0, 1	$(3R_1 + 2R_2 + R_4)/14$	0.218
K, L	2, 3, 1, 0	$(2R_1 + 3R_2 + R_3)/14$	0.190
M	2, 2, 1, 1	$(2R_1 + 2R_2 + R_3 + R_4)/14$	0.168
N	1, 3, 2, 0	$(R_1 + 3R_2 + 2R_3)/14$	0.140
molecule[a]	42, 26, 12, 4	$(42R_1 + 26R_2 + 12R_3 + 4R_4)/14$	3.107

[a] The last row gives the expression for molecular RE.

tions to the molecular RE. The situation is similar to simple computations of HMO and VB methods. For example, in the HMO approach one assumes all CC bonds to be of equal length, but as a result of calculations, one obtains different Coulson's bond orders (and similarly different Pauling bond orders) for different bonds. In such a situation, one may consider an iterative procedure that would result in internal consistency between the assumed and the resulting CC bond lengths. In analogy, the same approach can be applied to conjugated circuits and molecular RE by weighting individual Kekulé valence structures so that, in the result, the computed weights agree with those assumed in the calculations. Hence, instead of "bond orders" we would have "Kekulé structure orders". After a close look at the expressions and the numerical values for various Kekulé valence structures of benzo[*ghi*]perylene, one can notice that the first Kekulé valence structure shown in Figure 15, the Fries structure, makes the dominant contribution to the molecular RE. In fact, the first eight structures, all of which have $df = 3$, make the largest contributions to RE. The next important contributions come from Kekulé valence structures having $df = 2$, and finally the smallest contribution comes from the last, the "anti-Fries" valence structures, having $df = 1$.

A. Monocyclic Conjugated Systems

The great success of the Hückel MO method was not in quantitative predictions of molecular UV spectra, or in predicting variations in CC bond lengths or NMR chemical shifts, but in that it offered insights on the stability of $4n + 2$ monocyclic conjugated systems while predicting instability for $4n$ monocyclic conjugates systems. These predictions have been well justified with, on one side, a synthesis of [18]annulene and related compounds[550,551] and, on the other side, the elusiveness of the synthesis of cyclobutadiene. We can view as a great success of the VB method the postulate of Clar, that no polycyclic conjugated system can exist unless it possesses a Kekulé valence structure. Finally, we add as an outstanding successes of the GT method (graph theory) the prediction of stability of systems having only $4n + 2$ conjugated circuits while predicting reduced stability for systems having, in addition to $4n + 2$, also $4n$ conjugated circuits. The above GT result represents a true extension of the Hückel $4n + 2$ rule from monocyclic to polycyclic systems.

B. Polycyclic Conjugated Systems

For benzenoid hydrocarbons like naphthalene, anthracene, and phenanthrene, there is general agreement, between different approaches to aromaticity, that these molecule are aromatic and rather stable. Difficulties arise with polycyclic conjugated systems for which simple MO, simple VB, simple free-electron model, and graph theory may disagree. First, we should mention that simple calculations of these kinds of molecules need not give reliable results. Molecules having odd-member rings (non-alternants for which the starring process of Coulson and Rushbrooke[552] cannot be carried through) have a nonuniform distribution of charge on various carbon atoms. For such systems, simple theoretical treatments like the HMO method turn out not to be computationally consistent.

Hafner and Schneider[553,554] synthesized a dimethyl derivative of aceheptylene (which is build by fusing a five-member ring with two seven-member rings, the three rings having a single central common carbon atom). On the basis of the properties of the compound (deep red color, spectrum in the visible region resembling that of azulene though displaced to even longer wavelengths, solubility in 50% sulfuric acid, undergoing acylation by a Friedel–Crafts reaction), Hafner and Schneider concluded that aceheptylene is aromatic. A superficially related molecule, cyclopent[*cd*]azulene, also built from three fused odd-member rings, two five-member rings and one seven-member ring, by contrast lacks the stability and aromaticity of aceheptylene. It undergoes dimerization and shows reactions that have some similarity to those of dibenzpentalene. Clearly, the two molecules show considerable differences in their properties, and the second one is definitely less aromatic, but does this makes the first one aromatic? Asgar Ali and Coulson[555] considered the properties of Hafner's new heptalene and pentalene derivative from the theoretical point of view. In the abstract of their paper, they state: "*All agree that I (aceheptylene) should be genuinely aromatic, and II (cyclopent-[c,d]azulene) should not*."[555] Well, that may have been the case then, but it is not quite true now, as we do not agree that aceheptylene is "genuinely aromatic", though it may be "aromatic" to a degree. A close look at the Kekulé valence structures of aceheptylene show that there are present in this molecule 4*n* conjugated circuits involving two seven-member rings. We do agree that there is considerable difference between *I* and *II* and agree that *II* should not be viewed as aromatic as aceheptylene is. The difference between *I* and *II* is that, while both molecules have destabilizing 4*n* conjugated circles, in the case of *I* we have 12 π-conjugated circuits while in *II* we have conjugated circuits involving eight π-electrons. Smaller 4*n* conjugated circuits have greater destabilizing antiaromatic contributions in comparison with molecules having larger 4*n* conjugated circuits. When referring to aceheptylene, we agree that it is more aromatic than *II*, but we would like to reserve the label "genuinely aromatic" for polycyclic conjugated hydrocarbons having *only* $4n + 2$ conjugated circuits (vide infra). On this ground we agree that compounds like azupyrene and *as*-azupyrene, which are related to Hafner's aceheptylene and cyclopent[*c*,*d*]azulene, may deserve "*the designation aromatic*",[556,557] but according to our analysis of their conjugated circuits, the label "genuinely aromatic" is better kept for compounds having only $4n + 2$ conjugated circuits.

XI. Expression for Molecular Resonance Energy

> *By following well laid paths some forgotten flower may be gathered, but nothing essentially new will be found.*
>
> A. Kekulé[558]

Molecular resonance energy (RE) is generally accepted as a valid indication of the "extra" stability of cyclic systems compared to hypothetical acyclic systems having the same structural components. Conjugated circuits turn out to be among the most important structural components of Kekulé valence structures because they lead to expressions for the molecular RE. Recall the ambiguities associated with the calculation of RE in MO approaches, in that one has to choose between various standards, several of which may be equally plausible. Trinajstić and coworkers,[99,100] and Aihara,[101] elegantly solved the problem of selecting a RE standard, as already mentioned, for MO theories. Their approach, although it was illustrated on Hückel molecular orbitals, applies equally to other MO models in which electron interaction is represented by a single Hamiltonian matrix. The difference between the HMO and some other MO models can be viewed as introducing different weights to different CC bonds in the HMO model.

We should also mention a scheme attributed to Jiang, Tang, and Hoffmann,[559] in which the π-electron energy of the acyclic reference system is based on bond additivity:

$$E_\pi(\text{reference}) = n_{12}E_{12} + n_{13}E_{13} + n_{22}E_{22} + n_{23}E_{23} + n_{33}E_{33}$$

where E_{ij} is the π-electron energy for a bond $i-j$, in which the labels *i* and *j* indicate the degrees *i* and *j*, and n_{ij} is the number of such bonds in the reference structure. Bartell[560] has considered CC bond additivity of RE and has shown that such a scheme can account for the major trends in RE. Similarly, Aida and Hosoya,[561] Gutman,[562] and Herndon[563] considered the ring additivity of RE by differentiating benzene rings on the basis of their immediate environments. The conjugated circuits approach, one can say, represents a "fine-tuning" of the bond and ring RE additivity, replacing the crude bond and ring additivities, which give only approximate results, with the conjugated circuit additivity, which gives an exact expression for RE.

XII. Benzenoids: Systems with Only $4n + 2$ Conjugated Circuits

Conjugated circuits offer an elegant solution to ambiguities concerning the definition of RE for various VB models. In the case of benzenoid hydrocarbons, the decomposition of Kekulé valence structures in conjugated circuits eventually leads to an expression of the form RE = $(n_1R_1 + n_2R_2 + n_3R_3 + ...)/K$, where n_1, n_2, n_3, ... give the count of conjugated circuits R_1, R_2, R_3, ..., respectively, and K is the number of Kekulé valence structures of the molecule. It is known that benzenoid hydrocarbons can have only $4n + 2$ conjugated circuits. The expression for RE in fact represents the conjugated circuit content of the "average Kekulé structure".

In Table 13, under the heading "RE expression", we show the decomposition of Kekulé valence structures for a dozen smaller benzenoid hydrocarbons for which Dewar and de Llano[45] calculated SCF MO resonance energies. By using the computed RE values of Dewar and de Llano[45] obtained from the SCF MO method, one can determine the relative roles of conjugated circuits R_1, R_2, and R_3, which can be viewed as undetermined parameters in a multivariate linear regression. One obtains a correlation of very respectable quality, as evidenced by the high regression coefficient ($r = 0.9993$), the low standard error ($s = 0.029$), and the high Fisher ratio ($F = 2270$). In Table 14, in row 3, we have listed the coefficients of the regression equation (including the constant term, which is almost negligible). As we can see, the largest contribution to molecular RE comes from the smallest conjugated circuits, R_1. As the size of the conjugated circuits increases, their contribution to RE decreases by a factor of approximately 1/3. By using $R_1 = 0.815$ eV, $R_2 = 0.302$ eV, and $R_3 = 0.085$ eV, we obtained the RE for smaller benzenoids, as shown in Table 13.

The agreement between the SCF MO resonance energies and the RE obtained from the regression equation is outstanding. This result is remarkable if one takes into consideration the fact that conjugated circuits were found "accidentally" and had no prior connection to quantum chemical considerations. In Figure 51 we show the linear correlation between the graph theoretically computed RE and the Dewar and de Llano SCF MO resonance energies. The message that Figure 51 gives is that conjugated circuits represent an important structural component and that the *average Kekulé valence structure* offers a valid representation of benzenoid hydrocarbons. For

Table 13. Expressions for Molecular RE for Smaller Benzenoids, the SCF MO Computed RE, and the Graph Theoretical RE[a]

benzenoid	RE expression	SCF	RE(calcd)	residual
benzene	$(2R_1)/2$	0.869	0.864	0.002
naphthalene	$(4R_1 + 2R_2)/3$	1.323	1.324	−0.016
anthracene	$(6R_1 + 4R_2 + 2R_3)/4$	1.600	1.618	−0.018
tetracene	$(8R_1 + 6R_2 + 4R_3)/4$	1.822	1.752	+0.070
phenanthrene	$(10R_1 + 4R_2 + R_3)/5$	1.933	1.940	−0.007
pyrene	$(12R_1 + 8R_2 + 4R_3)/6$	2.098	2.141	−0.043
benzanthracene	$(16R_1 + 8R_2 + 3R_3)/7$	2.291	2.296	−0.005
chrysene	$(20R_1 + 10R_2 + 2R_3)/8$	2.483	2.488	−0.005
benzo[*a*]pyrene	$(22R_1 + 14R_2 + 7R_3)/9$	2.594	2.579	+0.015
perylene	$(24R_1 + 12R_2)/9$	2.619	2.628	−0.009
triphenylene	$(26R_1 + 6R_2 + 3R_3)/9$	2.654	2.636	+0.018
benzo[*d*[pyrene	$(32R_1 + 14R_2 + 7R_3)/11$	2.853	2.861	−0.008
dibenz[*a*,*h*]anthracene	$(36R_1 + 8R_2 + 6R_3)/12$	2.948	2.942	+0.006
benzo[*ghi*]perylene	$(42R_1 + 26R_2 + 12R_3)/14$	3.128	3.130	−0.002

[a] The contributions of conjugated circuits R_1, R_2, and R_3 were obtained from multiple regression with the SCF MO resonance energies.

Table 14. Statistical Data for a Stepwise Regression of SCF MO Resonance Energies and Parameters R_1, R_2, and R_3[a]

	R_1	R_2	R_3	const	r	s	F
1	0.9693			0.0744	0.9831	0.1249	346
2	0.8151	0.3403		0.0427	0.9990	0.0327	2 614
3	0.8153	0.3017	0.0848	0.0513	0.9993	0.0286	2 270
4	0.8359	0.2747	0.0929	0.0254	0.99984	0.0137	9 660
5	0.8291	0.2794	0.1042	0.0337	0.99994	0.0093	20 587
6	0.8352	0.2720	0.0997	0.0288	0.99999	0.0034	142 516

[a] Rows 4−6 give data for cases when one, two, and four “outliers” were removed from regression.

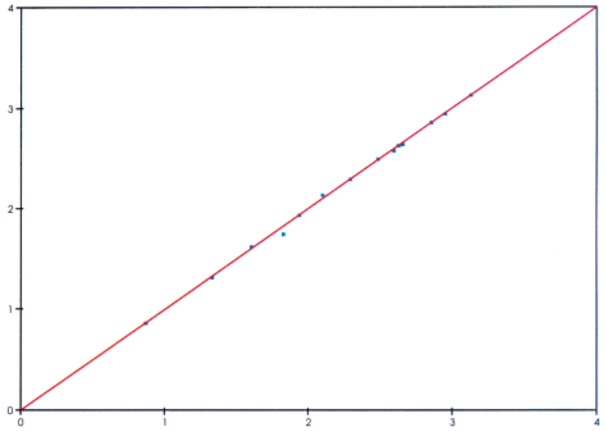


Figure 51. Linear correlation between the graph theoretically derived RE and the Dewar and de Llano SCF MO resonance energies.

several of the benzenoids listed in Table 13, we have depicted in Figure 52 their alternative pictorial representation based on the expressions for the average Kekulé valence structure, as derived from the count of conjugated circuits R_1, R_2, and R_3. The inscribed fractions are the coefficients of the average Kekulé structure in the expression for molecular RE as shown in Table 13. As we can see from Figure 52, in this model perylene is simply characterized as two naphthalene molecules, because there are no conjugated circuits involving the central ring that would combine the two naphthalene moieties that are separated by the essentially single CC bonds.

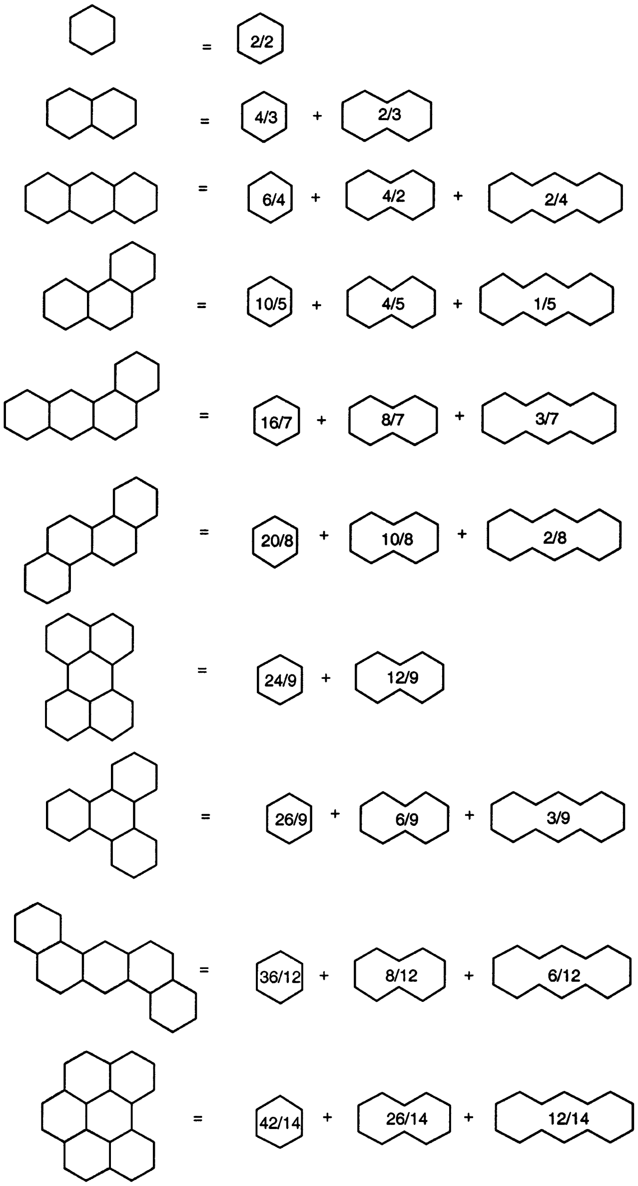


Figure 52. Pictorial representation of the benzenoids of Table 13, based on the count of conjugated circuits R_1, R_2, and R_3.

Additional Benzenoid Systems. Having thus a *recipe* for calculating molecular RE, we are in a position to find the RE for arbitrary benzenoid and non-benzenoid hydrocarbons. In Table 15 we have

Table 15. Expressions for Molecular RE for the Benzenoid Hydrocarbons Shown in Figure 53

molecule	RE expression	RE (eV)	REPE	RE (J)	REPE
1/53	$(2R_1)/2$	0.869	0.145	0.3034	0.0506
2/53	$(4R_1 + 2R_2)/3$	1.323	0.132	0.4519	0.0452
3/53	$(6R_1 + 4R_2 + 2R_3)/4$	1.600	0.114	0.5765	0.0412
4/53	$(10R_1 + 4R_2 + R_3)/5$	1.955	0.140	0.6403	0.0457
5/53	$(8R_1 + 6R_2 + 4R_3)/5$	1.766	0.098	0.6983	0.0388
6/53	$(16R_1 + 8R_2 + 3R_3)/7$	2.311	0.128	0.7763	0.0431
7/53	$(20R_1 + 10R_2 + 2R_3)/8$	2.506	0.139	0.8168	0.0454
8/53	$(26R_1 + 6R_2 + 3R_3)/9$	2.708	0.150	0.8549	0.0475
9/53	$(12R_1 + 8R_2 + 4R_3)/6$	2.133	0.133	0.7237	0.0452
10/53	$(10R_1 + 8R_2 + 6 R_3)/6$	1.876	0.085	0.8207	0.0373
11/53	$(22 R_1 + 12 R_2 + 7R_3)/9$	2.531	0.115	0.9010	0.0410
12/53	$(26R_1 + 16R_2 + 5R_3)/10$	2.705	0.123	0.9157	0.0416
13/53	$(36R_1 + 16R_2 + 6R_3)/12$	2.986	0.136	0.9723	0.0442
14/53	$(30R_1 + 18R_2 + 6R_3)/11$	2.828	0.129	0.9529	0.0433
15/53	$(40R_1 + 20R_2 + 5R_3)/13$	3.092	0.141	1.0004	0.0455
16/53	$(42R_1 + 14R_2 + 5R_3)/13$	3.111	0.141	0.9980	0.0454
17/53	$(46R_1 + 18R_2 + 5R_3)/14$	3.209	0.146	1.0242	0.0466
18/53	$(32R_1 + 14R_2 + 7R_3)/11$	2.906	0.145	0.9401	0.0470
19/53	$(22R_1 + 14R_2 + 7R_3)/9$	2.585	0.129	0.8890	0.0445
20/53	$(36R_1 + 24R_2 + 14R_3)/13$	2.970	0.124	1.0519	0.0438
21/53	$(24R_1 + 18R_2 + 12R_3)/10$	2.650	0.120	0.9638	0.0438
22/53	$(42R_1 + 26R_2 + 12R_3)/14$	3.150	0.143	1.0469	0.0476
23/53	$(96R_1 + 34R_2 + 12R_3)/24$	3.876	0.149	1.2253	0.0471
24/53	$(64R_1 + 48R_2 + 27R_3)/20$	3.509	0.146	1.1871	0.0495
25/53	$(76R_1 + 24R_2 + 14R_3)/20$	3.669	0.153	1.1560	0.0482
26/53	$(192R_1 + 48R_2 + 12R_3)/40$	4.498	0.150	n/a[a]	
27/53	$(56R_1 + 40R_2 + 22R_3)/18$	3.375	0.130	1.1846	0.0456
28/53	$(140R_1 + 90R_2 + 46R_3)/35$	4.243	0.141	n/a	
29/53	$(48R_1 + 32R_2 + 16R_3)/16$	3.201	0.114	1.2445	0.0445
30/53	$(108R_1 + 78R_2 + 49R_3)/30$	3.934	0.131	n/a	

[a] n/a = not available.

collected the expressions for RE for the 30 smaller benzenoid hydrocarbons depicted in Figure 53. We calculated RE and REPE (resonance energy per electron) using the following parameters (all in eV): $R_1 = 0.869$, $R_2 = 0.247$, and $R_3 = 0.100$, assuming contributions from larger conjugated circuits to be negligible. As expected, the molecular RE increases with the size of the molecules. If one is interested in comparing molecules of different size, then REPE, the RE per π-electron, is of more interest, as Hess and Schaad pointed out.[564] REPE values for the benzenoids shown in Figure 53 may be as high as 0.153 for dibenzopyrene (**25/53**), and as low as 0.085 for pentacene (**10/53**). Observe that some calculated REPE values are even slightly higher than the REPE of benzene. Besides dibenzopyrene (**25/53**), triphenylene (**8/53**) and tetrabenzantrhacene (**26/53**) also have large REPE, all three molecules being Clar's "fully benzenoid" hydrocarbons, the Clar structures of which have only aromatic π-sextets and "empty" rings and no rings with CC double bonds. The low REPE value for pentacene reflect the known fact that the stability of linear acenes, molecules built from linearly fused benzene rings, steadily decreases. In Table 16 we have collected the RE and REPE for linearly fused benzene systems having from 2 (naphthalene) to 10 fused rings. In view of the fact that the largest known linearly fused benzenoid hydrocarbon has 8 rings, we see that a REPE of approximately 0.060 is apparently the low boundary for a molecule to exist. This amounts to about two-thirds of the REPE value for benzene. With this insight, we can supplement Clar's postulate, that conjugated systems for which one cannot draw Kekulé valence structure do not exist, by adding the following:

Postulate: *Conjugated systems for which one can write Kekulé valence structure but locally REPE is less than two-thirds of the value for benzene will not exist (will not be stable).*

We had to add the attribute "locally" in order to eliminate structures in which the average REPE may be above the limiting value of approximately 0.060 eV but in which some fragments have a value below 0.060 eV and some have a value above 0.060 eV. A close look at Table 15 shows additional regularities concerning the relative values of REPE among different benzenoid hydrocarbons. For example, we find that benzenoid hydrocarbons having a single Clar structure tend to have above-average REPE values. Thus, for example, phenanthrene (**4/53**), the Clar structure of which has two π-sextets and a ring with an isolated CC double bond, has a REPE of 0.140, and tetrabenzonaphthalene (**23/53**) has a REPE of 0.146.

In the last two columns of Table 15, we show RE and REPE for 30 benzenoids, as calculated by Jiang and Li, who recently reported RE and REPE values for 89 medium-sized benzenoid hydrocarbons.[37] Their work represents accurate VB calculations based on the use of all Rumer diagrams (that is, all valence bond structures in which there is non-crossing of π-electron couplings). The values of Jiang and Li are expressed in units of J (which is the absolute value of the exchange integral). In Figure 54 we show a linear regression of REPE (J) against REPE (eV), that is, REPE as calculated by the accurate VB

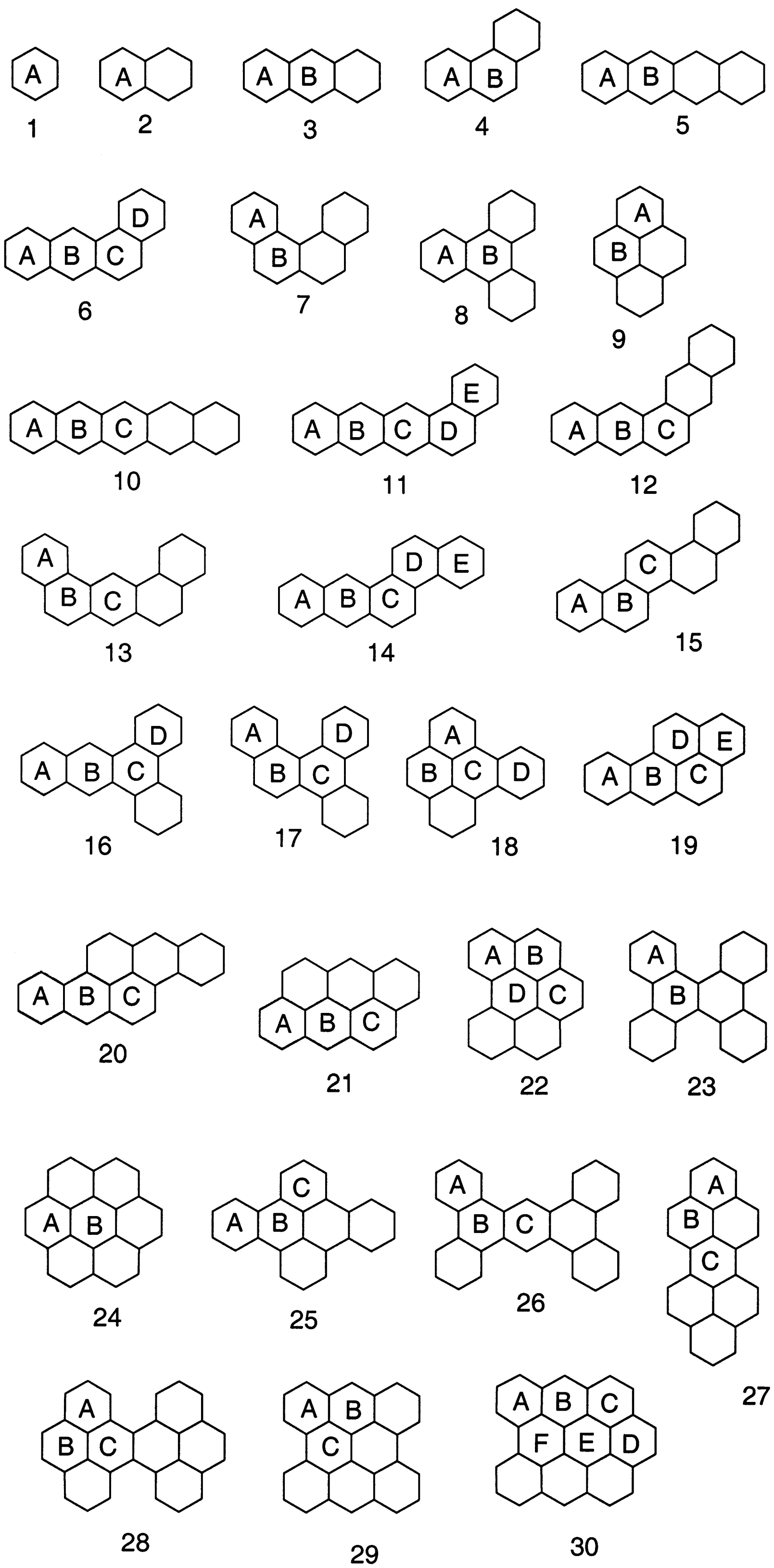


Figure 53. Thirty smaller benzenoid hydrocarbons for which RE values are listed in Table 15. Labels for symmetry-non-equivalent rings are included for a discussion of local aromaticity in a later part of the review.

approach of Jiang and Li versus REPE based on parametrized values of conjugated circuits' contributions R_1, R_2, and R_3 (based on the SCF MO calculations of Dewar and DeLano). Overall, as we can see from Figure 54, the agreement between the two sets of REPE values is quite satisfactory. The regression coefficient is $r = 0.911$, standard error $s = 0.0013$, and Fisher ratio $F = 122.2$. From Table 15, we see that three of the compounds shown in Figure 54 show a large deviation from the regression line. They are benzene, coronene (**24/53**), and bisanthene (**29/53**). Several factors can cause differences in the calculated

Table 16. RE and REPE for Linearly Fused Benzene Systems Having $N = 2-10$ Fused Rings

N	R_1, R_2, R_3	K	n	RE (eV)	REPE
2	4, 2, 0	3	10	1.323	0.132
3	6, 4, 2	4	14	1.601	0.114
4	8, 6, 4	5	18	1.767	0.098
5	10, 8, 6	6	22	1.878	0.085
6	12, 10, 8	7	26	1.957	0.075
7	14, 12, 10	8	30	2.016	0.067
8	16, 14, 12	9	34	2.062	0.061
9	18, 16, 14	10	38	2.099	0.055
10	20, 18, 16	11	42	2.130	0.051

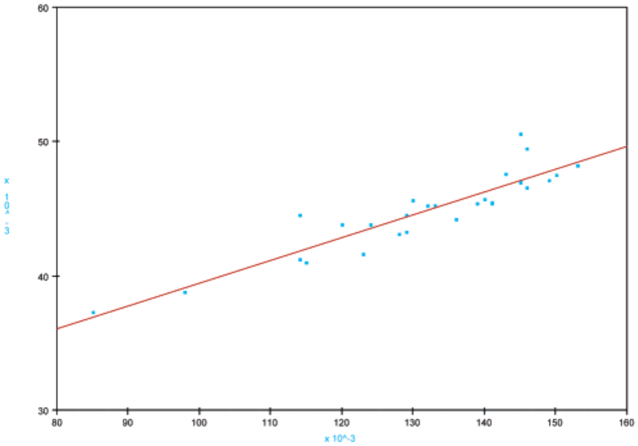


Figure 54. Linear regression of REPE, as calculated by Jiang and Li[37] (in units of J), and REPE, as derived from the conjugated circuits model (in units of electronvolts), for 27 of the benzenoids shown in Figure 53.

REPE values between the two models, besides the differences due to the different formalism of the underlying quantum chemical calculations. One is the difference due to the assumption of an acyclic reference structure, made by Jiang and Li. One of characteristics of their approach is the bond additivity approach to RE. As a consequence, compounds like bisanthene, in which the central CC bonds are essentially single, may show a larger departure from REPE values based on conjugated circuits, in which such bonds do not make contributions. A full comparison of the REPE values calculated by Jiang and Li and those computed from the conjugated circuits shows some discrepancies that have yet to be understood. For example, the conjugated circuits model always predicts fully benzenoid Clar's hydrocarbons to have the largest REPE value, but this is not the case with the REPE values Jiang and Li computed for medium-sized benzenoids. According to Jiang and Li, the highest value of REPE belongs to benzene, but the next highest value belongs to a coronene (**24/53**), which is not a "fully benzenoid Clar's hydrocarbon". Among four benzenoid hydrocarbons for which Jiang and Li found the highest REPE, we find two fully benzenoid hydrocarbons, dibenzopyrene (**25/53**) and triphenylene (**8/53**), to rank as third and sixth, respectively, after benzene. The conjugated circuits model ranks dibenzopyrene and triphenylene ahead of benzene; in fact, the two benzenoid hydrocarbons are found to have the highest REPE values, 0.153 and 0.150 eV, respectively, while the values for coronene and benzene are 0.146 and 0.145 eV, respectively.

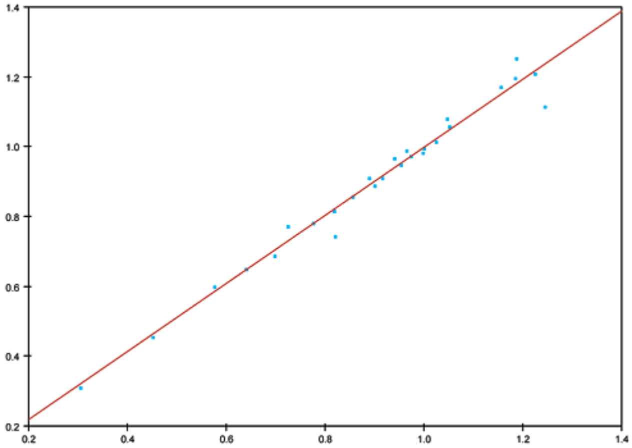


Figure 55. Linear regression of RE, as calculated by Jiang and Li[37] (in units of J), and RE, obtained from the conjugated circuits model (with $R_1 = 0.2277J$, $R_2 = 0.1008J$, and $R_3 = 0.1472J$) for 27 of the benzenoid hydrocarbons shown in Figure 53.

In order to compare the results of Jiang and Li with those based on the conjugate circuits model, we show in Figure 55 regression of RE as calculated by Jiang and Li and as obtained by reparametrizing the conjugated circuits contributions R_1, R_2, and R_3 using their computed REPE values. The regression is characterized by the following statistical parameters: $r = 0.9876$, $s = 0.0385$, and $F = 303.2$, while the computed contributions for R_1, R_2, and R_3, respectively, are

$$R_1 = 0.2277J \qquad R_2 = 0.1008J \qquad R_3 = 0.1472J$$

Observe first that, according to these VB calculations, the relative contributions of the conjugated circuits R_1, R_2, and R_3 have visibly changed. We see that now 14-π-electron conjugated circuits play a more prominent role than 10-π-electron conjugated circuits, which is contrary to expectations. It is difficult to assess, without detailed analysis, to what extent this may be an artifact of the selection of the standard used for calculation of RE in the VB computations of Jiang and Li and to what extent it is a result of possible differentiation of 14-member conjugated circuits of different shapes, or a result of neglecting contributions from higher order conjugated circuits.

Let us return to the four benzenoids shown in Figure 26, which all have the same number of Kekulé valence structures, for which the simple proportionality RE = $k \log K$ would predict identical RE. The count of conjugated circuits for those four benzenoids is given in Table 17. As we can see from Table 17, among the four compounds, the cata-condensed benzenoid has the largest number of contributing R_1, which may suggest that this compound would have largest the RE. However, the cata-condensed benzenoid also has many large conjugated circuits, which make little, if any, contribution to the RE. It is therefore not surprising to see that this compound has the smallest RE. Moreover, because it has two more carbon atoms than the three peri-condensed benzenoids, its REPE is visibly smaller than the REPE of the remaining compounds. From the same table, we can see that the last two compounds have

Table 17. Expressions for Molecular RE for the Four Benzenoid Hydrocarbons Shown in Figure 26, Which All Have the Same Number of Kekulé Valence Structures

molecule		RE expression	RE[a]	REPE
1/26	$C_{30}H_{16}$	$(74R_1 + 30R_2 + 21R_3 + 13R_4 + 5R_5 + 3R_6 + R_7)/21$	3.477	0.1159
			3.376*	0.1125*
2/26	$C_{28}H_{16}$	$(72R_1 + 40R_2 + 22R_3 + 10R_4 + 3R_5)/21$	3.555	0.1270
			3.493*	0.1248*
3/26	$C_{28}H_{16}$	$(72R_1 + 42R_2 + 21R_3 + 9R_4 + 3R_5)/21$	3.573	0.1276
			3.516*	0.1256*
4/26	$C_{28}H_{16}$	$(70R_1 + 48R_2 + 23R_3 + 5R_4 + R_5)/21$	3.571	0.1275
			3.536*	0.1263*

[a] $R_1 = 0.869$, $R_2 = 0.247$, $R_3 = 0.100$, $R_4 = R_5 = R_6 = R_7 = 0$. $R_1^* = 0.815$, $R_2^* = 0.302$, $R_3^* = 0.118$.

Table 18. Expressions for Molecular RE for the Benzenoids Shown in Figure 56

molecule	RE expression	RE[a]	RE/ring	REPE
1/56	$(10R_1 + 8R_2 + 6R_3 + 4R_4 + 2R_5)/6$	1.878	0.376	0.0853
2/56	$(22R_1 + 12R_2 + 7R_3 + 3R_4 + R_5)/9$	2.531	0.506	0.1151
3/56	$(36R_1 + 16R_2 + 6R_3 + 2R_4)/12$	2.986	0.597	0.1357
4/56	$(12R_1 + 10R_2 + 8R_3 + 6R_4 + 4R_5 + 2R_6)/7$	1.957	0.326	0.0753
5/56	$(28R_1 + 16R_2 + 11R_3 + 7R_4 + 3R_5 + R_6)/11$	2.671	0.445	0.1027
6/56	$(52R_1 + 24R_2 + 12R_3 + 6R_4 + R_5)/16$	3.270	0.545	0.1258
7/56	$(58R_1 + 22R_2 + 13R_3 + 5R_4 + 3R_5 + R_6)/17$	3.361	0.560	0.1293
8/56	$(76R_1 + 24R_2 + 14R_3 + 6R_4)/20$	3.669	0.611	0.1411
9/56	$(52R_1 + 28R_2 + 10R_3 + 4R_4 + 2R_5)/16$	3.319	0.553	0.1277
10/56	$(56R_1 + 40R_2 + 22R_3 + 8R_4)/18$	3.375	0.482	0.1298
11/56	$(192R_1 + 48R_2 + 26R_3 + 12R_4 + 2R_5)/40$	4.533	0.648	0.1511
12/56	$(140R_1 + 90R_2 + 46R_3 + 42R_4)/35$	4.243	0.530	0.1414
13/56	$(228R_1 + 168R_2 + 100R_3 + 40R_4 + 4R)/54$	4.623	0.462	0.1284
14/56	$(212R_1 + 80R_2 + 47R_3 + 21R_4)/45$	4.638	0.580	0.1546
15/56	$(120R_1 + 76R_2 + 40R_3 + 12R_4)/31$	4.098	0.512	0.1576
16/56	$(568R_1 + 236R_2 + 142R_3 + 64R_4)/101$	5.603	0.560	0.1648

[a] $R_1 = 0.869$, $R_2 = 0.247$, $R_3 = 0.100$, $R_4 = R_5 = 0$.

the largest RE. We included results for RE based on two alternative parametrizations of the contributing conjugated circuits R_1, R_2, and R_3. Observe that, because the two compounds differ in the number of R_1 and R_2 conjugated circuits, slightly different parametrizations can reverse the relative magnitudes of their RE values (as shown with the RE* values of Table 17). The difference in RE between the two compounds is $(2R_1 - 6R_2 - 2R_3)/21$, which is almost zero (being 0.0027 and 0.0084 eV, respectively, for the two sets of parameters given at the bottom of Table 17). In comparison with the cata-condensed benzenoid, the three peri-condensed benzenoids have an increased number of conjugated circuits R_2 and have fewer non-contributing larger conjugated circuits; consequently, they show increased molecular RE. In summary, we have seen that variations in RE among benzenoid hydrocarbons having the same number of Kekulé valence structures should not be ignored, though particularly among isomers having the same K (the case of the three peri-condensed benzenoids shown in Figure 26) the differences in RE are rather small. In contrast, differences in RE among isomers having different K can be considerable, as is already visible by comparison of anthracene and phenanthrene, which has only one additional Kekulé valence structure.

In Table 18 we report RE values for additional benzenoid hydrocarbons which are illustrated in Figure 56. Besides RE and REPE, we have listed for these compounds also the RE/ring, the average RE per ring, which corresponds to the average ring RE. As we can see, linear benzenoids **1/56** and **4/56** have rather low average ring RE, while “fully benzenoid” hydrocarbons (those having only π-aromatic sextets or empty rings, in the terminology of Clar), compounds **8/56**, **11/56**, **14/56**, and **16/56**, have the largest average ring RE. The intermediate RE/ring values belong to compounds having a single Clar structure (e.g., **3/56**, **10/56**, **12/56**, and **13/56**) and to compounds having migrating π-sextets (the remaining compounds shown in Figure 56). It is interesting that these average ring RE values point to differences between benzenoid hydrocarbons having a different number of aromatic π-sextets, migrating sextets, and “empty” rings. Hence, the significance of the model of benzenoids based on Clar’s notions of aromatic π-sextets, migrating sextets, and “empty” rings could have been detected from quantum chemical calculations if the total molecular resonance energy and the average ring energy contributions had been examined more closely.

In Table 19 we show the expressions for RE for miscellaneous benzenoid hydrocarbons shown in Figure 57. Among the compounds included are zethrene **9/57** and its higher analogue **14/57**, both of which have “fixed” double and single CC bonds, which can therefore be viewed as weakly coupled “double” naphthalene and “double” phenanthrene units. The corresponding RE values are twice as big as those of naphthalene and phenanthrene, respectively. The compounds **6/57** and **7/57** have identical expressions for RE as they are isoconjugated: all the rings after the terminal rings are “kink” rings of the Gordon and Davison algorithm for enumeration of K. Again, the largest ring RE belongs to the “fully benzenoid”

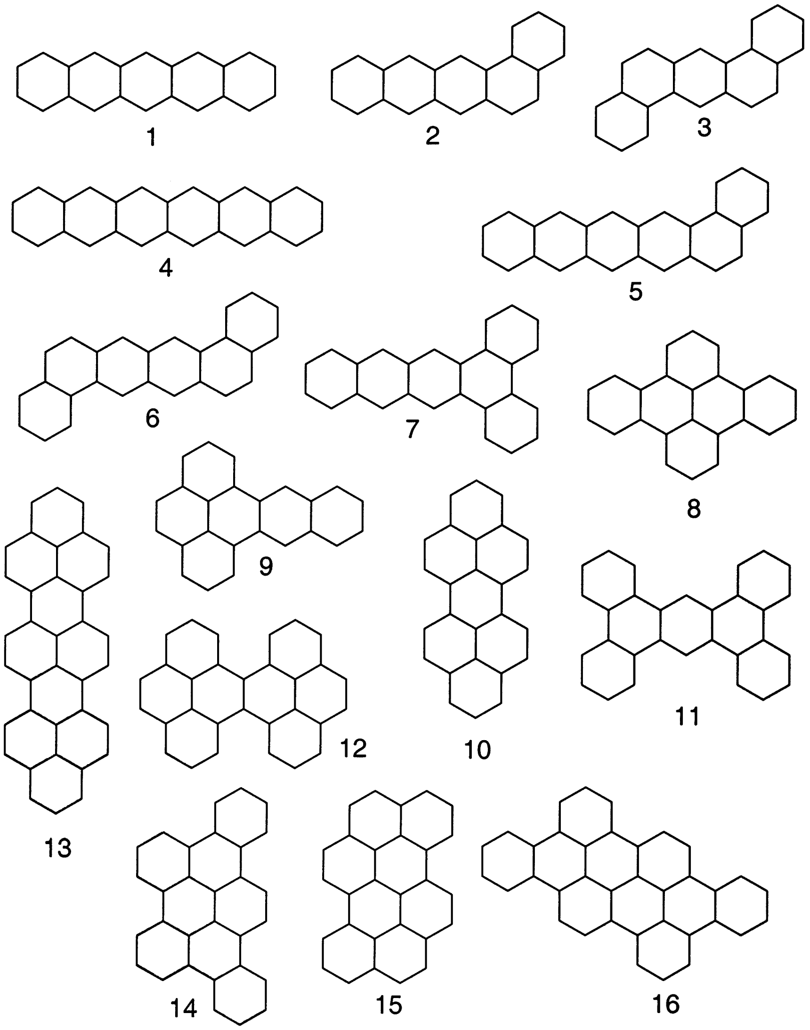


Figure 56. Benzenoid hydrocarbons for which RE is listed in Table 18.

hydrocarbon **15/57**, having six π-aromatic sextets. In the lower part of Table 19 we give RE values for a selection of benzenoids having nine rings, illustrated in Figure 58. Observe the dramatic decrease in the number of Kekulé valence structures and the dramatic decrease in molecular RE as we move from cata-condensed benzenoid to peri-condensed benzenoid. Observe also the much greater variation in K for peri-condensed benzenoids, which can be as low as 20 and as high as 60.

In Table 20 we have listed RE values for the benzenoid hydrocarbons shown in Figure 27, which are the structures with the largest K values among cata-condensed benzenoids having the same number of benzene rings. They were reported by Balaban and co-workers for benzenoids having 46 or less fused benzene rings.[434] The smaller members of this class were already known to Cyvin and Gutman.[435] It is not surprising to see that all the internal rings in the benzenoids shown in Figure 27 are the so-called "kink" rings (in the terminology of Gordon and Davison[439] (GD). The GD algorithm suggests higher K values for cata-condensed benzenoids molecules having more "kink" benzene rings.

It is of interest to see that, among these benzenoids that have the maximal K values, there are some that do not have the maximal RE as computed by the conjugated circuits method. In Figure 59 we show two cata-condensed benzenoids having seven benzene rings with $K = 41$ and $K = 38$, the former being the cata-condensed benzenoid having the maximal K among cata-condensed benzenoids having seven rings. The expressions for RE for the two benzenoids shown in Figure 59 are respectively

$$4.537R_1 + 1.366R_2 + 0.659R_3 + 0.195R_4$$

$$4.474R_1 + 1.895R_2 + 0.553R_3 + 0.079R_4$$

These expressions lead to RE values of 4.346 and 4.411 eV, respectively. If we use the values $R_1 = 0.815$, $R_2 = 0.302$, $R_3 = 0.085$, and $R_4 = 0$ as an alternative, we obtain slightly reduced values for the RE of these two benzenoids, 4.166 and 4.266 eV, respectively. However, as we can see, the relative magnitudes of the RE values have not changed. Hence, the benzenoid hydrocarbon having the largest K is not necessarily one that has the largest RE, contradicting predictions based on the simple proportionality of RE with log K, which suggests the opposite. This is an unexpected and somewhat surprising result because the first of the two structures represents a "fully benzenoid" system, according to Clar, while the second structure involves a migrating

Table 19. Expressions for Molecular RE for a Selection of Miscellaneous Benzenoid Hydrocarbons (Shown in Figure 57) and Benzenoid Hydrocarbons Having Nine Fused Benzene Rings (Shown in Figure 58)

molecule	RE expression	RE[a]	RE/ring	REPE
1/57	$(26R_1 + 16R_2 + 5R_3 + 2R_4 + R_5)/10$	2.705	0.541	0.1229
2/57	$(68R_1 + 30R_2 + 7R_3 + 3R_4 + 5R_5 + R_6)/19$	3.537	0.589	0.1360
3/57	$(110R_1 + 60R_2 + 9R_3 + 7R_4 + 6R_5 + 3R_6 + R_7)/28$	3.975	0.568	0.1325
4/57	$(86R_1 + 28R_2 + 12R_3 + 4R_4 + R_5 + R_6)/22$	3.766	0.628	0.1448
5/57	$(90R_1 + 34R_2 + 12R_3 + 2R_4)/23$	3.818	0.636	0.1468
6/57	$(76R_1 + 40R_2 + 10R_3)/21$	3.663	0.611	0.1409
7/57	$(76R_1 + 40R_2 + 10R_3)/21$	3.663	0.611	0.1409
8/57	$(44R_1 + 30R_2 + 14R_3 + 2R_4)/15$	3.136	0.523	0.1206
9/57	$(24R_1 + 12R_2)/9$	2.647	0.441	0.1018
10/57	$(42R_1 + 24R_2 + 12R_3 + 4R_4 + 2R_5)/14$	3.116	0.519	0.1298
11/57	$(24R_1 + 18R_2 + 12R_3 + 6R_4)/10$	2.650	0.442	0.1205
12/57	$(38R_1 + 29R_2 + 18R_3 + 10R_4 + 3R_5)/14$	2.999	0.428	0.1153
13/57	$(76R_1 + 52R_2 + 29R_3 + 4R_4)/23$	3.556	0.508	0.1368
14/57	$(100R_1 + 40R_2 + 10R_3 + 6R_4)/25$	3.911	0.489	0.1222
15/57	$(567R_1 + 249R_2 + 152R_3 + 52R_4)/102$	5.583	0.558	0.1551
16/57	$(200R_1 + 160R_2 + 110R_3 + 26R_4 + 4R_5)/50$	4.486	0.449	0.1402
1/58	$(592R_1 + 256R_2 + 76R_3 + 126R_4)/104$	5.628	0.625	0.1481
2/58	$(560R_1 + 256R_2 + 72R_3 + 12R_4)/100$	5.571	0.619	0.1466
3/58	$(618R_1 + 228R_2 + 90R_3 + 18R_4)/106$	5.683	0.631	0.1495
4/58	$(60R_1 + 48R_2 + 36R_3 + 24R_4 + 12R_5)/20$	3.380	0.376	0.1127
5/58	$(158R_1 + 108R_2 + 66R_3 + 24R_4 + 4R_5)/40$	4.264	0.474	0.1254
6/58	$(109R_1 + 78R_2 + 47R_3 + 27R_4 + 9R_5)/30$	4.025	0.447	0.342
7/58	$(132R_1 + 86R_2 + 48R_3 + 6R_4)/34$	4.140	0.460	0.1294
8/58	$(202R_1 + 116R_2 + 74R_3 + 26R_4 + 2R_5)/60$	3.527	0.392	0.1037

[a] $R_1 = 0.869$, $R_2 = 0.247$, $R_3 = 0.100$, $R_4 = R_5 = 0$.

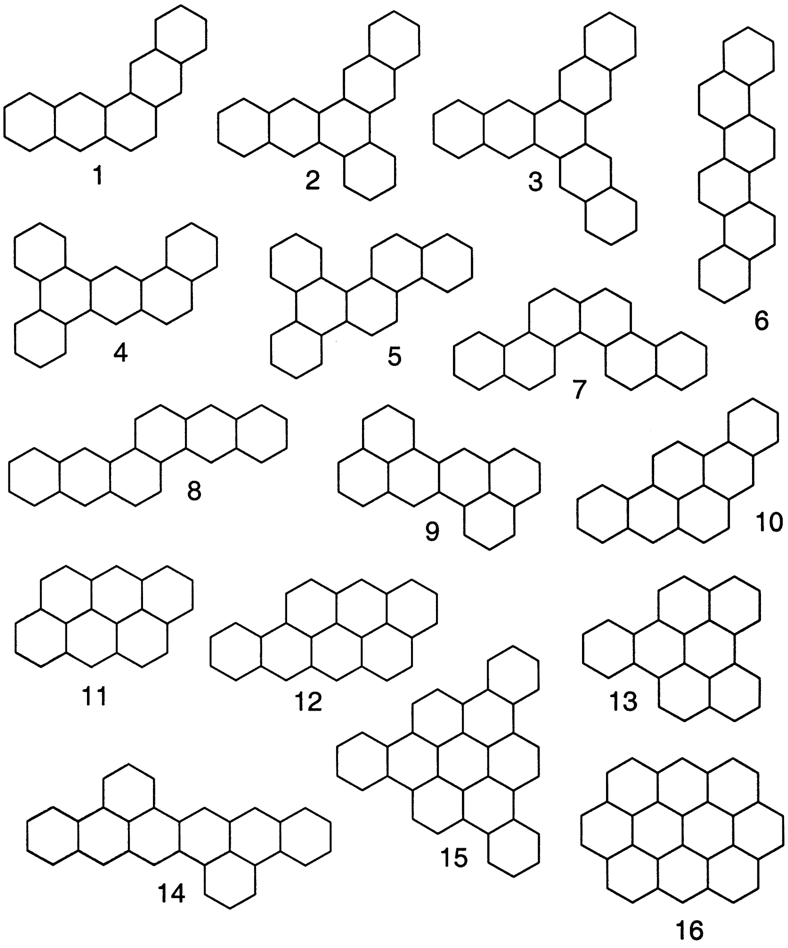


Figure 57. Miscellaneous benzenoid hydrocarbons for which RE is listed in the upper part of Table 19.

π-sextet, which is expected to show reduced stability. However, if we look more closely at the expressions for their RE, we see that, although the first structure has larger R_1 contributions, these are more than outweighed by the contributions from conjugated circuits R_2, for which the second structure has 72

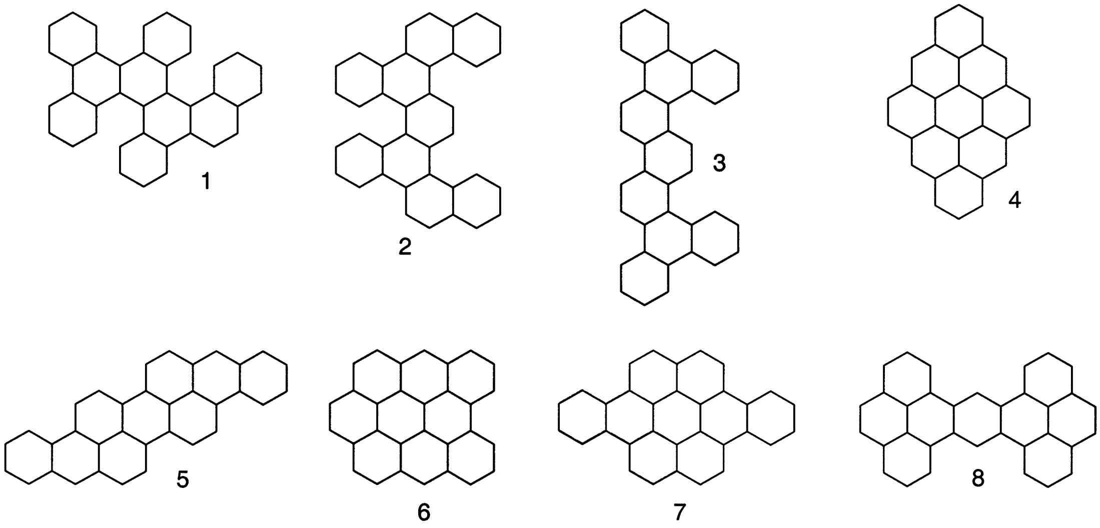


Figure 58. Benzenoid hydrocarbons having nine rings, for which RE is listed in the lower part of Table 19.

Table 20. Expressions for Molecular RE for the Benzenoid Hydrocarbons Shown in Figure 27, Which Are the Structures with the Largest *K* Values among Cata-condensed Benzenoids Having the Same Number of Rings

molecule	no. of rings	RE expression	RE[a]	REPE
1/27	3	$(10R_1 + 4R_2 + R_3)/5$	1.956	0.1397
2/27	4	$(26R_1 + 6R_2 + 3R_3)/9$	2.708	0.1505
3/27	5	$(46R_1 + 18R_2 + 5R_3 + R_4)/14$	3.209	0.1458
4/27	6	$(96R_1 + 34R_2 + 12R_3 + 2R_4)/24$	3.876	0.1491
5/27	7	$(186R_1 + 56R_2 + 27R_3 + 8R_4)/41$	4.346	0.1449
6/27	8	$(346R_1 + 128R_2 + 45R_3 + 8R_4)/66$	5.103	0.1501
7/27	9	$(650R_1 + 230R_2 + 91R_3 + 23R_4)/110$	5.734	0.1509
8/27	10	$(1262R_1 + 396R_2 + 183R_3 + 49R_4)/189$	6.417	0.1528

[a] $R_1 = 0.869$, $R_2 = 0.247$, $R_3 = 0.100$, $R_4 = R_5 = 0$.

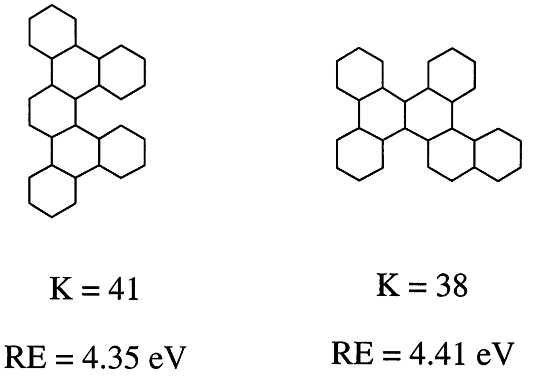


Figure 59. Benzenoids with $K = 41$ and $K = 38$, respectively, illustrating a disagreement in the prediction of RE on the basis of the empirical log *K* relationship and the conjugated circuits model.

compared with 56 for the first structure. Hence, while characterization of Kekulé valence structures with maximal *K* appears to be solved, finding benzenoids which have the maximal RE among systems having the same number of fused benzene rings appears to present a bigger challenge.

In the case of strictly peri-condensed benzenoids, it is less obvious to identify the benzenoids associated with the maximal *K*. Cyvin and Gutman[435] reported that the maximal *K* for a general peri-condensed system occurs for compounds in which various cata-condensed branches are added around the pyrene nucleus. It is therefore of more interest to consider benzenoids that do not have cata-condensed benzene rings, that is, each fused benzene ring must have at least two adjacent already fused benzene rings. Such benzenoids define the “strictly” peri-condensed systems. In Figure 60 we show strictly peri-condensed benzenoids having 10 or fewer fused rings, which have the maximal *K*. The expressions for RE, and the RE and REPE values, for these compounds are listed in Table 21.

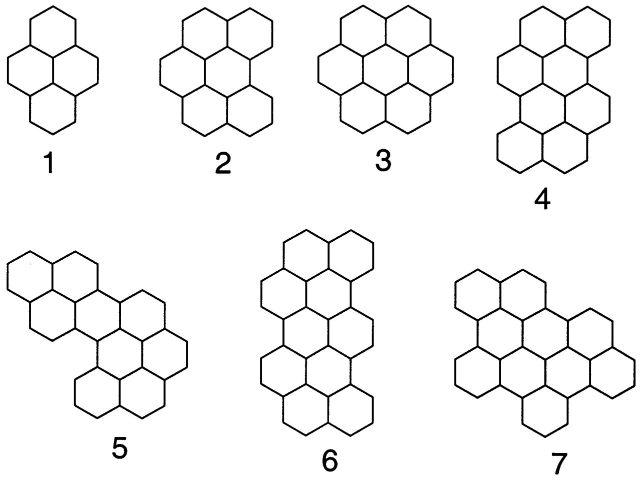


Figure 60. “Strictly” peri-condensed benzenoids having 10 or less fused rings and having the maximal *K*, as reported by Cyvin and Gutman.[79] (RE values are shown in Table 21.)

Finally, in Table 22 we give the expressions for RE for a family of benzenoid compounds, shown in Figure 61, that are the initial members that model a ben-

Table 21. Expressions for Molecular RE for the Benzenoid Hydrocarbons Shown in Figure 60, Which Are the Structures with the Largest K Values among Strictly Peri-condensed Benzenoids Having the Same Number of Rings

molecule	RE expression	RE[a]	REPE
1/60	$(12R_1 + 8R_2 + 4R_3)/6$	2.134	0.133
2/60	$(42R_1 + 26R_2 + 12R_3)/14$	3.151	0.143
3/60	$(64R_1 + 48R_2 + 27R_3)/20$	3.151	0.143
4/60	$(120R_1 + 82R_2 + 30R_3)/31$	4.114	0.147
5/60	$(172R_1 + 118R_2 + 62R_3)/42$	4.400	0.138
6/60	$(336R_1 + 210R_2 + 113R_3)/70$	5.0736	0.1492
7/60	$(343R_1 + 191R_2 + 100R_3)/70$	5.0749	0.1493

[a] $R_1 = 0.869$ eV, $R_2 = 0.247$ eV, $R_3 = 0.100$ eV, $R_4 = R_5 = 0$.

zenoid polymer made of fused pyrene units, referred to as "polypyrene fusenes" by Klein, Hite, and Schmalz.[481] The top part of Table 22 shows the fast growth of K and the increase in the number of conjugated circuits as the number of pyrene units in such compounds increases. In the middle part of the table are given the same formulas, but expressed in the decimal format, which allows one to see the rate of increase in the RE as the size of the polymer increases. From the coefficients of R_1, R_2, R_3, and R_4, one can immediately verify that there is a constant increment in molecular RE between the successive members of the family, given by

$$\Delta\text{RE} = 2R_1 + 1.233R_2 + 0.657R_3 + 0.111R_4$$

In the lower part of Table 22 we give the expressions for the average ring RE, which is almost constant. This is not surprising, in view of the constant increment in the RE for the successive members of the family of compounds. When comparing results on molecules of different sizes, it is more appropriate to consider REPE, the quantity introduced by Hess and Schaad,[564] rather than RE. In the last column of Table 22 we give RE, REPE, and RE/ring based on the values $R_1 = 0.841$ eV and $R_2 = 0.336$ eV, recommended by Herndon and used by Klein, Hite, and Schmalz, who used the transfer matrix approach for calculation of RE. They derived an asymptotic value for REPE, which is given by

$$\text{REPE}_\infty = R_1/7 + (12 - 5\sqrt{2})R_2/56$$

which gives as the limiting REPE for polypyrene fusene 0.1497 eV.

We end the discussion of RE of benzenoid hydrocarbons by examining more closely cata-condensed benzenoid hydrocarbons having seven benzene rings. In Figure 62 we show the molecular structures of these benzenoids, where only one of several possible isoconjugated isomers is shown. In Table 23 we have listed the expressions for RE and computed RE assuming $R_1 = 0.869$ eV, $R_2 = 0.427$ eV, and $R_3 = 0.100$ eV. We listed benzenoids starting with those with the smallest K and ending with the largest K values. Because all compounds have the same empirical formula, $C_{30}H_{18}$, there is no need to consider REPE, which varies from 0.071, which is close to the lower bound on REPE, to 0.152, which is close to the upper bound on REPE in benzenoid conjugated hydrocarbons. For benzenoid hydrocarbons having the same K, we see that, as a rule, the RE increases with the increase in the count of R_1. The only exception for molecules of Table 23 is the pair of benzenoids **16/62** and **17/62**. Which of the two compounds will have the larger RE depends on whether the difference $(2R_1 - 6R_2 - 3R_3)/K$ in RE between the two is positive or negative. With the adopted numerical values for R_1, R_2, and R_3 we find the difference to be rather small, hardly significant: 0.002 eV.

Having expressions for RE for a larger number of benzenoid isomers allows us to observe regularities

Table 22. Expressions for Molecular RE for Benzenoids Representing the Initial Members of a Polymeric Family (Shown in Figure 61)

molecule	RE expression	RE	RE[a]
$C_{16}H_{10}$	$(12R_1 + 8R_2 + 4R_3)/6$	2.134	2.130
$C_{30}H_{16}$	$(140R_1 + 90R_2 + 46R_3 + 4R_4)/35$	4.243	4.2276
$C_{44}H_{220}$	$(1\,224R_1 + 776R_2 + 402R_3 + 46R_4)/204$	6.351	6.323
$C_{58}H_{28}$	$(9\,512R_1 + 5\,988R_2 + 3\,124R_3 + 400R_4)/1\,189$	8.459	8.422
$C_{72}H_{34}$	$(69\,300R_1 + 43\,440R_2 + 22\,760R_3 + 3\,100R_4)/6\,930$	10.571	10.519
$C_{86}H_{40}$	$(484\,692R_1 + 302\,958R_2 + 159\,186R_3 + 22\,548R_4)/40\,391$	12.675	12.616

molecule	numerical expression for molecular RE	REPE	REPE[a]
1/61	$2R_1 + 1.333R_2 + 0.667R_3$	0.1334	0.1331
2/61	$4R_1 + 2.571R_2 + 1.314R_3 + 0.144R_4$	0.1414	0.1409
3/61	$6R_1 + 3.804R_2 + 1.971R_3 + 0.225R_4$	0.1443	0.1437
4/61	$8R_1 + 5.036R_2 + 2.627R_3 + 0.336R_4$	0.1458	0.1452
5/61	$10R_1 + 6.268R_2 + 3.284R_3 + 0.447R_4$	0.1468	0.1461
6/61	$12R_1 + 7.501R_2 + 3.941R_3 + 0.558R_4$	0.1474	0.1467

molecule	RE per benzene ring	RE/ring	RE/ring[a]
$C_{16}H_{10}$	$0.5R_1 + 0.333R_2 + 0.167R_3$	0.534	0.533
$C_{30}H_{16}$	$0.5R_1 + 0.321R_2 + 0.164R_3 + 0.014R_4$	0.530	0.528
$C_{44}H_{220}$	$0.5R_1 + 0.317R_2 + 0.164R_3 + 0.019R_4$	0.529	0.527
$C_{58}H_{28}$	$0.5R_1 + 0.315R_2 + 0.164R_3 + 0.021R_4$	0.529	0.526
$C_{72}H_{34}$	$0.5R_1 + 0.313R_2 + 0.164R_3 + 0.022R_4$	0.529	0.526
$C_{86}H_{40}$	$0.5R_1 + 0.313R_2 + 0.164R_3 + 0.023R_4$	0.528	0.526

[a] Based on calculations of Klein, Hite, and Schmalz.[481]

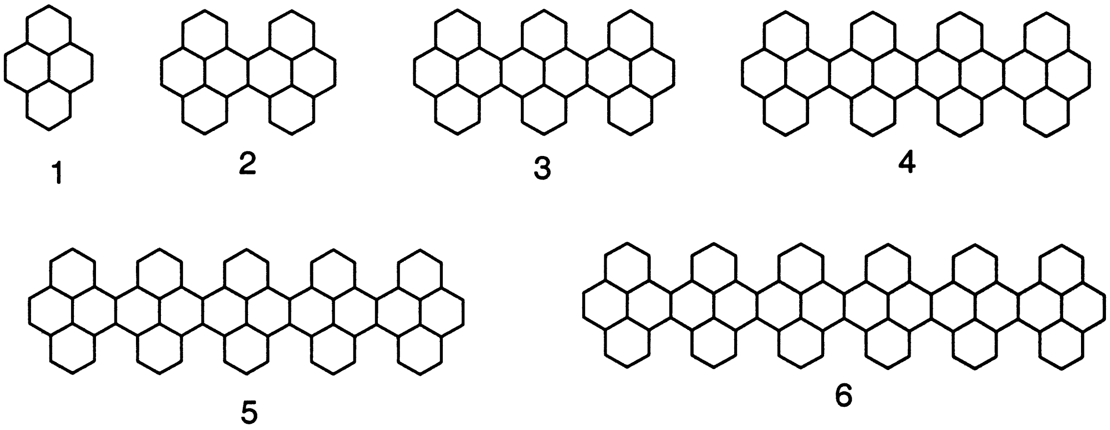


Figure 61. Initial members of a family of benzenoid hydrocarbons. (RE values are shown in Table 22.)

in their RE. First, we observe that when two benzenoids have the same K, the isomer that has shorter linearly fused rings has a larger RE. This is the case with the pairs (**4/62**, **5/62**), (**17/62**, **18/62**), and (**19/62**, **20/62**). When isomers have linearly fused segments of the same length, the isomer with a "kink" ring has a larger K and consequently is expected to have a larger RE, as is illustrated with the pairs (**3/62**, **4/62**) and (**12/62**, **13/62**). We also observe a rather interesting fact that among isomers having the same K, isomers having a "migrating" Clar's π-sextet have larger RE than the isomers with a single Clar structure. This is illustrated by benzenoids **27/62**, **33/62**, and **36/62**, which have four π-aromatic sextets, when compared with **28/62**, the pair (**34/62**, **35/62**), and **37/62**, respectively. However, if we compare **27/62** with **26/62**, which has lower RE, this is due to the fact that **26/62** has only three π-sextets, while **27/62** has four. This particular observation points to an unexpected empirical rule:

Clar's Structure Rules: *Benzenoid having a single Clar structure with only aromatic* π*-sextets and empty rings, the fully benzenoid systems described by Clar, are the most stable; benzenoids having several Clar structures are the next most stable; and benzenoids having a single Clar structure with rings with isolated CC double bonds are the least stable.*

Of course, in cases with "mixed" composition, that is, benzenoids having "fully benzenoid" fragments, "migration" fragments, and "fixed" CC double bonds, a balance between the number of migrating sextets, the "length" of the migration of the π-sextets, and the number of isolated CC double bonds will play some role. The above rule strictly applies only when such factors are the same; when they are not, as we have seen when comparing **26/62**, which has three π-sextets, with **27/62**, which has four π-sextets, a reversal in the relative stability (that is, RE and REPE) can occur.

XIII. Non-benzenoid Systems

The benzenoid hydrocarbons considered thus far were built solely from fused hexagonal rings, and as a consequence all their conjugated circuits are necessarily of $4n + 2$ type, as proved by Cvetković, Gutman, and Trinajstić.[565] If we consider compounds built from fused benzene rings but allow the presence of larger interior "holes", we may encounter also $4n$ conjugated circuits. Such compounds, known as corannulenes, can be grouped into two classes: those having only $4n + 2$ conjugated circuits, illustrated in Figure 63, and those having both $4n + 2$ and $4n$ conjugated circuits, illustrated in Figure 64. In the top part of Table 24 we show enumeration of conjugated circuits for the compounds shown in Figure 63, including kekulene (the last structure in Figure 63). Observe that the two perimeters of these molecules, the inner and outer perimeters, have $4n + 2$ π-electrons ($n = 2$, 3, and 4), that is, conjugated circuits of 10, 14, and 18 π-electrons. These molecules contain only aromatic contributions of $4n + 2$ conjugated circuits. In contrast, the compounds shown in Figure 64 have on their peripheries $4n$ carbon atoms. Hence, conjugated circuits involving the peripheries of such structures will necessarily have contributions from the $4n$ conjugated circuits.[457] However, the smallest such circuits will have already 12 carbon atoms and will make a small, if any, negative contribution to the molecular RE. So, from the practical point of view, the corannulenes shown in Figures 63 and 64 will show little differences in their properties from the benzenoids already considered, except for properties associated with the presence of the inner hydrogen atoms. As can be seen from Table 24, the structures shown in Figure 64 have REPE values (RE per electron) similar to those of the compounds shown in Figure 63. The largest REPE values belong to corannulenes having fewer straight-line (linearly fused) benzene strips and more "kink" benzene rings (angularly fused benzene rings). Observe also that the largest REPE is found for corannulenes **1/63** and **3/63**, which have a single Clar structure, while as we can see, kekulene, which also has a single Clar structure, shows a reduced REPE. The "departure" of kekulene from the anticipated higher REPE values may be due not only to the fact that, from 200 Kekulé valence structures of kekulene, only 64 have the highest degree of freedom ($df = 6$), but also to the fact that kekulene has more linearly fused benzene rings. As previously mentioned, linearly fused rings make smaller contributions to RE.

Kekulene itself is an interesting compound. We find here that not only is the number of Kekulé

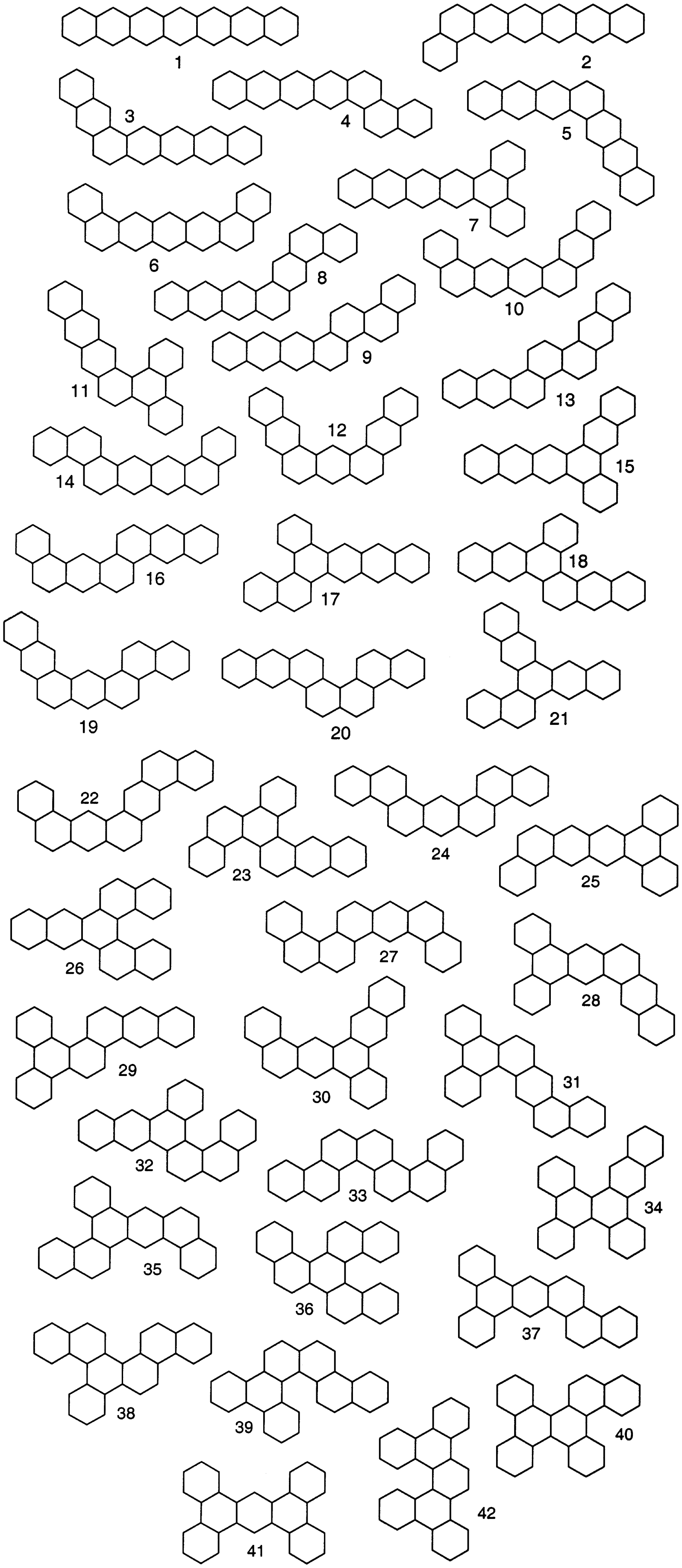
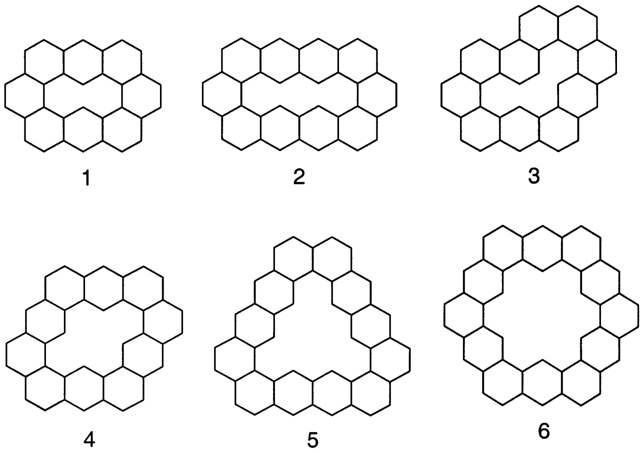


Figure 62. Cata-condensed benzenoid hydrocarbons having seven benzene rings. (RE values are shown in Table 23.)

Table 23. Expressions for Molecular RE for a Selection of Cata-condensed Benzenoid Hydrocarbons Having Seven Fused Benzene Rings (Shown in Figure 62)

molecule	RE expression	RE	molecule	RE expression	RE	molecule	RE expression	RE
1/62	$(14R_1 + 12R_2 + 18R_3)/8$	2.116	**15/62**	$(94R_1 + 46R_2 + 19R_3)/25$	3.798	**29/62**	$(134R_1 + 58R_2 + 19R_3)/32$	4.146
2/62	$(34R_1 + 20R_2 + 15R_3)/13$	2.768	**16/62**	$(96R_1 + 56R_2 + 24R_3)/26$	3.833	**30/62**	$(136R_1 + 56R_2 + 18R_3)/32$	4.182
3/62	$(46R_1 + 32R_2 + 17R_3)/16$	3.099	**17/62**	$(98R_1 + 50R_2 + 21R_3)/26$	3.831	**31/62**	$(140R_1 + 60R_2 + 24R_3)/33$	4.208
4/62	$(50R_1 + 34R_2 + 18R_3)/17$	3.156	**18/62**	$(102R_1 + 56R_2 + 24R_3)/27$	3.884	**32/62**	$(140R_1 + 62R_2 + 20R_3)/33$	4.211
5/62	$(50R_1 + 36R_2 + 21R_3)/17$	3.202	**19/62**	$(102R_1 + 60R_2 + 19R_3)/27$	3.902	**33/62**	$(142R_1 + 76R_2 + 20R_3)/34$	4.240
6/62	$(68R_1 + 32R_2 + 20R_3)/20$	3.450	**20/62**	$(112R_1 + 66R_2 + 22R_3)/29$	3.994	**34/62**	$(146R_1 + 62R_2 + 26R_3)/34$	4.258
7/62	$(74R_1 + 30R_2 + 21R_3)/21$	3.515	**21/62**	$(114R_1 + 64R_2 + 13R_3)/29$	4.006	**35/62**	$(146R_1 + 64R_2 + 20R_3)/34$	4.255
8/62	$(76R_1 + 44R_2 + 21R_3)/22$	3.591	**22/62**	$(116R_1 + 56R_2 + 22R_3)/29$	4.029	**36/62**	$(148R_1 + 78R_2 + 18R_3)/35$	4.277
9/62	$(80R_1 + 48R_2 + 23R_3)/23$	3.638	**23/62**	$(118R_1 + 66R_2 + 23R_3)/30$	4.038	**37/62**	$(154R_1 + 60R_2 + 21R_3)/35$	4.307
10/62	$(82R_1 + 46R_2 + 14R_3)/23$	3.653	**24/62**	$(118R_1 + 68R_2 + 20R_3)/30$	4.045	**38/62**	$(156R_1 + 74R_2 + 20R_3)/36$	4.329
11/62	$(86R_1 + 46R_2 + 25R_3)/24$	3.722	**25/62**	$(126R_1 + 44R_2 + 22R_3)/30$	4.085	**39/62**	$(164R_1 + 70R_2 + 22R_3)/37$	4.379
12/62	$(86R_1 + 52R_2 + 20R_3)/24$	3.732	**26/62**	$(124R_1 + 70R_2 + 17R_3)/31$	4.089	**40/62**	$(170R_1 + 72R_2 + 21R_3)/38$	4.411
13/62	$(90R_1 + 56R_2 + 23R_3)/25$	3.774	**27/62**	$(126R_1 + 64R_2 + 22R_3)/31$	4.113	**41/62**	$(192R_1 + 48R_2 + 24R_3)/40$	4.528
14/62	$(92R_1 + 50R_2 + 21R_3)/25$	3.776	**28/62**	$(130R_1 + 52R_2 + 23R_3)/31$	4.133	**42/62**	$(196R_1 + 56R_2 + 27R_3)/41$	4.557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4 5 6

Figure 63. Compounds built from fused benzene rings allowing the presence of larger interior "holes", in which we encounter only $4n + 2$ conjugated circuits. (RE values are shown in Table 24.)

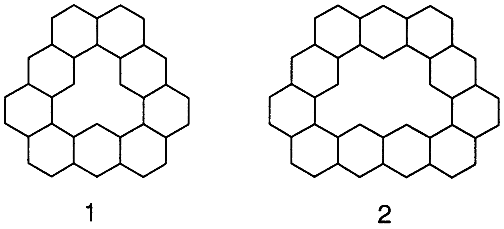
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Figure 64. Compounds built from fused benzene rings allowing the presence of larger interior "holes", in which we encounter both $4n + 2$ and $4n$ conjugated circuits. (RE values are shown in the lower part of Table 24.)

structures of maximal *df* smaller than the number of Kekulé structures with smaller *df*, but also in Kekulene there are Kekulé valence structures which have very different *df* values. In Figure 65 we illustrate Kekulé valence structures of kekulene showing different degrees of freedom, varying between $df = 6$ and $df = 2$.

A. Biphenylene and Related Non-benzenoid Systems

The occurrence of $4n$ conjugated circuits is quite common in non-benzenoid polycyclic conjugated hydrocarbons, both alternants and non-alternants. In Table 25 we show the decomposition of Kekulé valence structures for a selection of biphenylene derivatives, which are alternant non-benzenoid hydrocarbons (illustrated in Figure 66). We designated $4n$ conjugated circuits by Q_n and confined enumeration mostly to conjugated circuits of size 4, 8, and 12, that is, Q_1, Q_2, and Q_3. It is to be expected that such systems having $4n$ rings will necessarily have $4n$ conjugated circuits. However, in addition to $4n$ conjugated circuits, alternant non-benzenoid hydrocarbons not only may have $4n + 2$ conjugated circuits, but the $4n + 2$ conjugated circuits may dominate the overall properties of these compounds. The $4n + 2$ conjugated circuits may arise not only because of the presence of fused benzene rings that may occur in such structures but also from two or more fused $4n$ rings. Obviously, two adjacent $4n$ rings necessarily have $4n + 2$ perimeters. Because the contributions from Q_n conjugated circuits decrease molecular RE, we see that such structures will have a partially destabilizing anti-aromatic component.

Table 24. Expressions for Molecular RE for Benzenoid-like Compounds Built from Fused Benzene Rings but Having Non-benzenoid $4n + 2$ and $4n$ "Holes" (Shown in Figures 63 and 64, Respectively)

molecule		RE expression	RE[a]	REPE
$C_{32}H_{16}$	**1/63**	$(156R_1 + 100R_2 + 80R_3)/40$	4.207	0.131
$C_{40}H_{20}$	**2/63**	$(300R_1 + 192R_2 + 138R_3)/68$	4.734	0.118
$C_{40}H_{20}$	**3/63**	$(586R_1 + 366R_2 + 236R_3)/104$	5.993	0.150
$C_{40}H_{20}$	**4/63**	$(408R_1 + 264R_2 + 162R_3)/104$	4.192	0.105
$C_{48}H_{24}$	**5/63**	$(516R_1 + 402R_2 + 258R_3)/112$	5.121	0.107
$C_{48}H_{24}$	kekulene	$(1188R_1 + 696R_2 + 174R_3)/200$	6.108	0.085
$C_{36}H_{18}$	**1/64**	$(222R_1 + 256R_2 + 72R_3 + 4Q_3)/52$	5.064	0.141
$C_{44}H_{22}$	**2/64**	$(534R_1 + 408R_2 + 178R_3 + 4Q_4)/106$	5.4963	0.125

[a] $R_1 = 0.869$ eV, $R_2 = 0.247$ eV, $R_3 = 0.100$ eV.

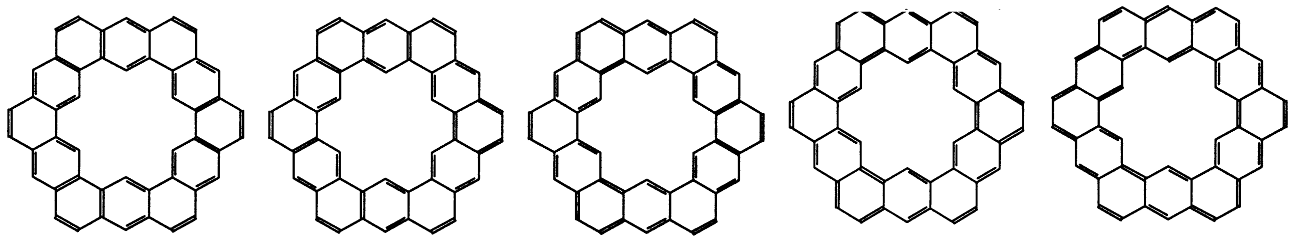


Figure 65. Kekulé valence structure of kekulene having different degrees of freedom.

Table 25. Expressions for Molecular RE for the Non-benzenoid Biphenylene Structures Shown in Figure 66

molecule	decomposition (average)	RE[a]	molecule	decomposition (average)	RE[a]
1/66	$(8R_1 + 2Q_1 + 4Q_2 + Q_3)/5$	0.877	**10/66**	$(90R_1 + 9R_2 + 2R_3 + 36Q_1 + 64Q_2 + 16Q_3)/31$	1.248
2/66	$(14R_1 + 5R_2 + 2Q_1 + 4Q_2 + 3Q_3)/7$	1.492	**11/66**	$(92R_1 + 6R_2 + 49Q_1 + 73Q_2 + 14Q_3)/34$	0.840
3/66	$(16R_1 + 4R_2 + 4Q_1 + 6Q_2 + 2Q_3)/8$	1.330	**12/66**	$(92R_1 + 6R_2 + 49Q_1 + 73Q_2 + 14Q_3)/34$	0.840
4/66	$(24R_1 + 12R_2 + 2Q_1 + 4Q_2 + 3Q_3)/12$	2.188	**13/66**	$(94R_1 + 6\mathrm{R}_2 + 54Q_1 + 78Q_2 + 13Q_3)/35$	0.734
5/66	$(26R_1 + 12R_2 + 4Q_1 + 6Q_2 + 6Q_3 + Q_4)/11$	1.976	**14/66**	$(290R_1 + 20R_2 + 180Q_1 + 249Q_2 + 44Q_3)/87$	0.722
6/66	$(32R_1 + 12R_2 + 8Q_1 + 5Q_2 + 2Q_3)/13$	1.880	**15/66**	$(38R_1 + 8R_2 + R_3 + 8Q_1 + 10Q_2 + 3Q_3)/14$	1.918
7/66	$(28R_1 + 2R_2 + 2R_3 + 8Q_1 + 16Q_2 + 4Q_3)/12$	1.238	**16/66**	$(56R_1 + 8R_2 + 20Q_1 + 32Q_2 + 10Q_3)/21$	1.355
8/66	$(28R_1 + R_2 + 12Q_1 + 20Q_2 + 4Q_3)/13$	0.837	**17/66**	$(80R_1 + 2R_3 + 20Q_1 + 41Q_2 + 14Q_3)/25$	1.778
9/66	$(88R_1 + 6R_2 + 2R_3 + 28Q_1 + 55Q_2 + 13Q_3)/29$	1.501	**18/66**	$(156R_1 + 68R_2 + 18R_3 + 52Q_1 + 67Q_2 + 40Q_3)/37$	2.779

[a] $R_1 = 0.841$ eV, $R_2 = 0.336$ eV. $Q_1 = -0.650$ eV, $Q_2 = -0.260$ eV.

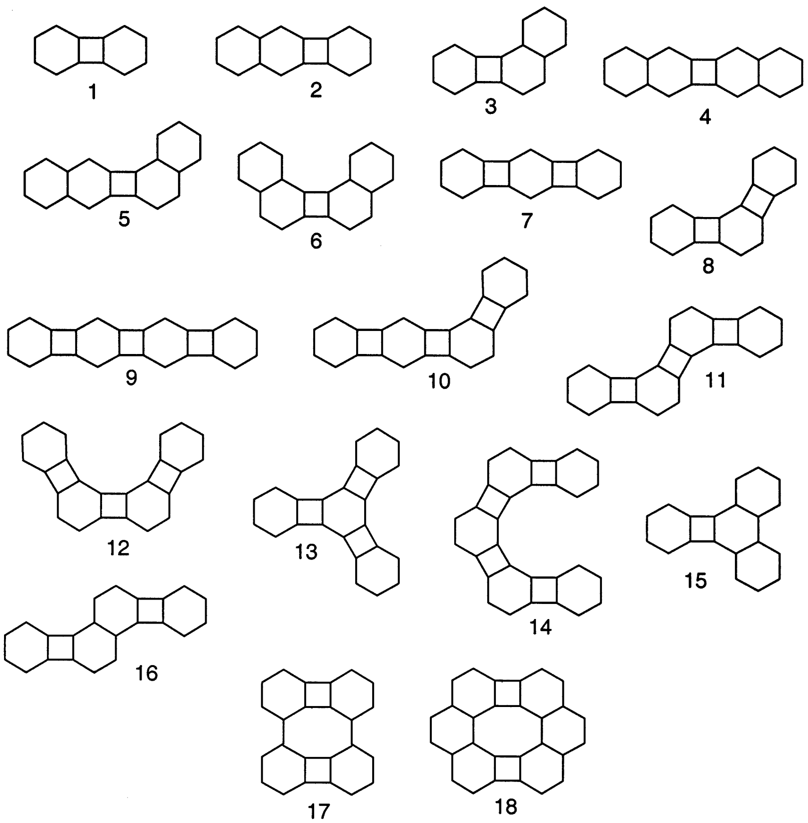


Figure 66. Selection of biphenylene derivatives representing *alternant* non-benzenoid hydrocarbons. (RE values are shown in Table 25.)

B. Non-benzenoid Systems with Odd Rings Having Only 4*n* + 2 Conjugated Circuits

In Table 26 we show the decomposition of Kekulé valence structures for a selection of non-alternant non-benzenoid hydrocarbons having odd rings (illustrated in Figure 67). They include azulene (**1/67**), acepleiadylene (**8/67**), and corannulene (**15/67**). Observe that all of the non-benzenoid systems shown in Figure 67, despite having odd-member rings, have only $4n + 2$ conjugated circuits. This suggests their stability and aromaticity. Corannulene, synthesized in 1966 by Barth and Lawton,[566] is an example of an aromatic non-benzenoid with high REPE, although it has an odd number of π-electrons on its periphery, thus defying the perimeter rule of aromaticity, which besides being wrong in some instances did not anticipate the possibility of molecules having neither $4n + 2$ nor $4n$ carbon atoms on their periphery.

Table 26. Expressions for Molecular RE for Non-alternant Non-benzenoid Hydrocarbons with Odd Rings Having $4n + 2$ Conjugated Circuits (Shown in Figure 67)

molecule	RE expression	RE	REPE
1/67	$(2R_2)/2$	0.317	0.032
2/67	$(2R_1 + 2R_2 + 2R_3)/3$	0.837	0.060
3/67	$(2R_1 + 2R_2 + 2R_3)/3$	0.837	0.060
4/67	$(2R_3)/2$	0.111	0.008
5/67	$(4R_2 + 2R_4)/3$	0.423	0.023
6/67	$(4R_2 + 2R_4)/3$	0.423	0.023
7/67	$(2R_3)/2$	0.111	0.008
8/67	$(4R_1 + 2R_2 + 6R_3)/4$	1.152	0.072
9/67	$(4R_1 + 4R_2 + 4R_3)/4$	1.255	0.078
10/67	$(4R_1 + 4R_2 + 4R_3)/4$	1.255	0.078
11/67	$(2R_3)/2$	0.111	0.008
12/67	$(8R_1 + 8R_2 + 4R_3 + 4R_4)/6$	1.599	0.080
13/67	$(8R_1 + 8R_2 + 4R_3 + 4R_4)/6$	1.599	0.080
14/67	$(8R_1 + 8R_2 + 4R_3 + 4R_4)/6$	1.599	0.080
15/67	$(30R_1 + 20R_2 + 5R_3)/11$	2.882	0.144

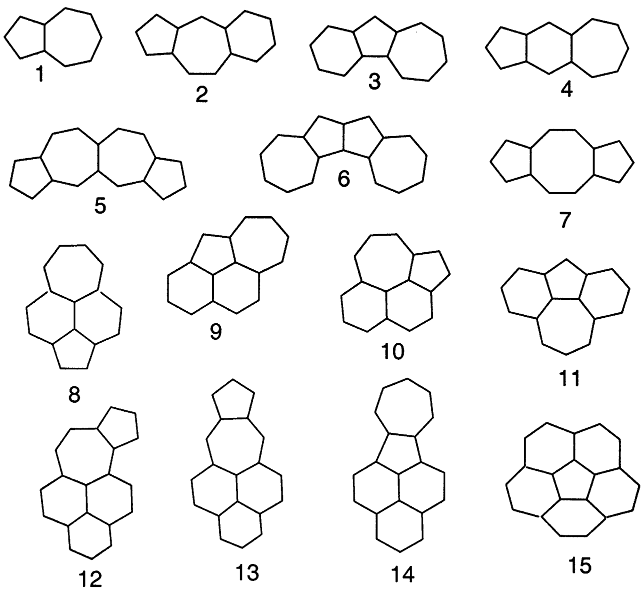


Figure 67. Non-alternant non-benzenoid hydrocarbons having only $4n + 2$ conjugated circuits. (RE values are shown in Table 26.)

Corannulene has 11 Kekulé valence structures, all having $df = 2$, and thus all 11 contribute to Clar's structure of corannulene, which has two migrating π-sextets.

Because all of the compounds shown in Figure 67 possess *only* $4n + 2$ conjugated circuits, they all are expected to be fully aromatic, even if they may show considerable departure in their properties from benzene − the prototype of aromaticity. However, we should add, although this may be viewed as a semantic question, that the similarity to benzene *should not be used to govern the characterization of aromaticity*, even though benzene may be prima facie an example of an aromatic compound. When we are interested in the similarity of a compound to benzene, we should use terms like benzenoid character or perhaps benzenoticity (if linguists do not object), and leave aromaticity as a broader concept encompassing compounds having $4n + 2$ conjugated circuits, which besides benzene includes, for instance, Sondheimer's 18 π-electron annulene, the smallest annulene after benzene that can attain planarity without severe non-bonded H−H interactions of the inner hydrogens. The [18]annulene, in contrast to benzene, in which all CC bonds are equivalent, has two types of symmetry-non-equivalent CC bonds. The MINDO calculations of Dewar et al.[567] and the molecular mechanics calculations[568] show slight differences between the non-equivalent aromatic CC bonds, although the difference is rather small.

We mentioned earlier the difficulty of the perimeter model, not only, as the case of corannulene illustrates, in that it gives wrong answers but also because *"it misleads one on believing that a large molecular periphery plays a critical role for determining aromatic and other molecular properties while the crucial role is played by smaller rings which can sustain conjugated circuits distribution."* [569]

C. Non-benzenoid Systems with Odd Rings Having 4*n* Conjugated Circuits

Non-alternant non-benzenoid hydrocarbons can have, besides $4n + 2$ conjugated circuits, also $4n$ conjugated circuits, as is the case with the structures shown in Figure 68, which include aceheptylene (**1/68**), azupyrene (**2/68**), aceazulene (**3/68**), dicycloheptapentalene (**4/68**), azulenoheptalene (**5/68**), *as*-azupyrene (**6/68**), pyracylene (**7/68**), and other systems built from five- and six-member rings. Decomposition of their Kekulé valence structure in conjugated circuits is shown in Table 27. Hence, structures that may appear visually similar to those shown in Figure 67 are in fact essentially quite different, at least when conjugated circuits of such structures are considered. Hafner[553−555,570,571] apparently was the first to observe difficulties in synthetic efforts toward obtaining some of these odd-ring systems, which, in contrast to the compounds shown in Figure 67, do have "anti-aromatic" contributing conjugated circuits.

It is regrettable that there are so few calculations of higher quality on a sizable collection of non-benzenoid hydrocarbons and non-alternant non-benzenoid systems that would allow a better estimate of the contributions made by $4n$ conjugated circuits. Therefore, better and more precise parametrization of various Q_n terms, which would be possible if there were reliable calculations of the resonance energies of these molecules, is lacking. The challenge here for theoretical chemistry is not so much in making quantum chemical calculations as such, but to be able to *extract* from such calculations a non-observable known as RE.

D. Summary on Applications of the Conjugated Circuits Method to Hydrocarbon and Carbon Chemistry

The conjugated circuits model was successfully applied to a variety of conjugated systems. In Table 28 we list the types of molecules studied so far using the conjugated circuits model. This table represents a slightly modified and updated version of a table first shown in a paper on quantum mechanical and computational aspects of the conjugated circuits model by Trinajstić, Nikolić, and Klein.[572] Incidentally, that paper was *"Dedicated to Professor Milan*

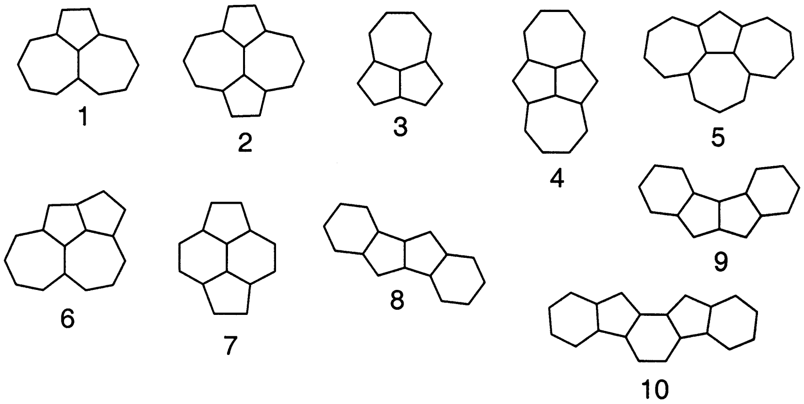


Figure 68. Non-alternant non-benzenoid hydrocarbons having both 4n + 2 and 4n conjugated circuits. (RE values are shown in Table 27.)

Table 27. Expressions for Molecular RE for Non-alternant Non-benzenoid Hydrocarbons Having Both 4*n* + 2 Conjugated Circuits and 4*n* Conjugated Circuits (Shown in Figure 68)

molecule	RE expression	RE	REPE	arom. (%)
1/68	$(4R_2 + 2Q_3)/3$	0.527	0.037	85.8
2/68	$(8R_2 + 2R_3 + 2Q_3)/4$	0.645	0.040	93.5
3/68	$(4R_2 + 2Q_2)/3$	0.275	0.023	61.9
4/68	$(8R_2 + 2R_3 + 2Q_2)/4$	0.579	0.036	83.9
5/68	$(6R_2 + 4Q_3 + 2Q_4)/4$	0.386	0.021	81.1
6/68	$(6R_2 + 2R_3 + 2Q_2 + 2Q_3)/4$	0.375	0.023	70.6
7/68	$(4R_1 + 2R_2 + 6Q_3)/4$	0.851	0.061	86.3
8/68	$(4R_1 + 2Q_2 + 4Q_3 + 2Q_4)/4$	0.626	0.039	66.2
9/68	$(8R_1 + Q_2 + 4Q_3 + Q_4)/5$	1.207	0.075	91.2
10/68	$(8R_1 + 4Q_4 + Q_5)/5$	1.323	0.066	100.0

Table 28. Types of Molecules Studied Using the Conjugated Circuits Model

Polycyclic Conjugated Hydrocarbons	
benzenoid hydrocarbons	polyacenes
macrocyclic benzenoid systems	benzoannulated annulenes
giant benzenoid hydrocarbons	phenylenes
helicenes	corannulenes
Related Systems	
excited benzene structures	polycyclic conjugated anions
benzenoid radicals	Möbius systems
polycyclic conjugated cations	
Extended Conjugated Systems	
benzenoid polymers	conjugated polymers
Elemental Carbon Systems	
buckminsterfullerene	2-D carbon networks
fullerenes	toroidal structures
graphite	conic structures
Heterocyclic Conjugated Systems	
heterocyclic — having oxygen	oxacarbanions
heterocyclic — having nitrogen	polycyclic quinones
heterocyclic — having sulfur	
Inorganic Systems	
superconductors	zeolites

Randić for enriching theoretical chemistry with the elegant concept of conjugated circuits." On that count, I would like to mention that a few of my papers dealing with conjugated circuits also have dedications. The paper on the resonance energy of very large benzenoid hydrocarbons[507] was "*Dedicated to Linus Pauling (Nobel Prize for Peace 1962 and Nobel Prize for Chemistry 1954) in appreciation of his outstanding contributions to structural chemistry and his untiring efforts to end war.*" A paper on "Local Aromatic Properties of Benzenoid Hydrocarbons" [508] was quite fittingly "*Dedicated to Professor Eric Clar, doyen of benzenoid chemistry, whose work inspired much of the recent graph theoretical interest in aromaticity.*" Finally, a more recent paper on "Giant Benzenoid Hydrocarbons. Supernaphthalene Resonance Energy" [573] was "*Dedicated to Professor Klaus Müllen, the pioneer of giant hydrocarbons,*" for obvious reasons.

XIV. Quantum Chemical Justification of the Conjugated Circuits Model

The mathematical equivalence of the quantum mechanical approach of Simpson and Herndon and the graph theoretical approach based on conjugated circuits offers a quantum chemical justification for the conjugated circuits model. Klein and Trinajstić were the first to outline an alternative, more traditional quantum chemical derivation of the conjugated circuits model via the Pauling–Wheland valence bond model, which follows from the usual Schrödinger equation in a sequence of steps.[7,8] As Klein has pointed, out this approach exhibits proper many-body size-extensivity for energies, "*with the present conjugated-circuit formulas being obtained as Hamiltonian expectations (for reasonable wave function ansatz).*" [545] In contrast, some semi-empirical quantum chemical approaches as well as some graph theoretical approaches fail to comply with size-extensivity. Thus, for example, "*the presumption that the total Kekulé structure count is proportional to the resonance energy so fails. Also the quantum-chemical technique of double-excitation-limited configuration interaction fail.*" (Footnote 8 in ref 545).

Size-extensivity is expected of good approximations. As Klein[534] pointed out in his paper on chemical graph theoretical cluster expansion, the "limited CI" (configuration interaction) fails in this regard in comparison with the single configuration (Hartree–Fock) wave function. Size-extensivity can be defined as follows:

Definition: *An approximation* X_a *for a general additive scalar quantity* X *is size-extensive relative to another approximation* X_b *if the difference* $X_a - X_b$ *scales linearly with the number of sites of the system as this number becomes large.*

Size-extensivity is just one of the requirements that a good model should satisfy — but that alone is not a guarantee of a good model. A model should offer an acceptable numerical characterization of molecules, even if they are of empirical origin. For example, there is no simple apparent understanding why log K should offer a quite good approximation for molecular RE for relatively smaller molecules — but, as shown be Sheldrake, Herndon, and Gutman,[432] it does. From this point of view, the model of conjugated circuits could also be viewed as an empirical scheme that offers satisfactory molecular RE. However, the fact that a model evolved from empirical considerations does not mean that it may not have deeper theoretical justification — that at the time of its "discovery" was not recognized. This is precisely the case with the conjugated circuits model, for which Klein, Trinajstić, and co-workers found the "missing" connection to quantum theory. In one of their contributions on the fundamentals of the conjugated circuits model, Trinajstić et al. wrote: "*The foundations of the conjugated-circuit model appear to be firmly rooted in the framework of the VB theory. However, the application of conjugated-circuit ideas to high temperature superconductors provides an opportunity for the further development and refinement of this model and its novel applications.*"[574]

It is important to bring the above messages of competent theoretical chemists who have been involved heavily in various aspects of VB theory to the attention of readers, so that there is no doubt left that the graph theoretical approach of conjugated circuits, although it was introduced through empirical considerations of molecular RE (itself a nonobservable quantity), represents a *legitimate* theoretical model which is rooted in traditional quantum chemical approaches. This is important not only to help to remove the notion of "qualitativeness" from the conjugated circuits model but also because later we will outline a quantum chemical justification of Clar's aromatic sextet approach using the conjugated circuits model: We have seen above that the conjugated circuits model is a bona fide theoretical tool for chemical structure, neither less nor more legitimate than most other quantum chemical approaches. Klein, Seitz, and Schmalz recently gave an overview of conjugated circuits computations for conjugated hydrocarbons.[575] In particular, they extend the core approach of the conjugated circuits method via a "transfer matrix" scheme for enumerations of Kekulé valence structures and conjugated circuits of different size. This is particularly important for large systems, including fullerenes, to ameliorate the explosive growth rate in computational time as sizes increase.

More on the Correlation of Quantum Chemical and Graph Theoretical RE. A closer look at the correlation shown in Figure 51 shows that two points appear slightly "off" the line. They correspond to tetracene and pyrene, with residuals +0.070 and −0.043, respectively, which are visibly larger than the residuals of the remaining benzenoids of Table 13. In line 4 of Table 14, we show the statistic for a regression in which tetracene, being an outlier, was removed. As we can see from a comparison of lines 3 and 4 of Table 14, which give the statistical parameters of the regression of RE computed quantum chemically and derived from graph theoretical considerations, after removal of tetracene the standard error has been halved, the correlation coefficient markedly improved, and the Fisher ratio increased by about a factor of 4. The improvement in the statistical parameters strongly suggests that there is something "peculiar" about tetracene. Hence, we may be justified in eliminating tetracene in order not to influence the computed parameters R_1, R_2, and R_3. In line 5 of Table 14, we show the statistic for a regression in which, besides tetracene, also pyrene, another outlier, was eliminated. Again, the standard error has been improved significantly, though not so dramatically as before. The correlation coefficient has further increased and the Fisher ratio increased by a factor of 2, which strongly suggests that pyrene also has been "unfairly" influencing the regression. The improvement in the statistical parameters again suggests that the SCF MO computed RE for pyrene deviates slightly from expectations based on conjugated circuits, or alternatively that pyrene (just as tetracene) may have *additional* structural features that are not captured by the model of conjugated circuits. Alternatively, both tetracene and pyrene may be lacking some typical characteristic that other benzenoids have. In either case, these two molecules influence the computation of parameters R_1, R_2, and R_3 used for computation of RE values of the other benzenoids of Table 13.

It is legitimate to eliminate outliers so that they do not influence regression if either data on them is in error or they have some structural features that are unique to them, not shared by other members of the set, and not described well by the descriptors used. The two cases illustrate the difficulties that one may encounter when one uncritically adopts properties of molecules *assumed* to be aromatic for definition of aromaticity, or for a selection of the standards for aromatic prototypes. Such molecules may have (or lack) some of the features that characterize the majority of aromatic compounds. For instance, among the benzenoid hydrocarbons of Table 13, tetracene is the *only* structure having four linearly fused benzene rings. It is possible that contributions from R_4, that are ignored here, have to be taken into account, but unless such contributions are assumed to be negative (destabilizing), such a "correction" will only make things worse for tetracene.

One should be aware that there is always a danger of "neglect of relevant evidence", or alternatively, "*Arguing in a way that ignores the importance of evidence unfavorable to one's position*",[91] when eliminating "outliers". To be on safe grounds, in Table 29 we have listed the residuals of the regression of SCF MO resonance energies against the graph theoretical RE when tetracene alone, and when tetracene and pyrene are eliminated as outliers (the two central columns having one and two asterisks as entries, respectively). As we can see, when we eliminate tetracene, not only does pyrene remain an outlier but an additional two compounds, benzo[*a*]pyrene and benzo[*e*]pyrene, which appeared "normal" when all

Table 29. Residuals in the Regression of SCF MO Resonance Energies and Parameters R_1, R_2, and R_3 for Smaller Benzenoids, and When One or More "Outliers" Were Removed from the Regression

benzenoid	res.	res.*	res.**	res.****	RE (calcd)
benzene	+0.002	+0.008	+0.006	+0.005	0.864
naphthalene	−0.016	+0.000	−0.003	−0.001	1.324
anthracene	−0.018	−0.000	−0.009	−0.003	1.603
tetracene	+0.070	*	*	*	*
phenanthrene	−0.007	−0.002	−0.003	−0.004	1.937
pyrene	−0.043	−0.027	*	*	*
benzanthracene	−0.005	+0.001	−0.002	−0.000	2.291
chrysene	−0.005	+0.001	+0.001	+0.001	2.482
benzo[*a*]pyrene	+0.015	+0.026	+0.018	*	*
perylene	−0.009	−0.002	+0.002	+0.000	2.619
triphenylene	+0.018	−0.000	+0.004	−0.002	2.656
benzo[*d*]pyrene	−0.008	−0.012	−0.015	*	*
dibenz[*a*,*h*]anthracene	+0.006	+0.002	+0.002	+0.001	2.947
benzo[*ghi*]perylene	−0.002	+0.005	−0.001	+0.003	3.125
regression coeff	0.99927	0.99959	0.99994	0.99999	
standard error	0.0286	0.0137	0.0093	0.0034	
Fisher ratio	2 270	9 660	20 587	142 516	

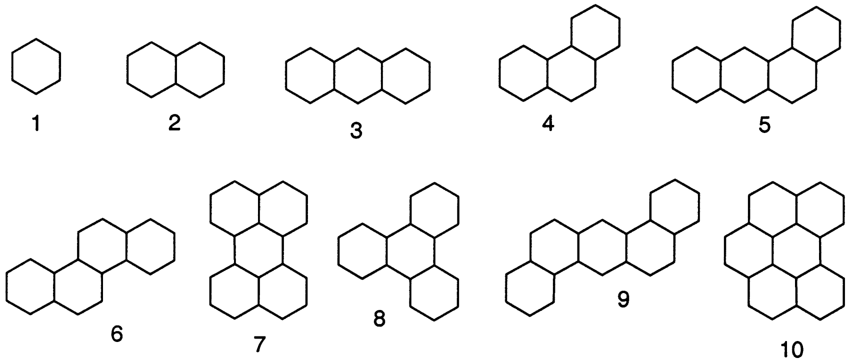


Figure 69. Ten benzenoids that show an outstanding correlation between the graph-theoretically computed RE based on the count of conjugated circuits and the SCF MO calculated RE of Dewar and de Llano.[45]

14 compounds of Table 14 were considered in multivariate regression, now show visible deviations (residuals): +0.026 and −0.012, respectively. When both tetracene and pyrene were eliminated, the two benzopyrenes still showed residuals that were visibly larger than the rest of the benzenoids considered (+0.018 and −0.015, respectively). Finally, in the next column of Table 29, we show the residuals when tetracene, pyrene, and two benzopyrenes are eliminated from the regression, leaving the regression based now on only 10 benzenoids of the original 14 considered. Removal of the four compounds made an enormous improvement in the statistical parameters (shown in the last three rows of Table 14). All the residuals are well within twice the magnitude of the standard error. The Fisher ratio (*F*) has increased by a factor of over 60 in comparison with the initial value of *F*. In the last column of Table 29 are given computed RE values for the 10 benzenoids that survived statistical "cleansing".

Observe the unprecedented improvement in the statistical parameters of the "cleansed" regression based on 10 benzenoids. The standard error is about 10 times smaller than when all 14 benzenoids are used in a regression, and the Fisher ratio has increased by a factor of 15. The numerical values for the parameters R_1, R_2, and R_3 changed somewhat when various outliers were disregarded, but these changes remained relatively small. In all cases, the relative magnitudes of R_1, R_2, and R_3 are approximately given by the ratio 1:1/3:1/9. Also, the constant term in all regressions of Table 14, which we have neglected to mention because it only shifts the scale for RE slightly and does not influence the relative RE values, is not changing much. We mention this "purification" of the correlation not because it is important for our estimates of the values for R_1, R_2, and R_3, because these have not changed much. Rather, we mention this to give credit to M. J. S. Dewar, who apparently was able to arrive at such fine-tuning of his MINDO computational schemes that display extraordinary internal consistency, at least when applied to the class of benzenoid hydrocarbons. Clearly, Dewar was able to identify the significant terms in his approximate quantum chemical calculations and ignore contributions that are insignificant for the calculation of molecular RE.

It may be worth mentioning that the "mystery" about pyrene and two benzopyrenes being outliers was also found in early calculations of ^{1}H NMR chemical shifts based on the model of ring currents using the Hückel−London−Pople−McWeeny method.[576] In summary, we could speculate that indeed there is something "peculiar" about tetracene and pyrene (which might have influenced the two benzopyrenes). The remaining 10 benzenoids, those shown in Figure 69, show an outstanding correlation between graph theoretically computed RE (as derived from the count of conjugated circuits R_1, R_2, and R_3) and RE obtained from quantum chemical calcula-

Table 30. Semi-empirical Quantum Chemical Calculations That Passed the Test by Producing the Correct Relative Magnitudes for the Graph Theoretical Parameters R_1, R_2, and R_3

method	benz.	naph.	anth.	R_1	R_2	R_3
SPO	1.32	2.28	3.08	1.32	0.78	0.63
SCF π-MO	1.32	2.28	3.09	1.32	0.79	0.64
SCF π-MO	2.05	3.69	5.17	2.05	1.44	1.33
SCF π-MO	0.87	1.32	1.60	0.87	0.25	0.10
DRE	0.93	1.48	1.90	0.93	0.36	0.29
ring additivity	0.91	1.48	1.90	0.91	0.40	0.27
SCF p-MO	0.90	1.46	1.77	0.98	0.23	0.16
resonance theory	0.84	1.35	1.60	0.84	0.35	0
log K	0.82	1.30	1.64	0.82	0.31	0.20
ISE	0.92	1.45	1.86	0.92	0.34	0.28
IMOSE	0.93	1.46	1.81	0.93	0.34	0.18
HMOSE	0.93	1.48	1.85	0.93	0.37	0.20

Table 31. Semi-empirical Quantum Chemical Calculations That Did Not Pass the Test by Producing the Correct Relative Magnitudes for the Graph Theoretical Parameters R_1, R_2, and R_3

method	benz.	naph.	anth.	R_1	R_2	R_3
VB	1.56	2.65	3.63	1.56	0.85	0.86
HMO*	2.00	3.68	5.31	2.00	1.53	1.58
VB	1.56	2.88	4.21	1.56	1.19	1.35
HMO + overlap	1.56	2.72	3.82	1.56	0.96	1.02
ring count*	1.56	2.60	3.64	1.56	0.78	1.04
additivity DRE	0.91	1.44	2.00	0.91	0.33	0.60
HMO variation*	0.39	0.55	0.66	0.39	0.05	0.06
HMO variation*	0.44	0.56	0.63	0.44	−0.04	0.02
IMOSE*	0.92	1.34	1.67	0.92	0.17	0.25
HMOSE*	0.92	1.49	1.97	0.92	0.40	0.40
Z number*	0.28	0.37	0.46	0.28	0	0.11
TRE*	0.27	0.39	0.48	0.27	0.04	0.06
TRE*	0.28	0.39	0.48	0.28	0.03	0.06

tions. While some may object to the “cleansing” procedure and may even challenge its legitimacy, and this is not the place to argue against or for that, the fact remains that the 10 benzenoid hydrocarbons in Figure 69 show a *remarkable internal agreement between graph theoretical and quantum chemical calculations*. Is this not worth serious attention in various quantum chemical circles? Should this not be enough to alert skeptics to pay attention to conjugated circuits, which have been ignored by most theoretical chemists for over 25 years?

XV. On a Diagnostic Use of Conjugated Circuits

The *diagnostic* potential of the conjugated circuits model has been tested on computed RE based on different quantum chemical models.[577] In Tables 30 and 31 we have summarized the results of various semi-empirical quantum chemical calculations of RE for benzene, naphthalene, and anthracene. All the methods listed in Table 30 *passed* the test based on the requirement that parameters R_1, R_2, and R_3 give the relative contributions of conjugated circuits decreasing monotonically with increasing circuit size, as calculated using the RE values for the three benzenoid hydrocarbons. This means that they satisfy the inequality $R_1 > R_2 > R_3$. Not all of the methods considered gave the approximate relative values R_1:R_2:R_3 = 1:1/3:1/9 found in the conjugated circuits method. The SCF π-MO method of Dewar and de Llano,[45] of course, satisfies the above condition because it was used to calibrate the parameters R_1, R_2, and R_3. The approach of George et al.,[578] based on SCF π-MO heats of atomization and resonance energy, again as computed by Dewar and de Llano, also shows a satisfactory performance. Less satisfactory results are obtained for the SPO method of Dewar and Gleicher[44] and an earlier version of the SCF π-MO method of Lo and Whitehead.[579] In both cases, the contributions of conjugated circuit R_3 appear exaggerated.

The approximate quantum chemical methods listed in Table 31 failed to satisfy the minimal requirement $R_1 > R_2 > R_3$ on the relative magnitudes of the contributing conjugated circuits rings when the RE values of benzene, naphthalene, and anthracene were calculated. Apparently, all the approaches listed in Table 31 overestimate the role of the contributions arising from R_3. Recall that the same thing happened with the calculations of Jiang and Li, which are exact VB calculations. This may suggest that the failure of the methods listed is not necessarily due to crudeness of the model but rather inadequacy of the procedure chosen for calculation of RE. The “lengthy” list of unsatisfactory approximate methods clearly points to subtleties involved in the development of approximate quantum chemical schemes. It is not surprising, then, that some such schemes, like Dewar’s MINDO, have undergone several modifications and revisions and apparently reached respectable internal consistency in the case of benzenoid hydrocarbons — judging by the high regression correlation shown in Table 29 for the 10 smaller benzenoids.

XVI. Resonance Graphs

We should recall that Herndon, in his structure–resonance theory,[164] employed two molecular integrals, γ_1 and γ_2, which give interaction terms between Kekulé valence structures differing in the location of three CC double bonds within the same benzene ring, and in the location of five CC double bonds in two adjacent benzene rings, respectively. Because the approach of Herndon and the conjugated circuits model could be made mathematically equivalent, Herndon’s molecular integrals γ_1 and γ_2 correspond to contributions from conjugated circuits R_1 and R_2, respectively (when they are identically parametrized). If we return to the upper part of Table 14, which shows the stepwise regression of RE when R_1, R_2, and R_3 are used as variables in multivariate regression, we see that R_1 and R_2, to a great extent, capture most of the contributions of various Kekulé valence structures to molecular RE. In his calculations of RE values of smaller benzenoid hydrocarbons, Herndon used only integrals γ_1 and γ_2. Inclusion of contributions from R_3 (or alternatively γ_3), as can be seen from Table 14, decreases the standard error for the regression somewhat, but not dramatically. Glidewell and Lloyd[580,581] came to the similar conclusion that only local “benzene” and “naphthalene” moieties play important roles. They based their considerations in describing the aromaticity of benzenoid hydrocarbons on the MNDO study of bond orders for select polycyclic benzenoid hydrocarbons. This suggests that γ_1 and γ_2 are dominant for determining aromatic contributions, just as we found earlier that Q_2 and Q_3 are dominant for anti-aromatic contributions (in view of the questionable presence of Q_1).

Models based on "benzene" and "naphthalene" moieties, or more correctly based on the molecular integrals γ_1 and γ_2 or the conjugated circuits R_1 and R_2, have an advantage in being simpler and avoiding ambiguities associated with larger conjugated circuits, which can be of different shapes. Already in the case of R_3, conjugated circuits having 14 π-electrons may the have shapes of the periphery of anthracene, phenanthrene, or pyrene. Do they make the same contributions to molecular RE? This problem was discussed by Trinajstić, Nikolić, and Klein,[534] who suggested that conjugated circuits of different shapes make different contributions to RE. There is no a priori reason that they make identical contributions, but before this question is firmly settled, it would be desirable to have very accurate quantum chemical calculations and a very reliable protocol for extracting RE from such calculations for large numbers of benzenoid hydrocarbons — both of which are currently unavailable. Again, the question is not whether very accurate computations on a larger collection of benzenoid hydrocarbons can be made, because sooner or latter they will be made. The question is how can one extract, with sufficient precision, a non-observable quantity to be interpreted as molecular RE from such calculations. What one needs here are well-defined algorithms that will "translate" results of ambitious MO calculations in terms of valence bond (VB) and graph theory (GT) concepts, such as conjugated circuits. That this is possible was demonstrated by Polansky and Derflinger 35 years ago in their pioneering work on the interpretation of MO results in terms of Clar structures.[582]

The first step, just the use of R_1 alone, already gives a fair correlation between graph theoretical and SCF MO resonance energy, as can be seen from the first row of Table 14. The numbers in the columns indicated by R_1, R_2, R_3, and "const", in Table 14 are the coefficient in the regression equation,

$$\mathrm{RE} = a_1R_1 + a_2R_2 + a_3R_3 + \text{constant}$$

respectively. Here RE is expressed in electronvolt units, and thus the constant term, being rather small, can practically be neglected. The regression using R_1 alone is satisfactory from a *qualitative* point of view. Thus, the count of only π-sextets in a set of Kekulé valence structures already captures the most important characteristics of benzenoids systems. We will see later that such a simple and elegant, but not simplistic, characterization of benzenoid hydrocarbons parallels to a great extent Clar's notion of aromatic π-sextets. Observe, however, the more visible change in the computed values for R_2 (or γ_2) contributions when instead of three parameters one uses two parameters. This illustrates why Herndon's approach based on only two parameters still work quite well. When the contributions of R_3 are neglected, R_2 compensates by increasing its value by approximately 10%. This apparently works because for many benzenoids the numbers of conjugated circuits R_2 and R_3 parallel each other to a considerable degree (see Table 15).

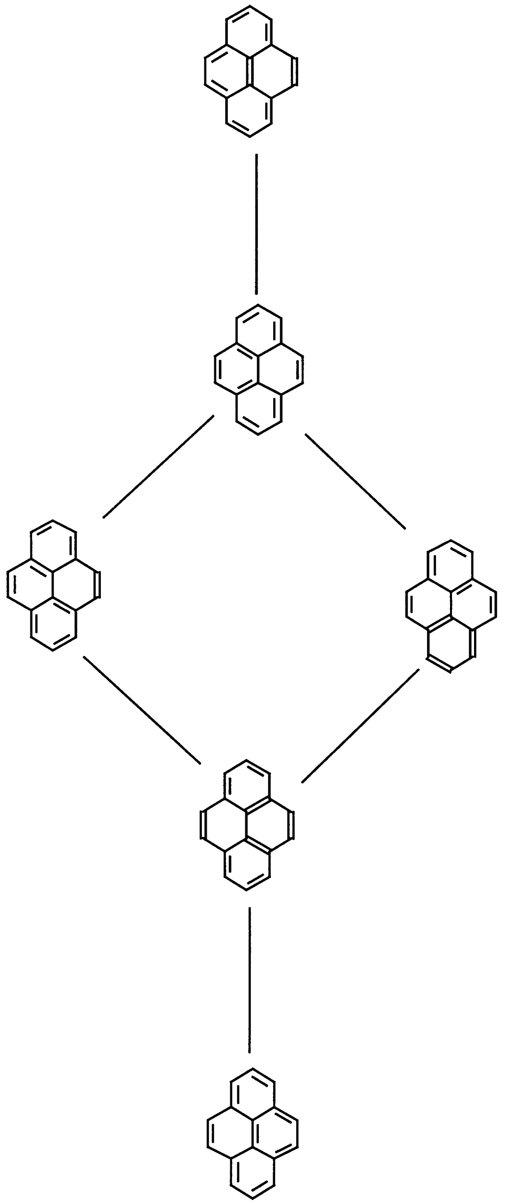


Figure 70. Simplified interaction graphs, referred to as "resonance" graphs, for the six Kekulé valence structures of pyrene.

In Figure 3 at the beginning of this review, we illustrated, for the six Kekulé valence structures of pyrene, the quantum chemical resonance interaction graphs of Herndon, in which the Kekulé valence structures used in the calculations are related by two kind of edges. Quantum chemical interactions between valence structures, which differ only in the position of CC double and single bonds in one benzene ring, are associated with the interaction integral γ_1, while if the structures differ in the positions of five CC double and single bonds in two adjacent benzene rings, they are characterized by the interaction integral γ_2. If we confine our attention only to the interaction integral γ_1, which is the same as confining our attention only to conjugated circuits R_1, then the interaction graphs of Herndon reduce to simpler graphs having only one type of edge. In

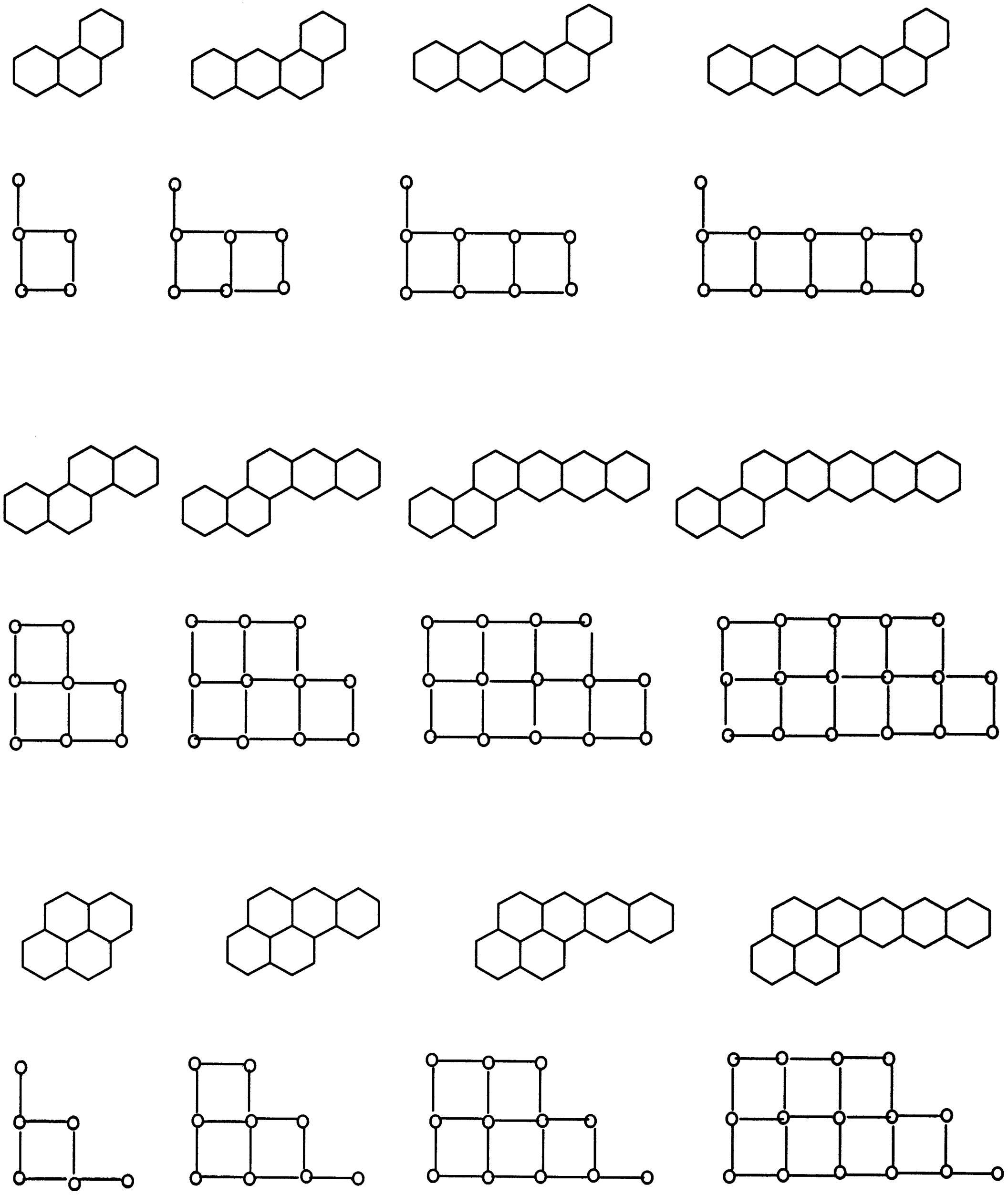


Figure 71. "Resonance" graphs for a selection of families of smaller benzenoid hydrocarbons.[337−339]

Figure 70 we show for the six Kekulé valence structures of pyrene the simplified interaction graph, referred to as the "resonance" graph. In Figure 71 we have illustrated a number of "resonance" graphs for a selection of families of smaller benzenoid hydrocarbons, as reported in refs 337−339. Observe from Figure 71 that resonance graphs of structurally related benzenoids, when similarly oriented, show some regularities. Once the regularity of the pattern characteristic of smaller graphs is recognized, one can construct resonance graphs for larger members of the family. Moreover, from the regularity of such patterns within a family of resonance graphs, one may even be able to construct recursion relations for the Kekulé structure count for larger members of the family.

These simplified resonance interaction graphs have interesting mathematical structures. The number of vertices is given by the number of Kekulé valence structures. In Figure 72 we have illustrated the resonance graph of benzo[*ghi*]perylene, the 14 valence structures of which are shown in Figure 15. In Figure 72, on the right, we used the same labels as in Figure 15 to identify the individual Kekulé valence structures that result in the resonance relationship.

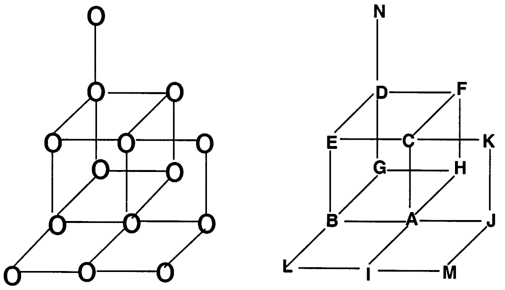


Figure 72. "Resonance" graphs of benzo[*ghi*]perylene. In the right diagram, all Kekulé valence structure of benzo[*ghi*]perylene have been identified using the labels of Figure 15.

The first thing to observe is that the degree of vertices in Figure 72 is determined by the number of the smallest conjugated circuits R_1 in each structure. Hence, the central vertex in the resonance graph with the degree $d = 5$ belong to the Fries valence structure A. The terminal vertex of degree $d = 1$ belongs to the anti-Fries valence structure N. From Figure 72 we see that all resonance graphs are built from fragments that represent *n-dimensional cubes.* For $n = 1$, the resonance graph reduces to an edge, which can be viewed as a "one-dimensional cube". For $n = 2$ we have a square graph or 2-D cube, for $n = 3$ we have a 3-D cube, for $n = 4$ we have a four-dimensional cube, etc. Graphs built by fusion of *n*-dimensional cubes are known in graph theory as "median" graphs.[583−586] They may involve combinations of cubes of different *n*, as is the case with the resonance graphs shown in Figure 72, which belong to benzo[*ghi*]perylene.

The resonance graphs of smaller benzenoid hydrocarbons were apparently first considered by Gründler of the Martin-Luther University of Halle-Wittenberg (then in East Germany), who published his work in the science journal of that University.[337] We rediscovered these graphs a dozen years later. Just as we were unaware of this work of Gründler for many years, apparently he was also not aware of our work. Thus, in the same publication, on what we now call resonance graphs, he reports on the graph theoretical ring indices for a few smaller benzenoids that he apparently rediscovered independently several years after our publication (and that of Aihara).[587]

Insights That Simple Models Offer. A question can be raised of why one should consider "simpler" models, such as calculation of RE by using only R_1, or only R_1 and R_2, when at not much greater effort one can consider models using R_1, R_2, and R_3 (and if necessary even higher contributions that are neglected here). Similarly, one can question why, in this age of ab initio calculations, one is still discussing semi-empirical MO and VB methods. We should remind the reader of the opening quotation, attributed to Parr, to the section of this review discussing approximate versus ambitious calculations. Apparently, what such critics overlook is not only the "diagnostic" value of simpler molecular approaches but also the fact that simpler computations are more likely to offer *interpretation* of the results obtained by elaborate calculations.

Let us illustrate the merits of simple approaches on a comparison of the bond orders as computed by the HMO method and the more elaborate Pariser−Parr−Pople (PPP) method, which represents an SCF MO model. That the two methods will give different results for the corresponding bond orders is to be expected. In Figure 73, on the left, we have indicated for phenanthrene the *differences* between the HMO and PPP bond orders. We have assigned the plus and the minus signs to CC bonds for which the bond orders have increased or decreased, respectively, when going from the HMO to the PPP. An increase in a bond order signifies a decrease in the corresponding CC bond length. Thus, CC bonds indicated by plus signs in Figure 73 have in fact became somewhat shorter in PPP calculations. In other words, such bonds have increased their C=C double bond character. The opposite is the case with CC bonds having the minus sign, which have increased their C−C single bond character. If we now replace the plus and minus labels of the CC bonds of phenanthrene by C=C and C−C signs, we obtain the Kekulé valence structures shown on the right in Figure 73.[588] Observe that the Kekulé valence structure of phenanthrene obtained in this way has three Kekulé benzene rings; that is, it is the valence structure that Fries recognized as "the most important". In Figure 74 we show similar results for a selection of smaller benzenoid hydrocarbons considered in ref 588. In all cases, comparison of the bond orders between the HMO and the PPP, when transformed to changes in CC bond character, results in a single Kekulé valence structure of each of the benzenoids considered, and the resulting structure is the Fries valence structure. In the case of molecules having two symmetry-equivalent Fries valence structures (e.g., pyrene, ovalene), the resulting valence structure is obtained by their superposition. We think that it is highly significant that all the resulting Kekulé valence structures, when comparing HMO with PPP, are the Fries Kekulé valence structures[5,6] of the benzenoids considered. Clearly, all this is not accidental.

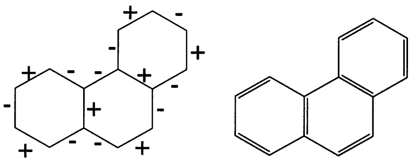


Figure 73. The *differences* between the HMO and the PPP bond orders illustrated on phenanthrene (left). Plus and minus signs indicate CC bond lengths that have decreased and increased, respectively. When the changes are interpreted as increased C=C and C−C bond character, the Fries structure (right) of the molecule is obtained.

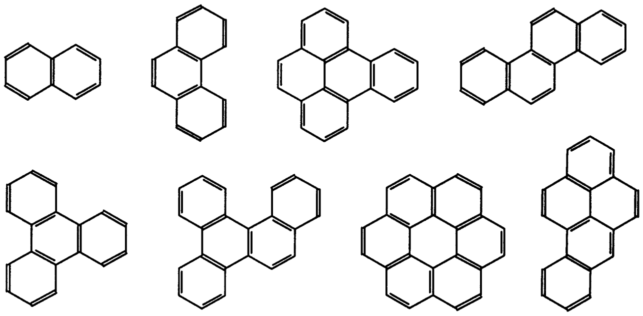


Figure 74. Dominant Kekulé structures (Fries structures) obtained from a comparison between the HMO and the PPP bond orders for smaller benzenoid hydrocarbons.[588]

The numerical details of both approximate methodologies, the HMO and the PPP methods, are not as important here as the *conceptual novelty* that relates two MO theories to a very special Kekulé valence structure. The comparison of the HMO and the PPP methods suggests that electron repulsion, which has been *incorporated* in the PPP approach but has been *absent* from the simple Hückel MO approach, may be a factor in contributing to the relative importance of Fries Kekulé valence structures. In other words, the comparison of the HMO and the PPP methods offers an *explanation* of the empirical Fries rule. The Fries rule has pointed toward the most important Kekulé valence structures *but did not say why* structures with the maximal number of benzene rings are the most important. From the above, it appears that the Fries structures, in comparison with other Kekulé valence structures, better accommodate electron−electron repulsion.

It is of interest to mention here that, besides the pioneering work of Polansky and Derflinger[582] on the interpretation of MO calculations in terms of Clar's structures, there have been several publications in which the results of MO calculations were related to Kekulé valence structures. Thus, for example, England and Ruedenberg[589−591] considered localization of molecular orbitals and found that local orbitals point to a single Kekulé structure or a superposition of symmetry-equivalent Kekulé structures. They raised the question, "*Why is the delocalization energy negative?*"[591] and reported that every one of the maximally localized π orbitals is still more delocalized than the ethylene π-orbital. Paniagua and Moyano have observed[592] for benzenoid conjugated hydrocarbons that the localized molecular orbitals of Edminston and Ruedenberg[593,594] can always be associated with the Fries Kekulé structure of the maximal Kekulé index value. The Kekulé index was introduced by Graovac et al.[595] as a measure of the overlap of a set of CC double bonds within a Kekulé valence structure with each of the occupied MO's. One may interpret the Kekulé index to indicate the importance of a Kekulé valence structure: the larger the index, the more important is the contribution of that particular structure in the total wave function. Such an interpretation is supported by the result that the valence structures with the largest number of benzene Kekulé structures are those with the greatest Kekulé index, in complete agreement with the empirical Fries rule.[5,6] Finally, we may add that Hosoya and collaborators[596−598] produced visual density maps which depict local features in benzenoid hydrocarbons. They considered the concept of partial electron density and drew contour maps slightly above the molecular plane. For a number of benzenoids, such maps show the characteristic features that parallel densities expected from Clar structures of these benzenoids.

XVII. Aromaticity versus Anti-aromaticity

> *Kekulé structures are of paramount importance for the stability of aromatic ring systems.*
>
> E. Clar, W. Kemp, and D. G. Stewart[599]

We start with the fact that we all agree that benzenoid hydrocarbons − that is, polycyclic conjugated hydrocarbons built from fused benzene rings − are aromatic. Some may be "more" aromatic than others, but they are all aromatic. Difficulties arise when we want to attribute "aromatic character" to the compounds that are built not from benzene rings but from rings of different sizes. Some of these non-benzenoid hydrocarbons show considerable similarity in various properties to benzene itself, and they themselves rarely cause problems. Non-benzenoid hydrocarbons that do not show any similarity whatsoever in their properties to benzene again do not cause much problems. The difficulties are with compounds that are, so to speak, the "border" case. They show some similarity to benzenoid hydrocarbons, but at the same time they display marked dissimilarities. Are they to be considered aromatic or not, or could we assign to them a partial aromaticity character?

Before trying to clarify these difficulties, we have to agree on the terminology to be used. We will first define *benzenoid hydrocarbons* as used in this review as follows:

Definition: *A benzenoid hydrocarbon is a conjugated polycyclic system having Kekulé valence structures built solely from fused benzene rings in such a way that no larger rings are formed.*

According to this definition, helicenes classify as benzenoids, even though larger helicenes are highly non-planar, with several rings overlapping other rings. As has been pointed out by Herndon,[600] although we may draw benzenoid hydrocarbons as fragments of a graphite lattice, many benzenoids are not planar because of hydrogen−hydrogen repulsion. This is particularly the case with benzenoids having the so-called "cove" or "fjord" regions on their perimeters. The descriptive terms "cove" and "fjord" were introduced by Gutman and Cyvin[452] to signify local concave regions on the periphery of benzenoids involving four and five CC bonds, respectively. While "cove" and "fjord" may be adequate descriptive labels, they have been overshadowed by the local regions known as the "bay". This term describes a concave fragment of the periphery of benzenoids involving three CC bonds close to the terminal benzene ring, which became prominent with their recognition by Jerina and co-workers[419−421] as the location of importance for carcinogenicity of benzenoid hydrocarbons.

We should mention that there are other definitions of benzenoid hydrocarbons. For instance, Gutman and Cyvin[452] excluded as "benzenoid" compounds that cannot be superimposed on a graphite lattice without overlapping (like larger helicenes). In addition, Gutman classified as "benzenoid" structures that represent fragments of a graphite lattice, even if they have no Kekulé valence structures. This is the case with the structures shown in Figures 75 and 76. Such structures have been referred to as "non-Kekuléan". The definition of benzenoids proposed by Gutman and Cyvin may be more suitable for mathematical than for chemical analysis. Our definition of benzenoid hydrocarbons excludes structures shown in Figures 75 and 76, because they do not have Kekulé valence formulas. In fact, such structures do not exist as chemical compounds. In his booklet *The Aromatic Sextet*, Clar[49] considered several hypothetical structures shown in Figure 75 and concluded that they cannot be prepared. It is not difficult to recognize that structures shown in Figure 75 cannot have Kekulé valence structures, because they have unequal numbers of "starred" and "non-starred" carbon atoms. Kekulé structures require an equal number of

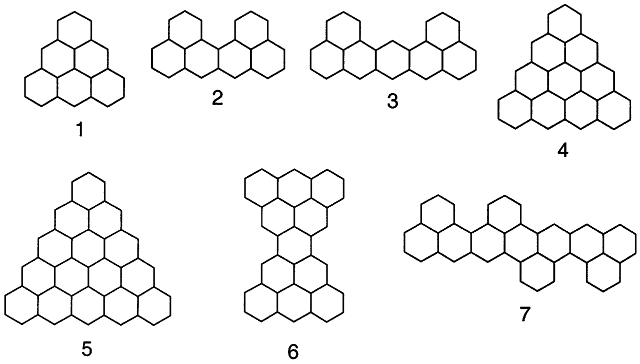


Figure 75. Benzenoid-like structures that represent fragments of a graphite lattice but have no Kekulé valence structures.

"starred" and "non-starred" carbon atoms because each CC double bond combines one "starred" and one "non-starred" carbons atom. However, it may be more difficult to recognize the structures shown in Figure 76 as "non-Kekuléan" (that is, as structures with $K = 0$). Structures built from fused hexagonal rings belong to the class of bipartite graphs. In such systems, carbon atoms can be labeled as "starred" and "non-starred" so that "starred" atoms are adjacent to "non-starred" atoms and vice versa. An equal number of "starred" and "non-starred" carbon atoms is a necessary but not sufficient condition for $K \neq 0$, as illustrated by **6/75** and **7/75**, the last two structures shown in Figure 75, and all the non-Kekuléan structures shown in Figure 76. The structures having an equal number of "starred" and "non-starred" carbon atoms and not having a Kekulé valence structure have became known as "concealed" structures, in view of the fact that in some cases it is more difficult to recognize such structures as having $K = 0$. The search for "concealed" structures received some attention in the literature.[601−606] Because such structures do not exist it may appear that they would be of limited interest in chemistry. However, some of the structures shown in Figures 75 and 76 represent carbon skeletons of stable dianions and dications. Murata and co-workers[607,608] synthesized both the dianion and the dication of triangulene (**1/75**) and dibenzopentacene (**3/75**).

Clar and co-workers[609,610] tried to synthesize a few of the "elusive" compounds, triangulene (**1/75**), $C_{22}H_{12}$, and dibenzo[*de*,*jk*]pentacene (**2/75**), $C_{24}H_{14}$, but without success. Clar came to the conclusion that compounds that have no Kekulé valence structure do not exist. One can refer to this conclusion of Clar as the "Clar postulate":

Clar Postulate: *Structures built from fused benzene rings for which one cannot draw a Kekulé valence structure do not exist.*

The significance of this postulate can be put in full parallel with the significance of the Hückel $4n + 2$ rule. The Hückel $4n + 2$ rule explained the difference between $4n + 2$ and $4n$ monocyclic conjugated systems, which was the first triumph of MO theory as applied to organic chemistry. The Clar postulate, which predicts the very existence of structures built from fused benzene rings, can be viewed as the first triumph of chemical graph theory applied to polycyclic conjugated systems! The Clar postulate can be extended to apply also for non-benzenoid hydrocarbons.

The structures shown in Figure 63, which include kekulene as the last structure, which was prepared in 1978 by Staab, Diderich, and co-workers,[611−614] have been excluded from both alternative definitions of benzenoids, although they are expected to show considerable similarities in their properties to benzenoid hydrocarbons. The reason for their exclusion from the class of benzenoids is that, although they can be viewed as derived by fusion of benzene rings, they also incorporate a larger (central) ring that does not represent benzene. Hence, such structures should not be taken as a standard for characterization of benzenoid hydrocarbons. Because of their considerable similarity to benzenoids, one may refer to these as pseudo-benzenoids. Such compounds have been of considerable theoretical interest,[615] particularly in view of the intriguing notion of "super-aromaticity" [616] that we will address later.

XVIII. On Classification of Polycyclic Conjugated Hydrocarbons

> *All the real knowledge which we posses, depends on methods by which we distinguish the similar from the dissimilar.*
>
> Carolus Linnaeus[617]

With so many compounds, it is only to be expected that one would like to classify them into groups, groups into subgroups, and subgroups into still smaller classes, if necessary. Several criteria for classifications of compounds continue to be considered in chemistry, such as cyclic ↔ acyclic, organic ↔ inorganic, hydrocarbons ↔ heteroatomic systems,

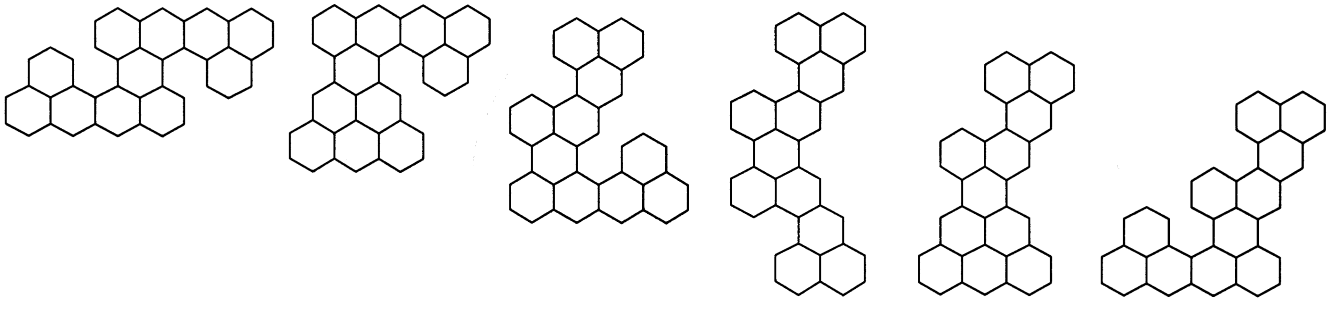


Figure 76. So-called "concealed" benzenoid-like structures (having an equal number of "starred" and "non-starred" carbons) that have no Kekulé valence structures.[601−606]

benzenoid ↔ non-benzenoid, alternant ↔ non-alternant, aliphatic ↔ aromatic, saturated ↔ unsaturated, carcinogenic ↔ non-carcinogenic, toxic ↔ non-toxic, etc. Each such classification has focused attention on a particular aspect of interest for the classification. Here we are interested in classification of compounds that will reflect their aromatic and/or anti-aromatic nature. Again, we will confine our attention to conjugated hydrocarbons and will not consider their ions or radicals. If we are going to extend the classification aromatic ↔ non-aromatic ↔ anti-aromatic to their ions or radicals, and then incorporate even heteroatomic counterparts, we must first wait for the proposed classification of polycyclic conjugated hydrocarbons to be accepted, ameliorated, or abandoned.

We propose to establish four classes of polycyclic conjugated hydrocarbons, as listed below:

fully aromatic (“aromatic−aromatic”)	**AA**	or	**AA**
aromatic	**A**		**A**
anti-aromatic	$\bar{\mathbf{A}}$		**1/A**
fully anti-aromatic (“anti-anti-aromatic”)	$\bar{\mathbf{A}}\bar{\mathbf{A}}$		**1/AA**

One may refer to the borderline cases between aromatic and anti-aromatic hydrocarbons as **A/A** (non-aromatic hydrocarbons).

Before each of the classes is fully described, let us explain why we have *four* classes and not two classes (aromatic and anti-aromatic), or why *three* classes (aromatic, non-aromatic, and anti-aromatic) will not suffice. There are no problems with the dichotomy “aromatic−anti-aromatic” based on the presence of only $4n + 2$ or only $4n$ conjugated circuits in the set of Kekulé valence structures of a compound, respectively. The problem is with the “non-aromatic” class, which would include structures having both $4n + 2$ and $4n$ conjugated circuits. Some structures in this class may show a greater similarity with benzene, and on the other hand they may show some similarity to anti-aromatic compounds. The problem is that the class of such “neither aromatic nor anti-aromatic” structures, that have both $4n + 2$ and $4n$ conjugated circuits, is so *large* and so broad that it becomes of little use.

With four classes of compounds − fully aromatic, aromatic, anti-aromatic, and fully anti-aromatic − we have the possibility to differentiate between the benzenoid hydrocarbons, which are the prototype of aromaticity, and compounds that may show properties similar to those of benzenoid hydrocarbons but may have some structural features that are not typical of “pure” aromatic compounds (such as the presence of a few $4n$ conjugated circuits that may contribute slight anti-aromaticity characteristics). Consider, for example, biphenylene, which one would tend to classify as aromatic, yet the compound has a four-member ring that one tends to associates with anti-aromaticity. By introducing four classes of compounds, we can resolve the difficulty arising from compounds that show aromatic properties but are not a 100% aromatic. By separating aromatic compounds into two classes − “pure” or “fully” aromatic and “aromatic” (implying some “impurities”) − we can classify biphenylene as “aromatic”, while benzenoids like naphthalene, anthracene, phenanthrene, etc. are considered “pure” aromatic compounds. The distinction between “fully aromatic” and “aromatic” alerts chemists to the presence of “less than aromatic” features in some aromatic compounds classified in this way. In particular, this allows one to differentiate compounds that should be viewed as the *standards* of aromaticity from aromatic compounds, the aromatic properties of which could have been compromised by the presence of a few $4n$ conjugated circuits.

The critical structural elements on which we base our classification are conjugated circuits that are “hidden” in the set of Kekulé valence structures of a molecule. We may have molecules that have only $4n + 2$ type conjugated circuits, molecules that have only $4n$ type conjugated circuits, or molecules that have both types of conjugated circuits. If both types of conjugated circuits are present in a molecule, we can distinguish cases when there are more $4n + 2$ type conjugated circuits than $4n$ type, and vice versa. Finally, we may have cases where the two types of conjugated circuits appear to be present in a similar quantity, which leads to ambiguous borderline cases of compounds that have aromatic/anti-aromatic character. Such compounds may, at the same time, be weakly aromatic or weakly anti-aromatic. Although one may refer to such compounds as non-aromatic, there is no need to form a special class of aromatic/anti-aromatic compounds by itself. Such compounds may be grouped when needed and referred to as the borderline cases of aromatic/anti-aromatic without formally setting them apart. Hence, in summary, we propose the following classes of hydrocarbons, identified by differences in their conjugated circuits content:

fully aromatic	only $4n + 2$ conjugated circuits
aromatic	$(4n + 2) > 4n$
anti-aromatic	$4n > (4n + 2)$
fully anti-aromatic	only $4n$ conjugated circuits

One may informally refer to the borderline cases (when the number of $4n + 2$ conjugated circuits equals the number of $4n$ conjugated circuits) as non-aromatic hydrocarbons, but it appears better to call them by their proper name: “borderline case of aromatic/anti-aromatic class”. This would allow us to reserve the label “non-aromatic” compounds for compounds in which there is no resonance, in which all CC bonds have a fixed CC double or CC single bond type. An example of non-aromatic compounds would be, besides the tub form of cyclooctatetraene, molecules like fulvene (**1/77**), heptafulvene (**2/77**), fulvalene (**3/77**), sesquifulvene (**4/77**), and heptafulvene (**5/77**), shown in Figure 77. In such molecules, there are no conjugated circuits. Instead, one can consider conjugated paths (conjugated chains), which may allow one to better characterize subtle differences in the kind of conjugation components present in the compounds illustrated in Figure 77. In Table 32 we give the count of conjugated paths of different length for the acyclic non-aromatic compounds shown in Figure 78. As we can see, the count of conjugated paths varies among isomers. However, as illustrated

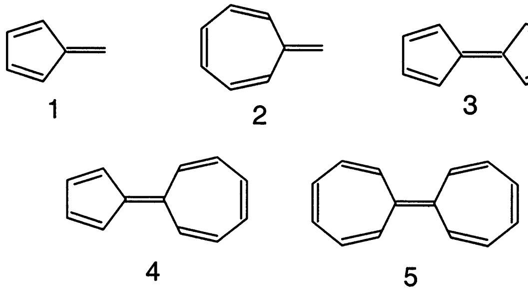


Figure 77. Cyclic benzenoid hydrocarbons with a single Kekulé valence structure.

Table 32. The Count of Conjugated Paths for the Acyclic Systems Shown in Figure 78

molecule	path 1	path 2	path 3	path 4	path 5
1/78	4	3	2	1	
2/78	4	3	2		
3/78	4	3	1		
4/78	4	3			
5/78	5	4	3	2	1
6/78	5	4	3	2	
7/78	5	4	3	1	
8/78	5	4	2	1	
9/78	5	4	4		
10/78	5	4	1		
11/78	5	4	1		
12/78	6	5	2	1	
13/78	6	5	2	1	
14/78	6	5	3	1	
15/78	6	5	3	2	

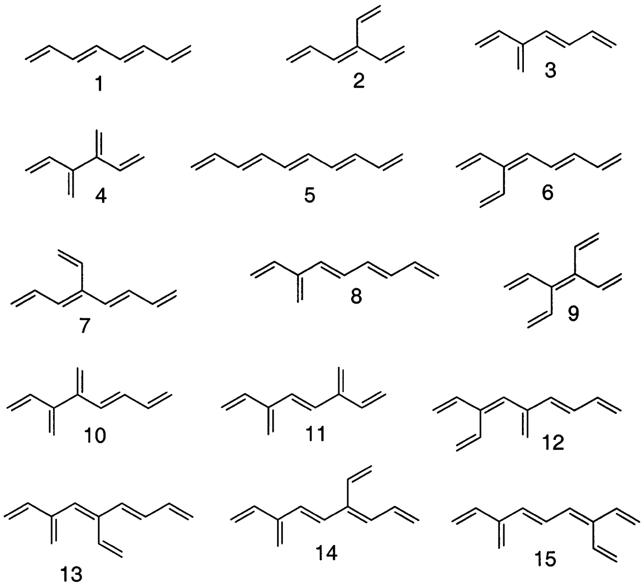


Figure 78. Acyclic conjugated hydrocarbons for which the count of conjugated paths is listed in Table 31.

by compounds **10/78** and **11/78**, there are compounds of different connectivity that are built having the same count of conjugated paths. This should not be surprising, because the same situation occurs with the count of paths in saturated alkanes.[322,323] On the other hand, the last four structures, **12/78**−**15/78**, isomers of $C_{12}H_{11}$, which have neither been discriminated by the cluster expansion method of Hess and Schaad,[618] nor by the method of Jiang, Tang, and Hoffmann,[559] as pointed out by Schmalz et al.,[619] are found to have different counts of conjugated paths. The method of Hess and Schaad discriminates three types of CC single bonds and five types of CC double bonds that can arise in unsaturated hydrocarbons in which carbon atoms may have as neighbors two, one, or no hydrogens. Jiang, Tang, and Hoffmann similarly consider five types of CC bonds, which can be single or double, which again differentiate only the immediate bond environment. Isomers necessarily have the same count of conjugated paths of length one and two, so to differentiate among them one has to increase the diameter of the neighborhood. As we can see from Table 32, there are many isomers that have the same count, even for paths of length three. As pointed out by Schmalz, Živković, and Klein, "*a framework for understanding these decompositions is provided by the concept of graph-theoretic cluster expansion.*" [619] A property of a molecule is written as a sum of contributions from progressively larger connected subgraphs of the molecular graph, but to be useful the expansion must converge relatively rapidly.[620−624] The critical step in such expansions is the selection of the class of subgraphs. For example, Moyano and Paniagua[625] considered a selection of the next-nearest-neighbor bond interactions, which apparently correspond to an increase (even if not systematic) of the diameter of the cluster expansion. As pointed out in ref 619, inclusion of all next-nearest-neighbor bond interactions would result in a large number of parameters that would need to be fitted to experimental data — so the "art" of the game is to recognize the smallest number of the expansion subgraphs that account for the most of variations in the properties. The conjugated paths may be of interest in some such expansions.

When considering expansions, some caution has to be exercised in allowing for a possibility that an apparently different form of an expansion may turn out to be mathematically equivalent. This has already been seen with Herndon's resonance theory and the conjugated circuits method, which can both lead to the same expressions for the molecular resonance energy. The distinction between such expansions may be in the interpretation of the terms used. This is well illustrated with a comparison of the quantum chemically computed diamagnetic susceptibilities of alkanes and the graph theoretical analysis of the same diamagnetic susceptibilities briefly outlined below.

Analysis of Diamagnetic Susceptibility of Alkanes. Hameka was[626] the first to develop a general theory of diamagnetic susceptibilities of saturated organic molecules. He used the MO formalism based on the following assumptions: (1) all CC and CH bonds are localized; (2) all CC bonds are identical and all CH bonds are identical; and (3) all CC and all CH bond lengths are constant for all alkane molecules.

Using the above assumptions, Hameka has shown that the diamagnetic susceptibility can be expressed by

$$\chi = N_C\chi_C + N_{CC}\chi_{CC} + N_{CH}\chi_{CH} - N_{CC,CC}\chi_{CC,CC} - N_{CC,CH}\chi_{CC,CH} - N_{CH,CH}\chi_{CH,CH}$$

Here, N_C is the number of carbon atoms, N_{CC} the number of CC bonds, N_{CH} the number of CH bonds,

$N_{CC,CC}$ the number of adjacent CC bonds, $N_{CC,CH}$ the number of adjacent pairs of CC and CH bonds, and $N_{CH,CH}$ the number of adjacent pairs of CH bonds. The quantities χ_C, χ_{CC}, χ_{CH}, $\chi_{CC,CC}$, $\chi_{CC,CH}$, and $\chi_{CH,CH}$ are formally defined through the corresponding quantum chemical integrals, which in semi-empirical approaches can be viewed as adjustable parameters.

The above theory of diamagnetic susceptibilities of alkanes is fully cast in the language of quantum chemistry. However, the assumptions of the model allow one to interpret the same results in the language of graph theory. Let us focus only on CC bonds, because CH bonds can be inferred from the connectivity of CC bonds. The assumptions that "all CC bonds are localized", that "all CC bonds are identical", and that "all CC bond lengths are constant for all alkane molecules" mean that small variations among CC bonds have been ignored in the calculations. But the same is true of *molecular graphs*, for which only *connectivity* matters and not the lengths of individual bonds. As we can see from the formula for χ, the *count* of bonds and the *count* of pairs of *adjacent bonds* are all that matter. In graph theoretical language, one speaks of paths of length one (bonds) and paths of length two (pairs of adjacent bonds). Hence, the result for the diamagnetic susceptibility can be equally well cast in graph theoretical format.

If we use the parameters A, B, and C of Hameka, defined as follows,

$$A = \chi_C + 4\chi_{CH} - 2\chi_{CC,CH} - 5\chi_{CH,CH}$$

$$B = \chi_C + \chi_{CC} + 2\chi_{CH} - \chi_{CC,CC} - 4\chi_{CC,CH} - \chi_{CH,CH}$$

$$C = -\chi_{CC,CC} + 2\chi_{CC,CH} - \chi_{CH,CH}$$

and use letters a, b, and c for the graphs representing carbon skeletons of methane, ethane, and propane, that is, paths of length zero, one, and two, respectively, we find that the two sets of descriptors are simply related:[627]

$$A = a - c, \qquad B = a + b + c, \qquad \text{and} \quad C = c$$

We see that by using the graph theoretical model, we can immediately understand, for example, why 2-methylpentane and 3-methylpentane have the same diamagnetic susceptibility, given by $A + 5B + C$, which is not apparent from the standard quantum chemical approach. For an extension of this approach to heteroatomic compounds, see ref 628.

XIX. Fully Aromatic Hydrocarbons

> *"Aromaticity," if to be used at all, should be a purely structural concept ...*
>
> E. Heilbronner [629]

Benzene and all benzenoid hydrocarbons have only $4n + 2$ conjugated circuits. Hence, these compounds should be viewed as prototypes of aromatic compounds. We have already shown in Tables 15−23 the RE values for the smaller benzenoid hydrocarbons illustrated in Figures 53−63, assuming in most cases and if not shown otherwise that $R_1 = 0.869$ eV, $R_2 = 0.247$ eV, and $R_3 = 0.1008$ eV. As already mentioned, when comparing molecules of different size, because RE increases with molecular size, better indices of relative aromaticity are RE/ring and REPE (the resonance energy per electron), the measure introduced by Hess and Schaad.[564] As we have seen from Tables 15−25, the values of REPE may vary appreciably. Benzenoid hydrocarbons with several linearly fused rings show reduced values of REPE in comparison with benzenoids having several "kink" rings. Among the compounds considered, the largest REPE, bigger even than the value for benzene, belongs to triphenylene and other fully benzenoid hydrocarbons considered. Clar was the first to advocate the concept of fully benzenoid hydrocarbons, which are benzenoid hydrocarbons of unusual stability.[49]

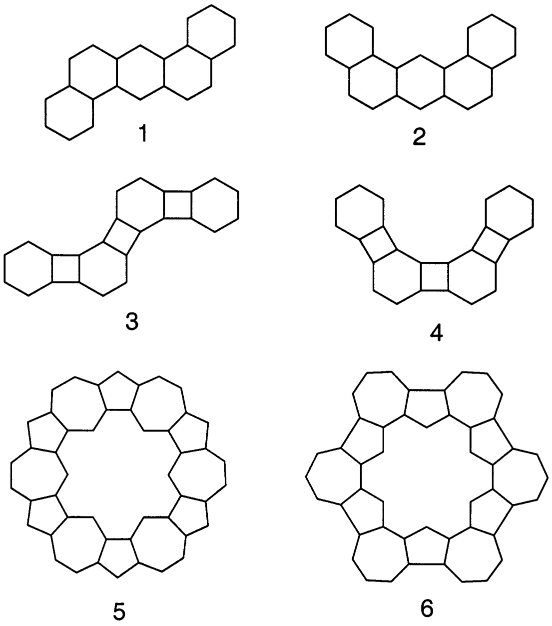


Figure 79. Isoconjugate structures. Top, benzenoids; middle, alternant non-benzenoids; and bottom, non-alternant non-benzenoid structures.

Definition: *Fully benzenoid hydrocarbons are 6n π-electron systems, which have the maximal number of disjoint benzene rings to which is assigned isolated π-sextets, mutually connected by CC single bonds only.*

There are benzenoid and non-benzenoid hydrocarbons that have identical decomposition of their Kekulé valence structures in conjugated circuits. One refers to such structures as *isoconjugate.*[53] In Figure 79 (top) we show dibenzo[*a*,*h*]anthracene and dibenzo[*a*,*j*]anthracene, a pair of benzenoid hydrocarbons that are isoconjugate. Such structures can be easily constructed from smaller benzenoids by attaching a benzene ring to symmetry-non-equivalent CC bonds that have the same Pauling bond order. For example, chrysene and benzophenanthrene, the smallest isoconjugate benzenoid hydrocarbons, can be constructed in this way from phenanthrene. In the middle part of Figure 79 is shown a pair of isoconjugate derivatives of biphenylene, while at the bottom is shown a pair of isoconjugate non-benzenoids built from azulene fragments. We included in Figure 79 two cyclic azulenoid structures; the structure on the

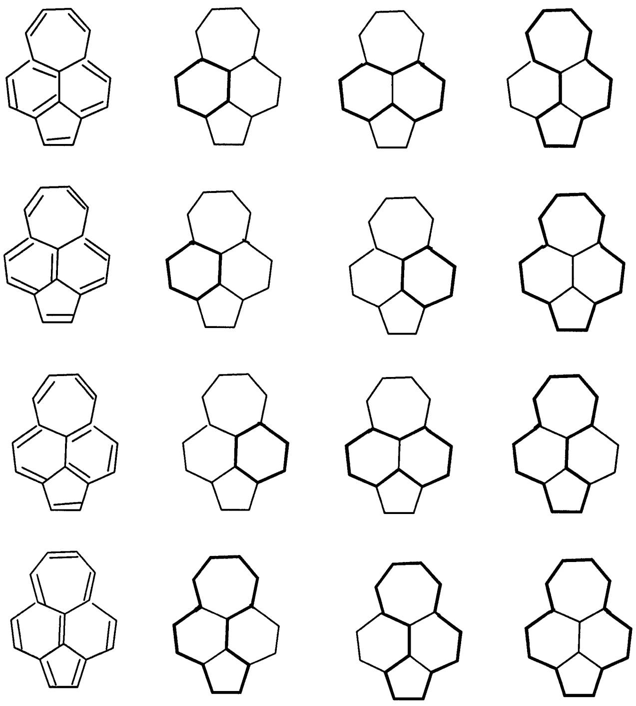


Figure 80. Kekulé valence structures for acepleiadylene, $C_{16}H_{10}$, and their decomposition in conjugated circuits.

left has been mentioned in the literature,[630] but the structure on the right apparently has been overlooked, and this may be the first time that it appears in the chemical literature. Both structures, which are isoconjugate, of course, would present an interesting challenge to synthetic chemists.

It may be of interest that isoconjugate benzenoid hydrocarbons necessarily have the same RE in Herndon's resonance theory VB model as in the conjugated circuits model, but generally they will have different RE in the HMO model and the TRE model, mentioned earlier. This clearly points to not only numerical but also conceptual differences between different graph theoretical models: those based on the adjacency matrix (HMO) and that based on Kekulé valence structures and conjugated circuits (VB).

That benzenoid hydrocarbons are generally viewed as aromatic is well known, but it is less known that there are a number of non-benzenoid hydrocarbons that also have *only 4n + 2 conjugated circuits*. A good example is acepleiadylene, $C_{16}H_{10}$, which has four Kekulé valence structures, illustrated in Figure 80. As we can see from Figure 80, each of the four individual Kekulé structures yields only $4n + 2$ conjugated circuits, which gives the following for the average conjugated circuits content of acepleiadylene: $(4R_1 + 2R_2 + 6R_3)/4$. This gives for molecular RE and REPE the values 1.143 and 0.071 eV, respectively. While the derived RE is somewhat smaller than that of naphthalene, the REPE is considerably smaller than the values found in benzenoid hydrocarbons having the same number of carbon atoms. In fact, we should compare the RE of acepleiadylene with that of pyrene, which has the same empirical formula $C_{16}H_{10}$: for pyrene, RE = 2.133 eV and REPE = 0.133, almost twice the values of acepleiadylene. Despite the reduced RE, acepleiadylene is as "blue blood" an aromatic compound as naphthalene and pyrene, because it has only $4n + 2$ conjugated circuits.

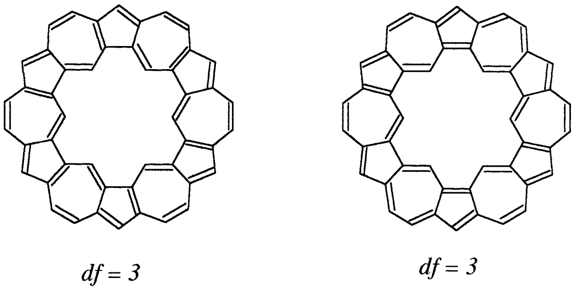


Figure 81. Two Kekulé structures of the cyclic azulenoid system shown in Figure 79, having $df = 3$ and having different numbers of disjoint conjugated circuits.

An interesting pair of non-benzenoid structures built from only five- and seven-member rings and having only $4n + 2$ conjugated circuits, and thus being prototypes of aromatic compounds, is illustrated at the bottom of Figure 79. They have only 36 Kekulé structures and are isoconjugate; that is, there is a one-to-one correspondence between their Kekulé structures and their conjugated circuits. Their expression for RE is $(120R_2 + 72R_4 + 24R_6)/36$; hence, essentially only the conjugated circuits within azulene units make significant contributions to molecular RE. A comparison with azulene shows that the REPE of the two cyclic azulenoids is about a half the REPE of azulene. This suggests that the synthesis of cyclic "azulenoids" is possible. In Figure 81 we show two Kekulé structures of the cyclic azulenoid, one of which has the maximal number (three) of disjoint conjugated circuits, and the other has the smallest number (two) of disjoint conjugated circuits. Both structures, as one can verify by trial and error, have $df = 3$, which indicates that in the case of *non-benzenoid* systems the number of disjoint conjugated circuits and the degree of freedom of a Kekulé structure need not be the same.

Non-benzenoid hydrocarbons having only $4n + 2$ conjugated circuits and built from five- and seven-member rings are illustrated in Figure 67. The structures **2/67** and **3/67**, then **5/67** and **6/67**, and again **4/67**, **7/67**, and **11/67** are isoconjugate. In Table 26 we listed the RE values of a number of fully aromatic non-benzenoid molecules (shown in Figure 67). Not surprisingly, these compounds also show large variations in REPE that are particularly visible in the case of compounds **4/67**, **7/67**, and **11/67**, which lack the contribution not only from R_1 conjugated circuits but also from R_2 conjugated circuits. Isoconjugate benzazulenes **2/67** and **3/67** represent bridged 14-annulenes having three Kekulé structures, and structures **4/67**, **7/67**, and **11/67** represent bridged 14-annulenes having only two Kekulé structures, while the bridge in structure **11/67** involves essentially single and essentially double CC bonds.

In summary, we see a clear-cut reduction in REPE for the fully aromatic molecules shown in Figure 67 with five- and seven-member rings in comparison with molecules built solely by fusion of benzene rings. Another significant reduction in REPE accompanies molecules having no fused benzene rings at all

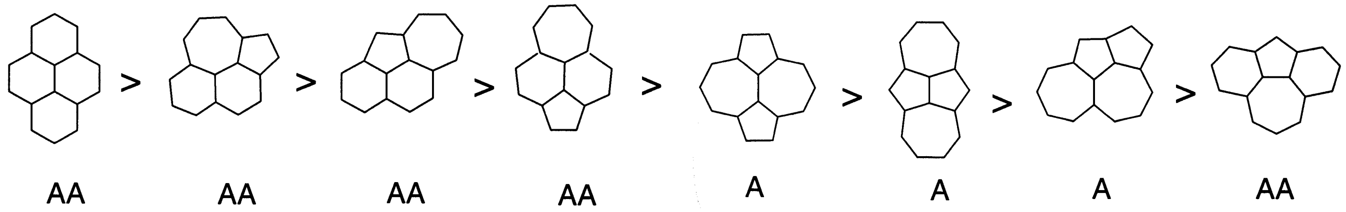


Figure 82. Non-benzenoid pyrene-like tetracycles studied by Aihara.[631] (RE values are shown in Table 33.)

Table 33. Expressions for Molecular RE, the Graph Theoretically Computed RE, and the Hückel Molecular Orbital (HMO) RE for Pyrene and Several Structurally Related Polycyclic Compounds (Shown in Figure 82)

molecule	description[a]	RE expression	RE	HMO RE
1/82	**AA**	$(12R_1 + 8R_2 + 4R_3)/6$	2.151	0.598
2/82	**AA**	$(4R_1 + 4R_2 + 4R_3)/4$	1.255	0.376
3/82	**AA**	$(4R_1 + 4R_2 + 4R_3)/4$	1.255	0.372
4/82	**AA**	$(4R_1 + 2R_2 + 6R_3)/4$	1.152	0.398
5/82	**A**	$(8R_2 + 2R_3 + 2Q_3)/4$	0.645	0.217
6/82	**A**	$(8R_2 + 2R_3 + 2Q_2)/4$	0.579	0.214
7/82	**A**	$(6R_2 + 2R_3 + 2Q_2 + 2Q_3)/4$	0.375	0.122
8/82	**AA**	$2R_3/2$	0.111	0.247

[a] **AA** = aromatic−aromatic (fully aromatic); only $4n + 2$ conjugated circuits. **A** = aromatic; $4n + 2 > 4n$ conjugated circuits.

(compounds 1−7 in Figure 67), which thus lack R_1 contributing conjugated circuits.

XX. Less than Fully Aromatic Hydrocarbons

Numerous compounds are generally viewed as aromatic although they contain, besides $4n + 2$ conjugated circuits, also a few $4n$ conjugated circuits. We have already mentioned aceheptylene and corannulenes with $4n$ periphery. If we are to restrict the label "aromatic" solely to compounds having only $4n + 2$ conjugated circuits, then on one hand there would be too few compounds besides benzenoid hydrocarbons that would qualify as aromatic, and on the other hand compounds that have many properties typical of aromatic compounds would not qualify. For example, compounds like biphenylene, generally considered aromatic, would then not qualify as aromatic. Therefore, we ought to broaden the definition of aromatic compounds so as to embrace compounds which have *dominant* contributions from $4n + 2$ conjugated circuits. However, in this way, in order to solve one "problem", that of widening the meaning of aromaticity, we have created a novel "problem", the problem of how to determine what constitutes the "dominant" aromatic features. More specifically: How many $4n + 2$ conjugated circuits in a molecule should be present to overshadow the adverse influence of $4n$ conjugated circuits?

In order to resolve this dilemma, we will examine structures having both $4n + 2$ and $4n$ conjugated circuits that are generally perceived as "aromatic", that is, in which $4n + 2$ conjugated circuits are presumed to play the dominant role. In Figure 64 we illustrated macrocyclic compounds obtained from fused benzene rings but allowing "holes" which involve larger $4n$ cycles. It seems plausible to expect here a dominant role of $4n + 2$ conjugated circuits. The smallest $4n$ conjugated circuits possible in such macrocyclic structures has 12 carbons atoms (designated as Q_3) which, at best, can make a small negative contribution to molecular RE. Recall also that aceheptylene, perceived by Coulson and others to be aromatic, has Q_3 conjugated circuits. Thus, it appears that conjugated circuits having 12 π-electrons already make weak "anti-aromatic" contributions to "threaten" the dominant features of $4n + 2$ conjugated circuits (here, R_2 conjugated circuits).

In Figure 82 we show pyrene and several non-benzenoid pyrene-like tetracycles, which Aihara[631] studied using the HMO approach. We have ordered these isomers of pyrene relative to their resonance energies. In Table 33 we have listed the expressions for the RE for these molecules in terms of conjugated circuits and computed RE using the following parametrization for conjugated circuits contributions:

$$R_1 = +0.827 \text{ eV} \quad R_2 = +0.317 \text{ eV} \quad R_3 = +0.111 \text{ eV}$$

$$Q_1 = -0.781 \text{ eV} \quad Q_2 = -0.222 \text{ eV} \quad Q_3 = -0.090 \text{ eV}$$

The above parametrization for $4n + 2$ conjugated circuits is based on the standard least-squares analysis[632] of 32 benzenoids for which Dewar and de Llano reported SCF MO resonance energies. The contributions of $4n$ conjugated circuits were based on the SCF MO computed resonance energy of cyclobutadiene, reported by Dewar and de Llano. The numerical values of the Q_2 and Q_3 parameters were obtained by assuming for Q_n contributions the same proportionality that holds for R_n contributions, i.e., the following approximations:[633]

$$Q_2 = (R_2/R_1)Q_1 \qquad Q_3 = (R_3/R_1)\,Q_1$$

We have to point out that future quantum chemical calculations of RE for these compounds may require a revision of the values assumed here for R_n and Q_n contributions.

Observe from Table 33 that pyrene, the only benzenoid compound among those considered, has RE considerably larger than the remaining compounds of Table 33. The next in magnitude of RE are the three "fully aromatic" compounds of Table 33: **2/82**,

3/82, and acepleiadylene **4/82**, the RE of which is about half that of pyrene. The three tetracyclic non-benzenoid isomers of pyrene undoubtedly owe their relatively high RE to the presence of the naphthalene moiety. All three compounds qualify as "fully aromatic" (or "aromatic−aromatic"), even though, as we see from Table 33, their RE values are about half that of pyrene. The next three compounds shown in Figure 82, **5/82**, **6/82**, and **7/82**, again show a dramatic reduction in RE in comparison with the three "fully aromatic" isomers of pyrene. The RE is now reduced by a factor of 2 compared to that of "fully aromatic" non-benzenoids. These three compounds have $4n$ conjugated circuits, but as we can see from the expression for RE, the reduction of RE is not so much due to the presence of $4n$ conjugated circuits as it is due to the *lack of the contributions from* R_1. Finally, the last structure of Table 33 not only lacks contributions from R_1 but also has no contributions from R_2 conjugated circuits, and although the structure qualifies as "fully aromatic" (having only $4n + 2$ conjugated circuits), its RE is practically negligible. For comparison, in the last column of Table 33 are listed HMO resonance energies for pyrene and its isomers as reported by Aihara,[631] which show a fair parallelism between the corresponding RE, except for the last two compounds.

There are two important messages from the comparison of the compounds listed in Table 33, First, RE alone does not offer a reliable criterion for classification of conjugated polycyclic compounds as aromatic, non-aromatic, or anti-aromatic. Second, the HMO computed RE values do not offer a reliable criterion for classification of polycyclic compounds as aromatic, non-aromatic, or anti-aromatic. The HMO computed RE for the last compound of Table 33 is apparently too high. Also, the relative values of RE as derived from the GT (graph theory) approach and the HMO method show minor discrepancies. According to the HMO method, the RE of isomer **4/82** is overestimated. A close examination of RE obtained by the HMO and the SCF MO approaches nevertheless may be instructive, particularly within families of structurally related compounds. It may give some insight into topological factors that are and that are not critical for molecular stability.

A. Degree of Aromaticity

> *(Cycloocta[1,2,3,4-def]benzo[3,4]cyclobuta[6,7]-biphenylene) appears to hover at the border line between olefinic, aromatic, and antiaromatic classification.*
>
> C. F. Wilcox, Jr., and G. D. Grantham[634]

Cycloocta[1,2,3,4-*def*]benzo[3,4]cyclobuta[6,7]biphenylene (shortly cycloocta[*def*]biphehylene), the first structure shown in Figure 83, built by fusing biphenylene and cyclooctatetraene, is one of several hydrocarbons involving unusual conjugations that were synthesized by Wilcox and collaborators in the period 1972−1976.[634−637] Cycloocta[*def*]biphenylene has an equal number of $4n + 2$ rings and $4n$ rings. Is it aromatic, olefinic, or anti-aromatic? Apparently, such molecules are less aromatic than biphenylene, which itself is less aromatic than any of the benzenoid hydrocarbons. It is then conceivable that the molecules shown in Figure 83 may have crossed "over the borderline between olefinic, aromatic, and anti-aromatic classification".

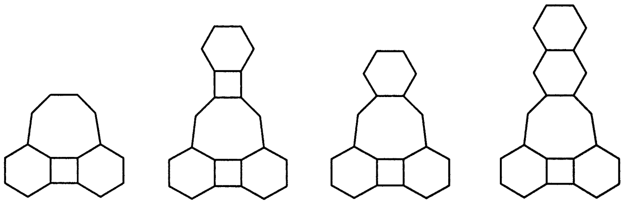


Figure 83. Cycloocta[1,2,3,4-*def*]benzo[3,4]cyclobuta[6,7]-biphenylene and related compounds described by Wilcox.[634−637]

In order to set a boundary between aromatic, non-aromatic, and anti-aromatic compounds, first we have to *define* a measure of the "degree of aromaticity" and then apply it to a series of structurally related compounds of apparently decreasing aromatic character in order to verify its adequacy. If we continue to consider RE as the prime indicator of aromatic characteristics of compounds, then we can define the "degree of aromaticity" to measure that portion of the total RE which is due to contributions from the aromatic $4n + 2$ conjugated circuits. This leads to the following:

Definition: *The degree of aromaticity A is given by the quotient*

$$A = [\mathrm{RE}(4n + 2) + \mathrm{RE}(4n)]/[\mathrm{RE}(4n + 2)] \\ = 1 + \mathrm{RE}(4n)/\mathrm{RE}(4n + 2)$$

where RE(4n + 2) are (positive) contributions of R_n conjugated circuits and RE(4n) are (negative) contributions of Q_n conjugated circuits.

This can be written as $A = 1 - Q$, where Q is the quotient of the absolute values of the negative and the positive contributions to RE. Hence, the degree of aromaticity is given by the fraction of RE derived from contributing $4n + 2$ conjugated circuits. Alternative definitions are possible. For example, one such "aromaticity scale" was defined as follows:[638]

Definition: *The degree of aromaticity is given by the quotient*

$$A' = [\mathrm{RE}(4n + 2) + \mathrm{RE}(4n)]/[\mathrm{RE}(4n + 2) - \mathrm{RE}(4n)]$$

where RE(4n + 2) are (positive) contributions of R_n conjugated circuits and RE(4n) are (negative) contributions of Q_n conjugated circuits.

Recollect that RE($4n$) is a negative quantity, so in both definitions the numerical values of the aromaticity index are less than one for compounds having $4n$ conjugated circuits. The two measures parallel each other to a degree.

We are now in a position to establish numerically the boundary between the aromatic and anti-aromatic compounds. A non-benzenoid hydrocarbon will qualify as aromatic or not, depending on whether, in such non-benzenoid hydrocarbons, there is a domi-

Table 34. Expressions for Molecular RE, the Graph Theoretically Computed RE, REPE, and the Percentage Aromatic Character for the Conjugated Hydrocarbons Shown in Figure 2, Which Illustrate a Gradual Transition from Fully Aromatic Benzene to Fully Anti-aromatic Hypothetical (Planar) Cyclooctatetraene

molecule	RE expression	RE	REPE	arom. (%)	non-dimensional	scaled RE	description[a]
1/2	$(2R_1)/2$	0.827	0.138	100	1.000	0.827	**AA**
2/2	$(4R_1 + 2R_2)/3$	1.314	0.131	100	1.555	1.286	**A**
3/2	$(8R_1 + 2Q_1 + 4Q_2 + Q_3)/5$	0.815	0.068	61.6	0.911	0.753	**A**
4/2	$(8R_1 + 2R_3 + 2Q_1 + 6Q_2 + 5Q_3 + Q_4)/6$	0.582	0.036	51.1	0.605	0.500	**A**
5/2	$(8R_1 + 4R_2 + 4R_3 + 2R_4 + 4Q_1 + 10Q_2 + 8Q_3 + 11Q_4)/9$	0.252	0.013	27.2	0.136	0.112	**A**
6/2	$(2R_1 + 2R_2 + R_4 + 2Q_1 + 10Q_2 + 4Q_3 + 3Q_4)/6$	−0.309	−0.017	−44.8	−0.531	−0.439	**1/A**
7/2	$(4R_2 + 2Q_1 + 8Q_2 + Q_4)/5$	−0.414	−0.026	−62.0	−0.674	−0.557	**1/A**
8/2	$(2R_3 + 4Q_2)/3$	−0.222	−0.014	−75.0	−0.370	−0.306	**1/A**
9/2	$(2Q_2)/2$	−0.222	−0.027	−100	−0.333	−0.275	**1/AA**

[a] **AA** = aromatic−aromatic (fully aromatic). **A** = aromatic. **1/A** = anti-aromatic. **1/AA** = anti-anti-aromatic (fully anti-aromatic).

nant role of $4n + 2$ or $4n$ conjugated circuits. In Figure 68 we collected a number of conjugated hydrocarbons having one or more odd-member rings. The structures considered included aceheptylene (**1/68**), azupyrene (**2/68**), dicycloheptapentalene (**4/68**), azulenoheptalene (**5/68**), pyracylene (**7/68**), and two isomers of dibenzpentalene (**8/68** and **9/68**). In Table 27 we listed their RE and A (%) values. As we can see from Table 27, the non-benzenoid non-alternant compounds in Figure 68 show a considerable variation in their RE values, which are as high as 1.323 eV and as low as 0.275 eV. The variation in the REPE for the same compounds also shows a considerable range: the highest value is 0.075 eV for **9/68,** and the smallest is 0.021 eV for pyracylene. However, the changes in their relative aromaticity is moderate: it decreases from the value found for an “almost” fully aromatic compound **10/68** to the dibenzpentalene **3/68**, which has an A index of about 62%. It is clear from Table 27 that the dominant role for all compounds shown in Figure 68 is played by the $4n + 2$ conjugated circuits.

B. On the Boundary of Aromaticity

At the very beginning of this review, in Figure 2, we illustrated a sequence of structurally related compounds starting with aromatic benzene and ending with hypothetical anti-aromatic (planar) cyclooctatetraene. A gradual variation of the relative content of $4n + 2$ and $4n$ conjugated circuits is expected as we move from the top to the bottom, from benzene to the planar hypothetical cyclooctatetrane. In Table 34 we show the aromaticity and anti-aromaticity indices for the compounds in Figure 2.

Finally, in the last two columns of Table 34, we computed a “non-dimensional” RE by assuming

$$R_1 = -Q_1 = 1, \qquad R_2 = -Q_2 = 1/3,$$
$$R_3 = -Q_3 = 1/9, \qquad R_4 = -Q_4 = 1/27$$

We have adjusted the scale so that it reproduces the RE of benzene, which facilitates comparisons with RE as calculated in the first numerical column of Table 34. An advantage of the dimensionless scale is that, though it is approximate, it is independent of fluctuations of the parameters R_1, R_2, R_3, and Q_1, Q_2, Q_3 when such would be based on quantum chemical computations from different sources and employing different approximations. As we can see, the two scales agree to a considerable degree. An additional advantage of the non-dimensional scale is that it allows one to include contributions of conjugated circuits R_4, R_5, R_6, etc., which were mostly neglected. We assume that they would make contributions of $1/3^3$, $1/3^4$, $1/3^5$, etc. Although these contributions are small in larger molecules, there are many of these conjugated circuits, so that they may not be negligible. Such would be the case of the giant benzenoids described by Müllen et al.[174−177] and the fullerenes described by Kroto et al.[153]

Even if such contributions cannot be established with sufficient confidence at this time, they have a conceptual value. Consider, for instance, the last compound of Table 27, for which we found the numerical aromaticity index A to suggest 100% aromaticity. However, we know that this is not a “full-blooded” aromatic compound, because the molecule has conjugated circuits Q_4 and Q_5, the contributions of which we have neglected. If we take into account the presence of these $4n$ conjugated circuits and use the extended “non-dimensional” scale, we find that the aromaticity index decreases to about 96% and is not 100%.

The “official” boundary between aromatic/anti-aromatic classification is a matter of convention, agreed upon between the users. One possibility is to consider $A = 1/2$ as the boundary of aromatic/anti-aromatic classification for the following reasons: *If* structures with $A = 0$ and $A < 0$ *do not exist,* because they would be unstable, while a structure close to $A = 1/2$ “*appears to hover at the borderline between olefinic, aromatic, and antiaromatic classification*”,[634] then the boundary $A = 1/2$ appears a plausible alternative choice. However, from a theoretical point of view, the case $A = 0$, which occurs for RE = 0, appears as a natural boundary between the aromatic and the anti-aromatic species. In the case of the compounds shown in Figure 2, which gradually change from aromatic to anti-aromatic, we see from Table 34 that RE for the compound which is in the middle of the list, cycloocta[*def*]biphenylene, is close to zero, as one would like to be the case. Although anti-aromatic compounds are elusive and often hypothetical, it may become possible to have a truly anti-aromatic compound by forcing a non-planar octatetraene ring to become planar, as is the case with tetrakis(bicyclo[2.1.1]hexeno)cyclooctatetraene reported by Fowler et al.,[639] a flattened cyclooctatetraene system which has D_{4h} symmetry and shows paratropic delocalized ring current while maintaining bond alternation.

C. Degree of Anti-aromaticity

We continue to report on the degree of aromaticity as given by the index A as previously defined and the degree of anti-aromaticity $1/A$, which can be defined analogously as follows:

Definition: *The degree of anti-aromaticity 1/A is given by the quotient*

$$\begin{aligned} 1/A &= [\mathrm{RE}(4n) + \mathrm{RE}(4n+2)]/[\mathrm{RE}(4n)] \\ &= 1 + \mathrm{RE}(4n+2)/\mathrm{RE}(4n) \end{aligned}$$

where RE(4n) are (negative) contributions of Q_n *conjugated circuits and RE(4n + 2) are (positive) contributions of* R_n *conjugated circuits.*

It follows from the definitions for the "degree of aromaticity" and the "degree of anti-aromaticity" that, for $A = 1$ or $A = 100\%$ compounds are "fully aromatic" and that for $1/A = 1$ or $1/A = 100\%$ compounds are "fully anti-aromatic". The quotients $[\mathrm{RE}(4n+2) + \mathrm{RE}(4n)]/[\mathrm{RE}(4n+2)]$ and $[\mathrm{RE}(4n+2) + \mathrm{RE}(4n)]/[\mathrm{RE}(4n)]$ will take values from $+1$ to -1. One can combine the "degree of aromaticity" and the "degree of anti-aromaticity" into a single index A by assigning positive values for aromatic compounds and using $A = -1/A$, i.e., negative A, for anti-aromatic compounds.

Although we based our classification of aromatic/anti-aromatic compounds on RE, other *properties* of such compounds may suggest a shift in the apparent characteristic perceived as making the compound aromatic. Thus, less aromatic compounds may appear more aromatic, or vice versa. Consider, for example, pyracylene or cyclopent[*fg*]acenaphthylene, prepared by Trost and co-workers.[640,641] This molecule shows an anomalously low half-wave reduction potential and has been characterized by Aihara: "*this compound is not obviously aromatic*".[631] We find that its aromaticity level based on RE is still quite respectable. When we use the three scales mentioned earlier, pyracylene's aromaticity index is 86.3%, 72.8%, and 75.0% aromatic, respectively. The count of conjugated circuits yields for molecular RE $(4R_1 + 2R_2 + 6Q_3)/4$, which clearly shows a dominant role of $4n + 2$ conjugated circuits. As we can see, while $4n + 2$ conjugated circuits make the dominant contribution to RE, it is possible that, for other properties (such as the half-wave reduction potential and magnetic properties), $4n$ conjugated circuits may play an important role.

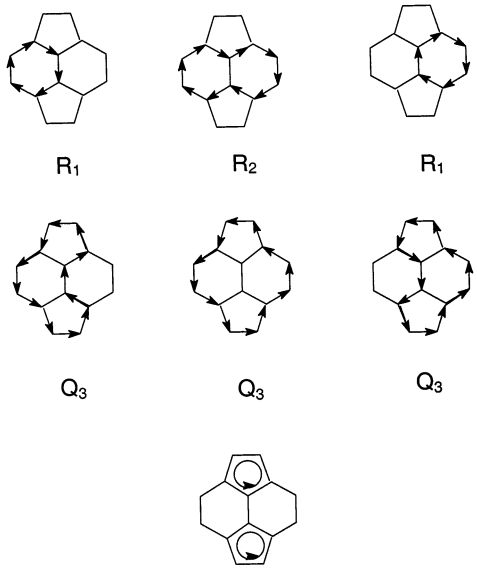


Figure 84. Schematic representation of diamagnetic and paramagnetic ring currents originating with $4n + 2$ and $4n$ conjugated circuits in pyracylene, respectively.

Pyracylene has been the subject of several quantum chemical calculations over a period of two decades. An early calculation of ring currents and magnetic properties of pyracylene is that of Coulson and Mallion[642] in the mid-1970s, based on iterative Hückel molecular orbitals. More recently, Fowler and co-workers[643] reported very advanced ab initio calculations on pyracylene based on the distributed-origin Hartree–Fock method. The results of such calculations, which are summarized in the article by Gomes and Mallion[644] in a recent issue of *Chemical Reviews* on aromaticity, point to difficulties of theoretical computations. The outcomes of such calculations are often sensitive to the level of sophistication of the computational method used. Nevertheless, the overall conclusion of these calculations points to dominant contributions coming from the "perturbed [4*n*]annulene". This indicates paramagnetic components of the ring current as opposed to diamagnetic components that originate with $[4n + 2]$annulene ring currents. In Figure 84 we indicate by arrows the direction in which CC bonds participating in different $4n + 2$ and $4n$ conjugated circuits in pyracylene contribute to ring currents. If we assume, for simplicity, that the accompanying ring currents are all of the same strength, then a simple superposition of all diagrams indicating ring current direction within individual conjugated circuits, corresponding to a superposition of all four Kekulé valence structures of pyracylene, gives as a result the diagram shown at the bottom of Figure 84. This simple schematic representation of the diamagnetic and paramagnetic ring currents leads to cancellations of ring currents in the peripheral CC bonds of the naphthalene moiety. The resulting ring currents qualitatively agree with more elaborate pictorial representations of induced current densities in pyracylene, as reported by Fowler and co-workers (and reproduced by Gomes and Mallion in their review article as Figure 18a). In their concluding remarks, Fowler and co-workers stated, "*Finally, the particular magnetic properties of pyracylene can be understood qualitatively in terms of its 'anti-aromatic' electron count of 12 electrons distributed around molecular periphery.*" [644] To this we may add that the same conclusion follows from the qualitative description based on the conjugated circuits model, with the distinction that the contributions from *the "anti-aromatic" electron*

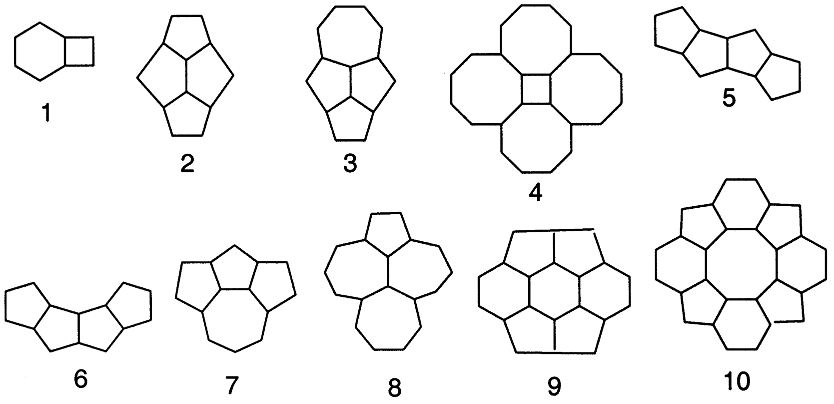


Figure 85. Molecular graphs of additional anti-aromatic structures and polycyclic conjugated hydrocarbons, for which it is difficult to determine by inspection if their RE is positive or negative.

Table 35. Expressions for Molecular RE, the Graph Theoretically Computed RE, and Percentage Anti-aromatic Character for a Selection of Additional Anti-aromatic Hydrocarbons (Shown in Figure 85)

molecule	RE expression	RE[a]	arom. (%)
1/85	$(2R_1 + 2Q_1 + 2Q_2)/3$	−0.047	−3.94%
2/85	$(2R_2 + 10Q_2)/4$	−0.482	−58.92%
3/85	$(4R_2 + 6Q_2 + 2Q_3)/4$	−0.054	−7.44%
4/85	$(8R_2 + 8R_3 + 4R_4 + 4Q_1 + 16Q_2 + Q_4 + 4Q_5)/9$	−0.452	−43.06%
5/85	$(2R_3 + 4Q_2)/3$	−0.347	−100%
6/85	$(2R_3 + 4Q_2)/3$	−0.347	−100%
7/85	$(6R_2 + 4Q_2 + 2Q_3)/4$	+0.244	+31.94%
8/85	$(4R_2 + 6Q_3 + 2Q_4)/4$	+0.336	+100%
9/85	$(8R_1 + 4R_2 + 8R_3 + 8Q_2 + 17Q_3)/9$	+0.666	+59.02%
10/85	$(16R_1 + 16R_3 + 20R_4 + 4Q_2 + 24Q_3 + 18Q_4 + 20Q_5)/14$	+0.887	+85.65%

[a] $R_1 = 0.841$ eV, $R_2 = 0.336$ eV. $Q_1 = -0.650$ eV, $Q_2 = -0.260$ eV.

count of 12 electrons comes not solely from the molecular periphery, but also from contributions of 12 electrons that include interior carbon centers, which involve a pair of central carbon centers. Indeed, if only the periphery were responsible for the density of the paramagnetic ring current, the density would be over the periphery and not along the circumference of the two pentagonal faces of pyracylene.

Be that as it may, we should tolerate compounds such as pyracylene as aromatic but use attributes such as "partially aromatic" and "not obviously aromatic" to indicate that their degree of aromaticity is lower than that of "fully aromatic" compounds. Whether the term "not obviously aromatic" used by Aihara is perhaps too strong is a matter of opinion, but clearly paracylene cannot be labeled as "genuinely aromatic". We see from the case considered that molecular properties may depend on different structural features, which again speaks in favor of using *structural* criteria to define aromaticity and not a selection of *properties*, which will to a different degree depend on or reflect the differences in the $4n + 2$ and the $4n$ conjugated circuits.

In Figure 85 we show molecular graphs of a selection of anti-aromatic structures which also have odd-member rings. All the structures are assumed to be planar, and all the CC bonds are assumed to be of similar length. The RE and the degree of anti-aromaticity, $\pm A$, are listed in Table 35. For the last four structures shown in Figure 85, it is difficult to guess by inspection whether they will have positive or negative RE.

D. Clar Valence Structures and Aromaticity

An interesting aspect of the present analysis of conjugated compounds via conjugated circuits is to see that *apparently similar* compounds may show different RE and *different levels of aromaticity*. For example, the "cis" isomer of dibenzpentalene (**8/68**) has RE about half that of the "trans" dibenzpentalene isomer (**9/68**). When we compare RE values of the two isomers, we see that the major cause for the "weakening" of the "cis" isomer is appreciable loss in RE due to reduced contributions of R_1 conjugated circuits. This becomes apparent from Figure 86, in which we have inscribed the π-sextet of Clar in the benzene rings of dibenzpentalenes. As we can see, the "trans" isomers can support two π-sextets, while the "cis" dibenzpentalene can have only one π-sextet (for which one can draw two symmetry-equivalent Clar's valence structures..

In view of the pivotal importance of Clar's aromatic π-sextets as well as Clar's valence structures of

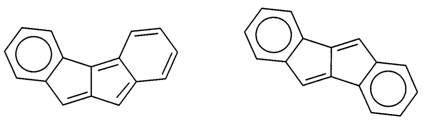


Figure 86. Clar structures for the "cis" and "trans" isomers of dibenzpentalene, showing why the "cis" isomer has a RE that is about half that of the "trans" isomer.

benzenoid hydrocarbons for characterization of aromatic compounds for a good proportion of this review, we will define them here formally:

Definition: *Aromatic π-sextets are defined as six π-electrons localized to a single benzene ring separated from adjacent benzene rings by formal CC single bonds.*

Definition: *Clar's valence structure of a benzenoid hydrocarbon is a valence structure having the maximal number of disjoint aromatic π-sextets. Carbon–carbon bonds of molecular fragments not involved in formation of aromatic π-sextets must necessarily have a unique CC double or CC single bond type.*

We will later devote more attention to Clar's structures, which, as we will see, can be viewed as a collection of a subset of Kekulé valence structures. As we have mentioned, in the early pre-quantum era of chemistry, Fries suggested that a *single* Kekulé valence structure having the maximal number of Kekulé benzene rings is dominant. The early VB calculations, on the other hand, assumed that *all* Kekulé valence structures contribute equally toward the description of conjugated polycyclic hydrocarbons. One can view Clar's approach as a compromise. According to Clar, *some* Kekulé valence structures apparently are more important for characterization of properties of benzenoid hydrocarbons than others! We can summarize the starting point of Clar by paraphrasing the well-known quotation of George Orwell from his *Animal Farm* by saying, "*All Kekulé structures are equal, but some are more equal than others.*" These "more equal than others", as we will see later, are Kekulé valence structures of the maximal degree of freedom. These are the very same Kekulé valence structures which, when superimposed, produce Clar's structure of a benzenoid hydrocarbon.

In Figure 64 we illustrated "macrocyclic" fused benzene rings, which give rise to 4*n* conjugated circuits. The smallest possible 4*n* conjugated circuit in macrocyclic benzenoids involves 12 carbon atoms, corresponding to Q_3. Large 4*n* conjugated circuits do not make a visible destabilizing contribution to molecular resonance energy, as we have already seen with aceheptylene. However, this is not to say that the larger conjugated circuits, be they $4n + 2$ or 4*n*, do not play a role in determining the properties of conjugated hydrocarbons. For example, [18]annulene, synthesized by Sondheimer[93,549−551] and considered properly as (fully) aromatic, is aromatic because of the 18-carbon conjugated circuits (R_4). The same is true of the largest yet reported monocyclic system of conjugated π-electrons, having 30 carbon atoms.[645]

XXI. Biphenylenes

We collected in Figure 66 non-benzenoid structures, derivatives of biphenylene, many of which are viewed as aromatic despite the presence of 4*n* circuits. The structures in the upper part of Figure 66 have a single cyclobutadiene ring, while those in the lower part of Figure 66 have two or more cyclobutadiene rings. In Table 25 we gave the expressions for the RE and the RE computed by the graph theoretical approach for the compounds shown in Figure 66. In Table 36 we compare the REPE for the same biphenylene derivatives with the computed aromaticity indices shown in the last column of the table. In Figure 87 we show a plot of REPE values against the aromaticity index *A*. We see a fairly good linear relationship between the computed REPE and the aromaticity index *A* given by [RE($4n + 2$) + RE(4*n*)]/RE($4n + 2$). The calculations of *A* and RE were based on the values $R_1 = 0.841$ eV, $R_2 = 0.336$ eV, $Q_1 = -0.650$ eV, and $Q_2 = -0.260$ eV.

The most aromatic among biphenylenes apparently are molecules with naphthalene and phenanthrene units. Among them, those with *linearly* fused rings have greater RE than the corresponding "bent" isomers. In particular, observe the difference in the RE between the "linear" 2,3,6,7-dibenzobiphenylene (**4/66**) and "bent" 1,2,7,8-dibenzobiphenylene (**5/66**). In contrast, in the case of benzenoid hydrocarbons built by fusing only hexagonal rings, the "bent" isomers have a greater stability (greater RE) than linear acenes having the same number of fused rings. Thus, phenanthrene has higher RE than anthracene. In the case of biphenylene derivatives, just the opposite is the case. Here we find that isomers having linearly fused rings (such as **9/66**) are relatively more aromatic than isomers in which rings are angularly fused (such as **10/66**). On this basis, we may conclude that, within such a model, the so-called anti-kekulene (compound shown in Figure 88) will not be particularly stable. Plavšić and collaborators[646] calculated RE for anti-kekulene and anticipated that its prepa-

Table 36. REPE and the Percentage Aromatic Character for a Selection of Biphenylene Derivatives (Shown in Figure 66)

molecule	REPE	arom. (%)	molecule	REPE	arom. (%)
1/66	0.073	48.4	**10/66**	0.052	32.6
2/66	0.099	70.4	**11/66**	0.035	21.9
3/66	0.083	56.1	**12/66**	0.035	21.9
4/66	0.109	82.4	**13/66**	0.031	18.8
5/66	0.099	72.3	**14/66**	0.024	15.9
6/66	0.094	65.3	**15/66**	0.096	63.2
7/66	0.064	44.3	**16/66**	0.062	40.0
8/66	0.047	29.5	**17/66**	0.074	51.9
9/66	0.063	40.1	**18/66**	0.099	60.5

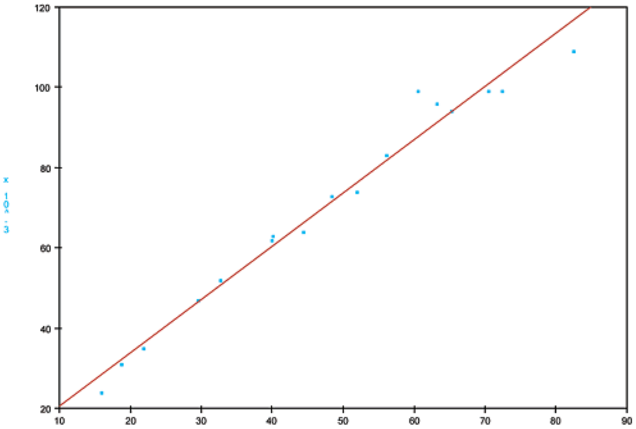


Figure 87. Plot of REPE values against the aromaticity index *A* for the biphenylene derivatives shown in Figure 66 (listed in Table 36).

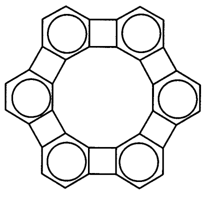


Figure 88. Clar structure of anti-kekulene.

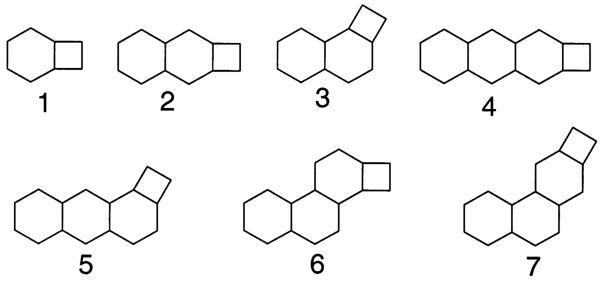


Figure 89. Derivatives of biphenylene having a terminal cyclobutadiene ring.

ration, though not impossible, would be difficult in view of its low RE.

However, *we have to emphasize that the conclusions drawn were based on* <u>*assuming*</u> *that all Kekulé valence structures make an equal contribution* to the molecular RE, just as we made the same assumption in calculating RE for benzenoid hydrocarbons. We also learned from RE for benzenoid hydrocarbons that, for a structure to exist, its REPE has to be above the critical value of about 0.060 eV. From Table 36 we see that bent [3]phenylene, according to our calculations, has REPE of only 0.047 eV — yet it exists, and it has been synthesized. Moreover, the even larger *cis*-[4]phenylene (**12/66**), with REPE 0.035 eV, and *cis*-[5]phenylene (**14/66**), with REPE 0.024 eV, for which the corresponding REPE values are still smaller, have been prepared. This clearly points to difficulties when one is extending the *present* model of conjugated circuits to non-benzenoid systems having, besides $4n + 2$, also $4n$ conjugated circuits based on the assumption that all Kekulé valence structures make equal contributions to molecular stability. Either the parametrization of contributing Q_1, Q_2, Q_3, etc. has to be *drastically modified*, or *not all the Kekulé valence structures make equal contributions* to molecular RE. We will see later (in section XXXII.B, Biphenylenes Revisited, as well as in the Epilogue) not only that different Kekulé valence structures do not play equally important roles in the characterization of molecules as benzenoid or non-benzenoid, but also that by extending the idea of Clar's aromatic π-sextets to non-benzenoid systems, we can obtain s*atisfactory* stability and REPE for non-benzenoid "bent" [*n*]phenylenes, which have been found to have too low REPE to exist.

In Figure 89 we illustrate a number of benzocyclobutadiene derivatives having cyclobutadiene as a terminal ring. In Table 37 we list the RE for the compounds shown in Figure 89. Observe that the biphenylene derivatives shown in Figure 66 that have cyclobutadiene rings situated between benzene rings are more aromatic than the biphenylene derivatives having the four-member ring at the "end" of the molecule. We will revisit biphenylene derivatives later, but it may be mentioned here that some caution has to be taken when considering RE and the degree of aromaticity of molecules, particularly those shown in Figure 89, in which contributions from benzenoid fragments may overshadow the local anti-aromatic features associated with the cyclobutadiene fragment. As we can see, the aromaticity index *A* increases with the size of the molecules shown in Figure 89, but all of them have the same local features found in benzocyclobutadiene, which as we can see has negative RE. So, while the remaining structures shown in Figure 89 may have the overall RE positive, locally they may all be unstable, and thus not able to exist — at least that follows if we assume that *all* Kekulé valence structures play an equal role in characterization of these molecules.

XXII. Fully Anti-aromatic Hydrocarbons

> *... the polymethines with 4n atoms should not only be less stable than those with (4n+2) atoms but should be less stable even than their open-chain counterparts; in other words the 4n-atom systems should not be aromatic but should actually be* ***antiaromatic****.*
>
> A. L. Chung and M. J. S. Dewar[647]

Elusive cyclobutadiene is the smallest prototype of anti-aromaticity, the concept introduced by Chung and Dewar and advanced by Breslow.[648,649] We will refer to structures that have only $4n$ conjugated circuits as "fully anti-aromatic" structures, in order to emphasize their anti-aromatic character in distinction to anti-aromatic structures, which contain also some $4n + 2$ "impurity". All the structures *illustrated* in Figure 90 are therefore "fully anti-aromatic", assuming that they are *planar* and that all CC bonds are of approximately *equal length*. Under such assumptions, we can calculate their RE and anti-aromatic character. The count of conjugated circuits gives the following expressions for their anti-aromatic destabilization energies:

$2Q_1/2$	$2Q_2/2$	$2Q_3/2$	$2Q_4/2$	$2Q_5/2$	$2Q_6/2$
1/90	**2/90, 3/90**	**4/90 - 8/90**	**9/90 - 15/90**	**16/90 - 18/90**	**19/90**

In all cases shown in Figure 90, we have only two Kekulé valence structures. However, "fully anti-aromatic" systems can have more than two Kekulé valence structures, as illustrated in Figure 91. The expressions for their anti-aromatic destabilization energy are listed in Table 38. We see that the presence of only $4n$ conjugated circuits is a *necessary* condition for a structure to be a candidate for being anti-aromatic, or "fully anti-aromatic". However, this is not sufficient. For such compounds to be truly anti-aromatic, they must be *planar* and have all CC bonds of approximately *equal length*.

To what extent formally classified anti-aromatic structures display anti-aromatic features will depend on the extent to which unfavorable destabilization due to $4n$ contributions can be relieved. Molecules like pentalene (**3/90**), heptalene (**4/90**), and *s*-indacene (**5/90**) are planar, but they can relieve the

Table 37. Expressions for Molecular RE and Percentage Aromatic Character for a Selection of Biphenylene Derivatives Having a Terminal Cyclobutadiene Unit (Shown in Figure 89)

molecule	RE expression	RE	arom. (%)
1/89	$(2R_1 + 2Q_1 + 2Q_2)/3$	−0.117	−17.3
2/89	$(6R_1 + 2Q_1 + 2Q_2 + 2Q_3)/4$	0.694	55.9
3/89	$(6R_1 + 2R_2 + 4Q_1 + 2Q_2 + Q_3)/5$	0.210	18.8
4/89	$(6R_1 + 4R_2 + 2R_3 + 2Q_1 + 2Q_2 + 2Q_3 + 2Q_4)/5$	0.853	66.1
5/89	$(10R_1 + 6R_2 + 3R_3 + 6Q_1 + 2Q_2 + Q_3)/7$	0.755	50.3
6/89	$(14R_1 + 6R_2 + R_3 + 6Q_1 + 4Q_2 + Q_3)/8$	0.991	58.3
7/89	$(12R_1 + 4R_2 + R_3 + 4Q_1 + 4Q_2 + 2Q_3 + Q_4)/7$	1.016	62.9

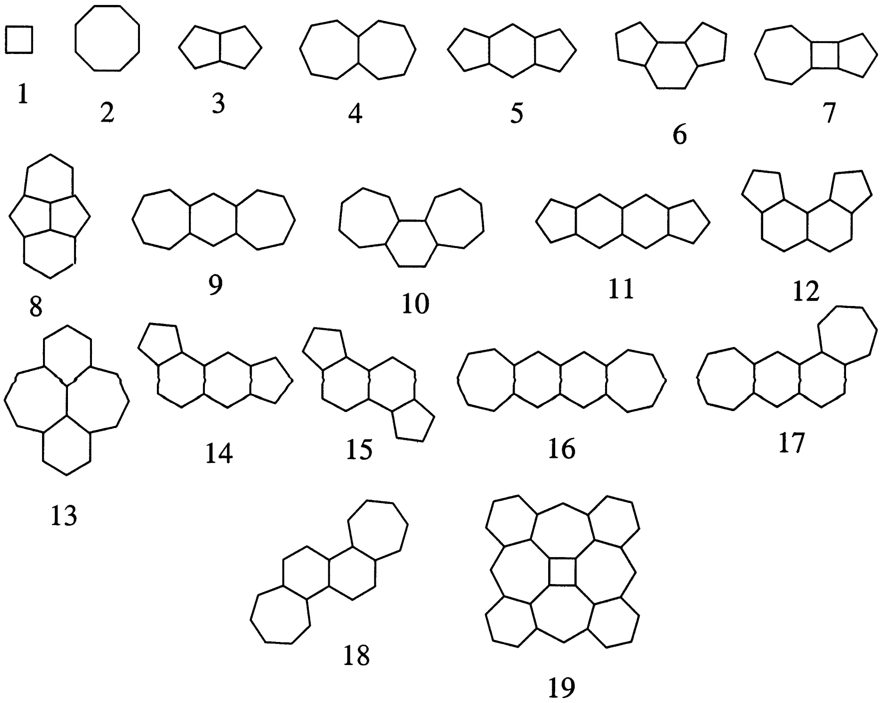


Figure 90. Fully anti-aromatic structures having $K = 2$.

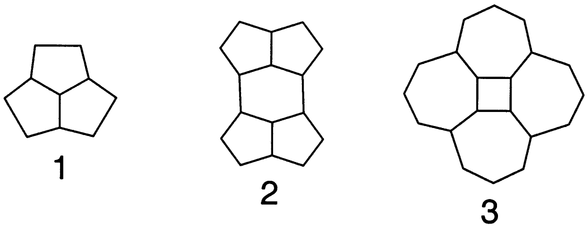


Figure 91. Fully anti-aromatic structures having $K > 2$.

Table 38. Expressions for Molecular RE and the Graph Theoretically Computed RE for the Fully Anti-aromatic Hydrocarbons Shown in Figure 91

molecule	RE expression	RE
1/91	$(6Q_2)/3$	−0.520
2/91	$(4Q_1 + 4Q_4)/4$	−0.650
3/91	$(8Q_2 + 7Q_3)/5$	−0.416

destabilizing role of $4n$ conjugated circuits by assuming *asymmetrical* forms. Thus, they no longer have all CC bonds of approximately equal length. The same would be true for a planar model of cyclobutadiene in which cyclobutadiene would assume a rectangular geometry (symmetry D_{2h}) rather than a regular square form (symmetry D_{4h}).[650,651] Cyclooctatetraene assumes a tub conformation,[652,653] in which unfavorable $4n$ conjugation is dramatically reduced compared with hypothetical anti-aromatic $4n$ contributions for a planar structure. In all the cases mentioned, the symmetrical (planar) form, which has the highest occupied MO degenerate, will undergo Jahn–Teller distortion[654] and produce two symmetry-equivalent less symmetrical geometries. In the case of *as*-indacene and other less symmetrical systems, the structures obtained as a result of the Jahn–Teller theorem need not be symmetry-equivalent. Nevertheless, they allow molecules to "escape" hypothetical anti-aromatic form and reduce the contributions of destabilizing $4n$ conjugated circuits.

Almost half of the potentially anti-aromatic structures shown in Figures 90 and 91 have rather small destabilization energy coming from the relatively large $4n$ conjugated circuits having 16, 20, and 24 π-electrons. These conjugated circuits are expected not to make significant contributions to destabilization, if any. It will be of interest to see if any of these structures can be synthesized and to see to what extent this prediction will be fulfilled.

XXIII. Aromaticity/Anti-aromaticity

The concept of anti-aromaticity remains useful and challenging to experimental as well as theoretical chemists, despite the difficulties in obtaining molecular systems that will show the full impact of the presence of anti-aromatic $4n$ conjugated circuits in a molecule. That the presence of 4*n* conjugated circuits is detrimental to molecular stability has been witnessed already for aromatic compounds in which 4*n* + 2 conjugated circuits dominate and enforce the planar geometry for the systems in which 4*n* conjugated circuits are also present. Hafner and Schneider[553] considered alkyl derivatives of aceheptylene and observed that these compounds depart somewhat in their properties from the "standard" non-benzenoid conjugated systems. Clearly this "departure" is due to the presence of anti-aromatic 4*n* contributing conjugated circuits.

For a compound to qualify as anti-aromatic, however, we must have a dominant anti-aromatic contribution. Hafner and co-workers[655] designed a clever way to arrive at anti-aromatic compounds by "forcing" a molecule that has undergone the Jahn−Teller distortion back into a more symmetrical geometric form. This was accomplished by introducing bulky *tert*-butyl substituents on the *s*-indacene skeletal frame. Calculations done by Gellini et al.[656] show that CC bonds in *s*-indacene alternate in length, assuming typical CC double (around 1.32−1.33 Å) and CC single (1.47−1.49 Å) bond lengths, respectively, and results in a structure having C_{2h} symmetry. This structure represents a more stable system than the hypothetical structure without bond alternation (having symmetry D_{2h}). In contrast, calculations on 1,3,5,7-tetra-*tert*-butyl-*s*-indacene (TTBI) show that the more stable system is the one with more equalized peripheral CC bond lengths (around 1.40−1.41 Å), in agreement with the available X-ray data. Hafner and co-workers, after careful analysis of infrared and Raman spectra of 1,3,5,7-tetra-*tert*-butyl-*s*-indacene, concluded that "*The tert-butyl effect on the TTBI structure results in a larger delocalization of the π-electron density over the indacene plane, giving rise to a molecular structure close to D_{2h} symmetry.*" [656]

Hence, because *tert*-butyl groups do not constitute conjugated fragments and are ignored in the conjugated circuits model, we may conclude that "modified" s-indacene, that is, 1,3,5,7-tetra-*tert*-butyl-*s*-indacene, represents an anti-aromatic species. More recently, Baldridge and Siegel[657] have theorized that cyclooctatetraene (COT) can similarly be forced to adopt a planar rather than a tub conformation. A flat form for COT would make contributions from 4*n* conjugated circuit be "felt" and thus would approach an anti-aromatic structure. According to calculations, the two annealed bicyclo[2.2.1]hexene fragments would result in a planar structure that would have localized π-electrons. Matsuura and Komatsu[658,659] synthesized the compound, and indeed the X-ray confirmed the calculations indicating the presence of CC double bonds in the endo conformation with respect to annealed bicyclo[2.2.1]hexeno fragments. Adding four annealed fragments resulted in a planar structure with exocyclic CC double bonds with respect to the fragments. Finally, by placing annealed bicyclo[2.2.1]hexeno fragments two bonds apart, one prevents CC double bond "fixation", and as a result one obtains a fully anti-aromatic "modified" cyclooctatetraene. These recent achievements show that anti-aromaticity that was for the most part "fictitious" is becoming "factual".

Table 39. *ABC*'s of Aromaticity

$A = \dfrac{\mathrm{RE}(4n+2) - \mathrm{RE}(4n)}{\mathrm{RE}(4n+2) + \mathrm{RE}(4n)}$	aromaticity
$B = \dfrac{\mathrm{RE}(\mathrm{R}_1) - \mathrm{RE}(\mathrm{R}_{n\neq 1})}{\mathrm{RE}(\mathrm{R}_1) + \mathrm{RE}(\mathrm{R}_{n\neq 1})}$	benzene character
$C = \dfrac{\mathrm{RRE}(\mathrm{R}_1) - \mathrm{RRE}(\mathrm{R}_{n\neq 1})}{\mathrm{RRE}(\mathrm{R}_1) + \mathrm{RRE}(\mathrm{R}_{n\neq 1})}$	Clar index

An indirect "proof" that anti-aromatic compounds are elusive comes from data on inter-stellar compounds.[660−662] In view of the low density of matter and extremely low temperatures in outer space, structures that would be difficult to observe in the laboratory may have long enough life in the inter-stellar space to be detected. Thus, for instance, among others, the smallest aromatic compound, cyclic $C_3H_3^+$, has been identified in the inter-stellar space. The search for anti-aromatic compounds in the inter-stellar space thus appears to be an interesting project. However, as of today, no anti-aromatic compounds have been detected in outer space,[663] although, as is well known, the inter-stellar space is rich in hydrocarbons.

In discussing aromaticity/anti-aromaticity, the problem that needs better understanding is why some aromatic compounds (having 4*n* conjugated circuits) have modified properties, as was the case with Hafner's hydrocarbons, and in other compounds, like biphenylene, 4*n* conjugated circuits apparently do not show a visible manifestation of the presence of 4*n* conjugated circuits. We will address this problem in section XXXII (Biphenylenes Revisited).

XXIV. ABC of Aromaticity

We can summarize the graph theoretical approach to aromaticity by focusing on the three important aspects pertaining to aromaticity: (*A*) classification of compounds as fully aromatic or less aromatic; (*B*) characterization of the degree of aromaticity of fully aromatic compounds; and (*C*) discrimination of the local aromatic features of larger compounds. We will briefly outline each of these three important steps for clarification of the concept of aromaticity as it applies to polycyclic conjugated hydrocarbons. From Table 39, which summarizes the *ABC* of aromaticity, one can immediately see that all the three indices are related. In particular, it follows that for aromatic compounds $A > 0$, for azulene and so-called "azulenoid" compounds, built from five- and seven-member rings, $B = 0$, while for rings not participating in conjugated circuits and thus not contributing to molecular RE, like the central rings of perylene and bisanthene, $C = 0$.

A. *A* of Aromaticity

As we have seen, aromaticity has been defined in terms of the presence and the absence of 4*n* + 2 and 4*n* conjugated circuits. The approach has led to a numerical index that estimates the degree of aromaticity for compounds having both 4*n* + 2 and the 4*n* conjugated circuits. It appears quite natural to expect that an index of aromaticity is sensitive to the relative roles of $4n + 2$ and $4n$ conjugated circuits. Construction of such an index is accomplished by partitioning RE into contributions arising from $4n + 2$ conjugated circuits, RE($4n + 2$), and destabilizing contributions arising from $4n$ conjugated circuits, RE($4n$). By following this reasoning, we arrive at the index A given in Table 39.

The index A assigns the value $A = 1$ to all benzenoid hydrocarbons, which are thus all characterized as "fully aromatic". However, as we know, there are variations of the degree of aromaticity even among benzenoid hydrocarbons, though they may be relatively small. We have already seen that "fully benzenoid" hydrocarbons, like triphenylene, dibenzopyrene, hexabenzocoronene, and other $6n$ π-electron systems, show unusual stability. Hence, we need a measure of aromaticity that can differentiate aromatic character among "fully aromatic" compounds.

B. *B* of Aromaticity

In order to characterize these small variations of aromatic features of benzenoid hydrocarbons, we consider another index that will measure the degree of similarity of a given benzenoid hydrocarbon to benzene. Such an index, referred to as the index of benzene character B of benzenoid hydrocarbons, was proposed in 1987 as follows:[664]

$$B = [\mathrm{RE}(R_1) - \mathrm{RE}(R_{n\neq1})]/[\mathrm{RE}(R_1) + \mathrm{RE}(R_{n\neq1})]$$

Here, RE(R_1) is the part of the computed resonance energy that comes from the presence of the conjugated circuits R_1, while RE($R_{n\neq1}$) is the part of the computed resonance energy that comes from the presence all other conjugated circuits. The denominator, [RE(R_1) + RE($R_{n\neq1}$)], is in fact the total molecular RE, which thus makes B a dimensionless number, always less than one, except for benzene, for which by definition $B = 1$.

In Table 40 we have collected B indices for a number of smaller benzenoid hydrocarbons. For comparison, we also show the corresponding aromaticity indices based on bond lengths. According to Julg,[665−667] one can derive an index of aromatic character from the differences between the actual CC bond lengths in a benzenoid hydrocarbon and the average CC bond distance $\langle d \rangle$ using the expressions

$$J = 1 - 255[\Sigma/\langle d \rangle]^2$$
$$\Sigma = \Sigma_i[d_i - \langle d \rangle]^2/N$$

The numerical value of index constructed in this way will depend on the bond lengths used, which could be experimental bond lengths or calculated ones. One of the two Julg's indices shown in Table 40 is based on experimental CC bond lengths, and the other is based on quantum chemical calculations using the AM1 model (which is attributed to Dewar). As we can see from Table 40, the magnitudes of the derived indices based on bond lengths vary somewhat in a relatively small interval, while graph theoretically derived B indices vary in the interval from about 1/2 to 1, the largest possible value assumed to belong to benzene. A comparison between the B index of aromaticity and indices based on the approach of Julg shows some differences for individual benzenoids. For example, the B indices for naphthalene, perylene, and quaterrylene, which are all formally built by connecting naphthalene units by essentially single CC bonds, are the same. The Julg indices based on AM1 calculations for the same compounds show a decreasing trend, the largest value belonging to naphthalene. Clearly, the decrease of Julg's index can be attributed to the increase in the number of essentially single CC bonds in perylene and quaterrylene, which do not participate in conjugation but nevertheless influence the average bond distance $\langle d \rangle$. For more details on Julg's bond length indices, the reader should consult a recent paper by Kiralj and Ferreira[668] on predicting CC bond lengths in planar benzenoid polycyclic hydrocarbons, where one can also find a list of over 300 experimental and calculated bond lengths for some 27 smaller benzenoid hydrocarbons.

Table 40. *B* Indices for a Number of Smaller Benzenoid Hydrocarbons

benzenoid	*B* index	Julg's values exptl	Julg's values calcd (AM1)
benzene	1.000	1.000	1.000
naphthalene	0.751	0.932	0.928
anthracene	0.630	0.889	0.878
phenanthrene	0.778	0.878	0.928
tetracene	0.561	0.870	0.849
triphenylene	0.801	0.906	0.946
chrysene	0.734	0.848	0.922
pyrene	0.630	0.916	0.899
perylene	0.751	0.877	0.890
dibenzo[*a*,*h*]anthracene	0.742	0.972	0.906
picene	0.670	0.900	0.921
benzo[*e*]pyrene	0.712	0.877	0.890
pentacene	0.522	0.880	0.826
dibenzo[*a*,*c*]anthracene	0.796	0.891	0.915
dibenzo[*fg*,*op*]tetracene	0.800	0.881	0.944
benzo[*ghi*]perylene	0.649	0.875	0.921
coronene	0.585	0.955	0.933
quaterrylene	0.751	0.889	0.877
hexabenzocoronene	0.741	0.910	0.848
kekulene	0.690	0.877	0.881

One can construct other indices for benzene character of benzenoid hydrocarbons, which we will designate as B' in order to differentiate them from the index B. For example, one can consider the Kekulé index,[595] which assigns to individual Kekulé valence structures an index derived from local properties of molecular orbitals, and take the average over all Kekulé structures. Even though for many Kekulé structures this index is bigger than the Kekulé index of benzene, the average Kekulé index appears smaller for polycyclic benzenoid hydrocarbons than it is for benzene. However, for an index to reflect benzene character, one expects certain trends among structurally related benzenoids to be satisfied, such as

$$B'(\text{naphthalene}) > B'(\text{anthracene}) > B'(\text{tetracene}) > \ldots$$

$$B'(\text{fully benzenoid hydrocarbons}) > B'(\text{benzenoid hydrocarbons})$$

While the average Kekulé index satisfies the first condition, it apparently fails to satisfy the second, because B'(naphthalene) > B'(triphenylene), naphthalene having migrating π-sextets and triphenylene being a fully benzenoid hydrocarbon.

Nevertheless, the Kekulé index, which assigns to individual Kekulé valence structures a numerical value, is of some interest, as it reflects the relative importance of individual Kekulé valence structures, a topic which has received some but apparently not sufficient attention in the literature.

C. *C* of Aromaticity

Some caution is required when considering bigger and bigger molecules, including benzenoid hydrocarbons, in which there could be considerable variations in local properties. Already in smaller benzenoids, such as perylene and bisanthene, in which the central CC bonds are essentially single (that is, they are single CC bonds in all Kekulé valence structures), we have portions of a molecule that are not contributing to RE, and thence to aromaticity. By averaging CC bond lengths, the contributions from various rings, or the contributions from different Kekulé valence structures, we may be diluting the aromatic characteristics of a molecule with spurious contributions. It does appear that useful characterization of benzenoid hydrocarbons may follow if we consider individual benzene rings, rather than taking the average of such contributions from all rings. This leads us to a ring index which we refer to as C of aromaticity, where C stands for Clar, which is defined as[539]

$$C = [\mathrm{RRE}(R_1) - \mathrm{RRE}(R_{n\neq 1})]/[\mathrm{RRE}(R_1) + \mathrm{RRE}(R_{n\neq 1})]$$

$\mathrm{RRE}(R_1)$ is the part of the computed ring resonance energy of individual benzene rings that comes from the presence of the conjugated circuits R_1, while $\mathrm{RRE}(R_{n\neq 1})$ is the part of the computed contribution to the resonance energy for the considered ring that comes from the presence of all other conjugated circuits contributing to RE to the particular benzene ring. The denominator $[\mathrm{RRE}(R_1) + \mathrm{RRE}(R_{n\neq 1})]$ is in fact the total ring resonance energy (RRE), which thus makes C a dimensionless number, always less than one, except for benzene, for which by definition $C = 1$. In the next section we give numerical examples of the RRE.

XXV. Local Aromaticity

It is not only among benzenoids that different molecules show different degrees of aromatic character, but within single polycyclic conjugated hydrocarbons, different rings show different local aromaticities. Dewar explicitly mentioned extending the notion of aromaticity criteria to individual rings in polycyclic systems.[669] The pioneering work on bridging the gap between calculated MO results and characterization of local aromaticity of benzene rings was attributed to Polansky and Derflinger,[582] whose work deserves more attention. They found some justification for Clar's model of localized benzenoid regions in polycyclic conjugated benzenoids, and they derived a ring index characterizing individual benzene rings of a molecule. This ring index is determined from computed MO coefficients when the MO's of the system are expanded in sets of MO's of each ring. The "benzene character" for benzene rings of numerous smaller benzenoid hydrocarbons reported by Polansky and Derflinger was based on using the HMO approach, but conceptually the approach is quite general and can be extended to more sophisticated MO calculations.

A. The Approach of Polansky and Derflinger

In the standard MO approach to conjugated hydrocarbons (e.g., in the HMO calculations), the molecular orbitals are expressed as a linear combination of atomic orbitals. However, it is possible, as Polansky and Derflinger outlined,[582] to express the same molecular orbitals in terms of molecular orbitals of the benzene ring. As a result, instead of obtaining information on the contributions of molecular orbitals to the bond orders, one obtains the contributions of a set of benzene orbitals to individual benzene rings of polycyclic benzenoid hydrocarbons. In other words, the "benzene character" described by Polansky and Derflinger, "*is the projection of occupied π-MO's in a given hexagon L of a polycyclic benzenoid hydrocarbon onto the three occupied MO's of a benzene molecule located on that position.*" [523]

In Figure 92 we illustrate for a collection of smaller benzenoid hydrocarbons the benzene ring indices as reported by Polansky and Derflinger.[582] The results are quite interesting, if not astounding. As one can see, there are considerable variations among individual rings within a molecule and between rings in different molecules. If we ignore diphenyl and hexaphenyl, in which benzene rings are bridged by a single CC bond rather than fused, and in which higher values for the ring indices were found than in benzene, the ring indices of Polansky and Derflinger are smaller than the value for benzene, varying between about 0.680 to 0.950. Observe also that the variations are more pronounced in some molecules than others. A more careful examination of the results of Polansky and Derflinger shows that the aromatic character of individual rings is far from uniform. Moreover, the variations show some anticipated and some unexpected regularities. As a rule, terminal rings in benzenoid hydrocarbons show greater similarity to benzene, suggesting that the local aromaticity may be influenced to a considerable degree by specifics of molecular periphery patterns. Highly significant are the observed large differences in benzene character among many adjacent rings. This is particularly visible in the cases of triphenylene (**6/92**), tetrabenzanthracene (**15/92**), dibenzopyrene (**13/92**), and hexabenzocoronene (**20/92**). Observe that all the mentioned benzenoids are those that Clar classified as "fully benzenoid". In comparison with rings in other benzenoids shown in Figure 92, they all show a large benzene character for benzene rings which are the sites of aromatic π-sextets. It is significant vindication for Clar's model of

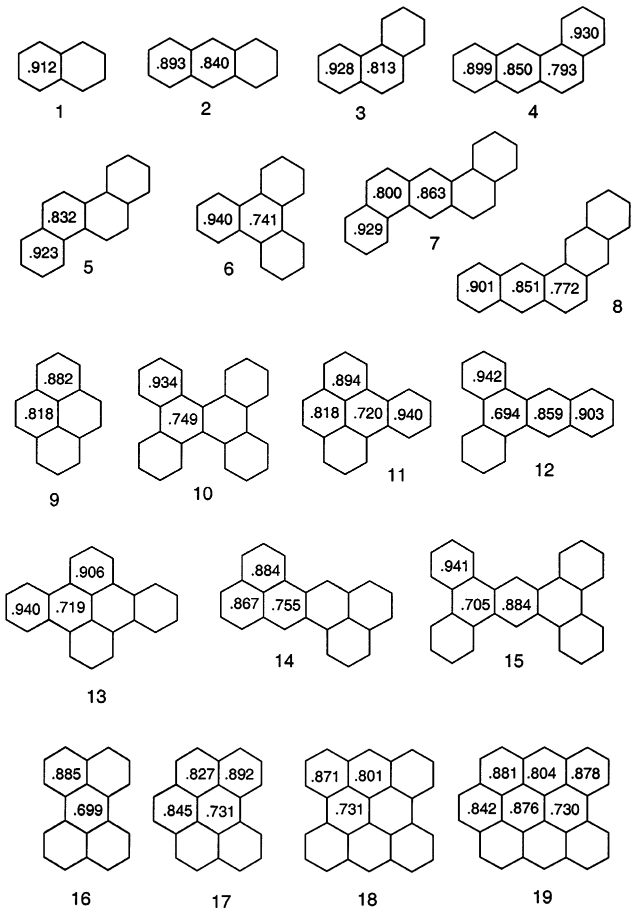


Figure 92. Benzene ring indices for a collection of smaller benzenoid hydrocarbons, as reported by Polansky and Derflinger.[582]

benzenoid hydrocarbons that in all cases the differences between ring indices parallel the expectation based on Clar's valence structure (which will be fully elaborated later).

It is somewhat tedious to follow the calculations of the "benzene character" of Polansky and Derflinger directly from HMO theory as described by the authors. Hosoya and co-workers reported that the benzene characters (BC) can be expressed as a linear combination of the Coulson bond orders for the six bonds of a ring and three para-bonds of the same ring using the expression

$$\mathrm{BC} = [(1/3)(2\sum p_{rs} - \sum pp_{rs}) - 2]/1000$$

Here, p is Coulson's bond order and pp is bond order for para-bonds. Both summations assume for indices that $r > s$. This is an interesting and much simplified approach to MO ring indices; however, the indices reported by Hosoya and co-workers are not quite identical to those of Polansky and Derflinger. Recently, Professor Hosoya informed me that the difference occurs because his group based their work on SCF MO rather than on HMO calculations.[670]

B. Approaches Based on Bond Orders

One can arrive at ring indices for benzenoid hydrocarbons (and not only for benzenoids) by considering CC bond orders rather than benzene MO components. In Figure 93 we show Pauling *fractional* bond orders for CC bonds in phenanthrene, which are 1/5, 2/5, or 3/5, depending on the location of the CC bond. Fractional bond order counts only the occurrence of CC double bonds in the collection of Kekulé valence structures, while the Pauling bond order is given by adding one to the fractional part. If we consider the fractional parts of CC bond orders for the six CC bonds within a single benzene ring, we obtain for the peripheral benzene ring 2(3/5) + 4(2/5) = 14/5, or 2.80. In contrast, when we add the fractional parts of CC bond orders for the six CC bonds of the central benzene ring, we obtain 4/5 + 2(2/5) + 3(1/5) = 11/5, or 2.20. The resulting quantities represent essentially the *average* CC bond orders for individual benzene rings. Clearly, the peripheral ring has a larger average bond order than the central ring, which means it has a smaller average CC bond, which again indicates a tighter ring or, to use the terminology of Eric Clar, more aromatic π-sextets. We will refer to benzene ring indices obtained from Pauling fractional bond orders simply as the Pauling ring indices, even though they have not been considered by Linus Pauling (or, as far as we know, anyone else for that matter).[671] The average bond orders of individual rings gives the corresponding molecular quantity, which when bond orders are converted to bond lengths will correspond to an index of benzene character analogous to Julg's structural aromaticity. For example, for phenanthrene we obtain in this way (1/3)(2.80 + 2.80 + 2.20) = 2.60. This differs slightly from the corresponding index based on the sum of bond orders, because CC bonds of fusion have been counted twice, once for each ring. At the very end of this review, in Appendix 4 on Prevention of Errors, we have briefly outlined the "correct" ring indices based on partitioning of π-electrons to individual rings so that contributions of π-electrons in CC double bonds belonging to two adjacent rings are not counted twice. We will see that in this way we maintain the correct count of π-electrons and, as a bonus, we obtain "numerical Kekulé valence structures", to be contrasted to the usual "geometrical" Kekulé valence structures. Even more importantly, in this way we can construct a *single* (numerical) valence structure to replace a set of Kekulé valence structures, to replace a subset of Kekulé valence structures such as those defining the Clar structure, or to replace several Kekulé structures when there are more than one Fries Kekulé structure.

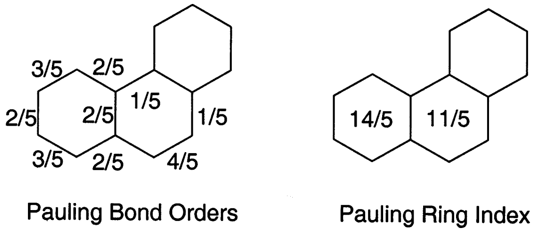


Figure 93. Pauling *fractional* bond orders for CC bonds in phenanthrene, and Pauling ring indices for two nonequivalent rings.

In Figure 94 we show the Pauling ring indices for a selection of smaller benzenoid hydrocarbons. A

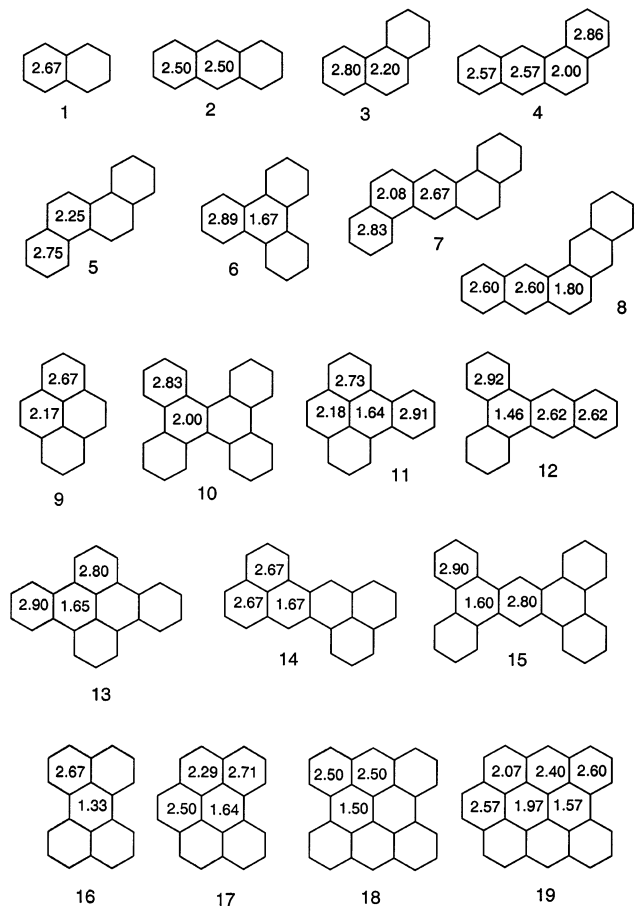


Figure 94. Pauling ring indices for a selection of smaller benzenoid hydrocarbons.

comparison of Figure 94 with the corresponding results of Polansky and Derflinger (Figure 92) shows an overall remarkable parallelism. Observe that in all cases the rings with the maximal "benzene character" are the same, just as the rings with the least "benzene character" again coincide in both approaches. This occurs even though Polansky and Derflinger's approach is based on the MO method and the Pauling ring indices can be viewed as a result of VB computations, or even more correctly, as the results of the graph theoretical considerations. The qualitative agreement between the two approaches shows that both schemes differentiate terminal rings as those with the "benzene character", which in Clar's model correspond to aromatic π-sextets. The next in relative magnitude are the rings that Clar referred to as "migrating π-sextets", which are benzene rings that in some Clar structures are shown as aromatic π-sextets but in other Clar structures of the same molecule are rings having CC double bonds. This is, for instance, the case with the benzene rings of naphthalene and anthracene. Still smaller "benzene character" belongs to benzene rings which in Clar structures have fixed CC double bonds, as is the case with the central bond in phenanthrene or pyrene. Finally, the smallest "benzene character" belongs to rings to which Clar refers as "empty", the rings which connect non-adjacent π-aromatic sextets, illustrated by the central ring of triphenylene or the two "branching" rings of tetrabenzanthracene.

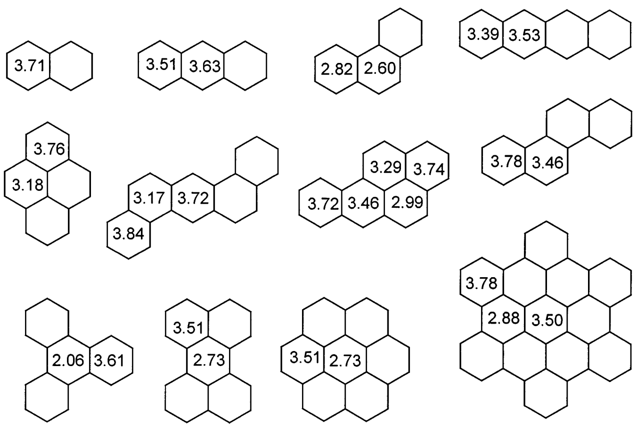


Figure 95. "Benzene ring characters" based on SCF MO calculations by Dewar and Trinajstić.[633]

Table 41. Comparison of the Ring Codes of Polansky and Derflinger[582] with Ring Codes Derived from the Pauling Bond Orders, SCF MO Calculated Bond Orders, and Graph Theory (GT) Bond Orders

	Polansky and Derflinger	Pauling bond orders	Dewar and Trinajstić	GT bond orders
naphthalene	0.912	0.890	0.928	0.667
anthracene	0.893	0.833	0.875	0.500
	0.840	0.833	0.908	0.500
phenanthrene	0.928	0.933	0.955	0.800
	0.813	0.733	0.650	0.400
chrysene	0.923	0.917	0.945	0.750
	0.832	0.750	0.865	0.500
triphenylene	0.940	0.963	0.903	0.899
	0.741	0.557	0.515	0.222
dibenzanthracene	0.929	0.943	0.960	0.833
	0.800	0.693	0.793	0.333
	0.863	0.890	0.930	0.667
pentaphene	0.901	0.867	0.975	0.600
	0.851	0.867	0.963	0.600
	0.722	0.600	0.931	0.200
pyrene	0.882	0.890	0.940	0.667
	0.818	0.723	0.795	0.333
perylene	0.885	0.890	0.878	0.667
	0.699	0.443	0.683	0

A parallelism between the magnitudes of the Pauling ring indices and the graph theoretical ring indices (to be discussed in the next section) should also be noticed. Observe in particular that in both cases linearly fused benzene rings, such as the rings of anthracene and the terminal rings of benzanthracene or dibenzanthracene, have the same ring index values. Instead of the Pauling bond orders, one can construct the benzene ring indices using the Coulson bond orders. They show the same main features that we have seen with ring indices based on the Pauling bond orders.[672] This approach of constructing ring indices from bond orders is open to other variants of the MO calculations, as illustrated in Figure 95, in which we show the "benzene ring characters" derived from SCF MO calculations of Dewar and Trinajstić.[673] In this case, the "benzene character" of a benzene ring is 4.000, the highest possible value for a benzene ring, which was in the case of the Pauling ring index 3.000. In order to facilitate comparison between the different schemes in Table 41, we collected for half a dozen smaller benzenoids normalized "benzene characters" which all assume benzene to have a ring index of magnitude 1.000. In the last column we included a simple graph theoretical index of "benzene character" proposed years ago by this author. Overall, there is considerable parallelism between different indices, with the GT approach displaying the greatest range of values. The range of values of the other indices can be increased by subtracting some "dead weight", a constant term, but although such steps are legitimate, they involve a degree of arbitrariness.

C. Graph Theoretical Approach to "Benzene Character" of Fused Benzene Rings

From a graph theoretical point of view, benzene character can be defined as the frequency of occurrence in the totality of Kekulé valence structures of a benzenoid hydrocarbon of a ring formally as a benzene ring. For example, as one can see from Figure 18, where Kekulé structures of phenanthrene are shown, the peripheral ring of phenanthrene occurs in four out of five Kekulé valence structures as a Kekulé benzene ring (having three CC double and three CC single bonds). In contrast, the central benzene ring of phenanthrene occurs as a benzene ring in only two out of five Kekulé valence structures. Hence, the corresponding graph theoretical indices of local aromaticity for the two benzene rings are 4/5 and 2/5, respectively. Similarly, the graph theoretical indices of benzo[*ghi*]perylene (Figure 15) are 6/14, 10/14, 8/14, and 2/14, the largest value belonging to the benzene rings of π-aromatic sextets (see Figure 96, structure 17). Such results follow from the following definition:

Definition: *The local aromaticity is given by the quotient of the number of time a ring appears in all Kekulé valence structures as a benzene Kekulé ring and the number of Kekulé valence structures.*

The graph theoretical approach to the local aromaticity of benzenoid hydrocarbons was outlined in ref 508. The local aromaticity can be extracted from the first entry in the ring codes[507] that enumerate conjugated circuits of different size for a single ring within the totality of Kekulé valence structures for benzenoid hydrocarbons. Dividing by K (the number of Kekulé valence structures) gives the sought-after graph theoretical "benzene character" for the ring considered. The graph theoretical "benzene character" is computationally simple and conceptually elegant. It may be viewed as a generalization of the very approach of Pauling characterization of CC bond orders, except that now it applies to rings rather than individual CC bonds.

In Figure 96 we show the ring indices for a selection of smaller benzenoid hydrocarbons. The ring indices show some interesting regularities. For example, rings that comprise a "linear part" of a benzenoid, e.g., all rings in naphthalene (**1/96**) and anthracene (**2/96**), and two rings in benzanthracene (**4/96**), pentaphene (**8/96**), and dibenzanthracene (**12/96**), have a constant index value. The ring at the "kink" position, however, as a rule shows a considerably reduced ring index value. This is the case with the central rings of phenanthrene (**3/96**), benzanthracene (**4/96**), and pentaphene (**8/96**). Interestingly, this very same regularity is also present in the "benzene characters" based on the Pauling bond orders. Finally, again terminal rings have the largest value for their ring indices. In the case of graph theoretical indices, the magnitudes of the "benzene character" are numerically smaller than for other approaches, and only the benzene rings of "fully benzenoid" hydrocarbons, e.g., triphenylene (**6/96**), dibenzopyrene (**13/96**), and tetrabenzanthracene (**15/96**), approach the value of one.

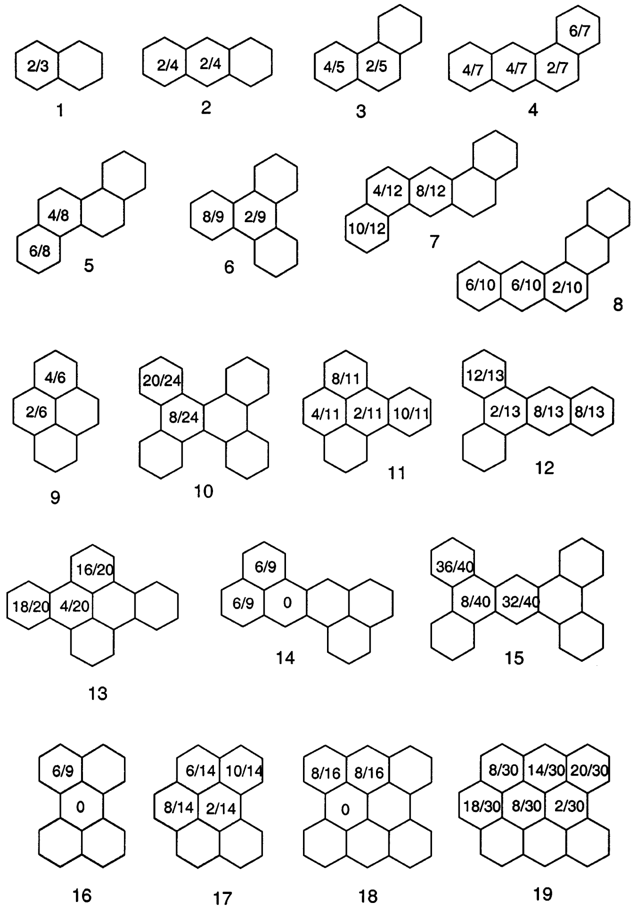


Figure 96. Graph theoretical ring indices for a selection of smaller benzenoid hydrocarbons.[765]

D. On Quantitative Interpretation of Clar Valence Structures

Clar structures, just as Kekulé valence structures, are first a novel pictorial representations of benzenoid hydrocarbons in which differences between individual benzene rings are emphasized. In Clar's formula, the benzene rings are shown either as the aromatic π-sextets, as the migrating sextets, as rings with a single CC double bond, or as the so-called "empty" rings. Hence, clearly Clar's pictorial representation of benzenoid hydrocarbons is necessarily *qualitative* in nature. However, by introducing the above graph theoretical characterization of local benzenoid character of individual rings in benzenoid hydrocarbon, we can assign to Clar's structures *quantitative* content. We can make a step further and *insist* that this link between Clar structures and their graph theoretical characteristics be viewed as the *definition of*

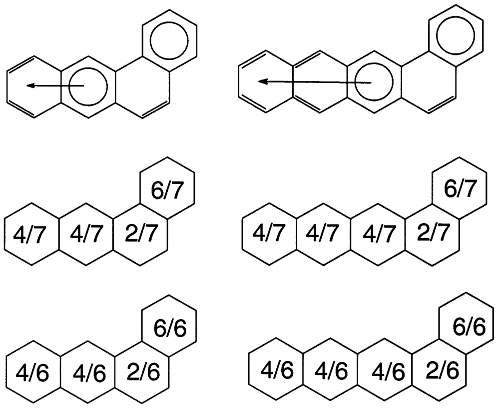


Figure 97. Clar structures and corresponding graph theoretical rings indices for benzanthracene and benztetracene, based on all Kekulé valence structures and based only on valence structures with maximal *df*.

quantitative Clar valence structures. Hence, quantitative Clar structures discriminate individual benzene rings by assigning them numerical values based on the value of the local aromatic index as outlined above.

Definition: *A quantitative Clar structure of a benzenoid hydrocarbon is given by assigning to individual benzene rings the numerical value R/K, where R indicates the number of times the ring appears as a Kekulé ring in the totality of Kekulé structures of the molecule.*

The numerator R is given by the count of the conjugated circuit R_1 for individual rings. Consider for example benzanthracene, the benzene rings of which have the ring indices 4/7, 4/7, 2/7, and 6/7, as illustrated in the middle on the left in Figure 97, where the Clar structure of benzanthracene is shown at the top. The terminal ring, having the local aromatic index of 6/7, belongs to the π-aromatic sextet of the Clar formula for benzanthracene. The Clar formula for benzanthracene also has a migrating sextet, which is located at the ring having local aromatic character of 4/7. Finally, the "kink" ring of benzanthracene, which has the local benzene character of only 2/7, corresponds in the Clar formula to an almost "empty" ring. The "empty" rings have no CC double bonds, but the benzene rings may have a single isolated C═C bond. In Figure 97 on the right, we also include Clar structures of benztetracene and show the corresonding ring indices for this molecule. As we can see, the numerical characterization of the rings has slightly changed: the migrating π-sextets are here associated with a smaller numerical ring value, which is a consequence of increased domain available for migration. Clearly, the less π-sextets are localized, the lesser contributions they make to RE and molecular stability, and the more π-sextets are localized, the greater contributions they make to RE and molecular stability.

At the bottom of Figure 97, we show the numerical characterization of Clar structures of benzanthracene and benzotetracene based on the use of only Kekulé structures contributing to the Clar structure. As we can see, and as is to be expected, in this case the numerical values that the aromatic π-sextets receive equal one.

A close look at Figure 96, in which there are several "fully aromatic" compounds, does show that the "empty" rings described by Clar are not quite "empty" but are associated with rather very low magnitudes for the ring indices. For instance, the "empty" ring of triphenylene has the value 2/9, that of dibenzopyrene has the value 4/20, and the same value in tetrabenzanthracene (written as 8/40) (structures **6/96**, **13/96**, and **15/96**, respectively). There are few rings with the graph theoretical index zero, e.g., the central rings in zethrene (**14/96**), perylene (**16/96**), and bisanthene (**18/96**), all of which are associated with the presence of essentially single and essentially double CC bonds. All that we did in this linkage between the qualitative and the quantitative Clar formulas was to assign numerical values to verbal descriptions, such as "π-sextet", "migrating sextet", and "empty ring". In different molecules, the same qualitative terms may have slightly different numerical values, but that is how it should be! When one considers *quantitative* models, there is no a priori reason why, for example, the π-aromatic sextet of triphenylene should be identical to the π-aromatic sextet in, say, phenanthrene, or why the empty ring in triphenylene should be identical to the empty rings of perylene.

We may add that, in a similar way, one can "upgrade" Kekulé valence structures by assigning to individual Kekulé structures a numerical parameter based on some structural considerations. In fact, enumeration of conjugated circuits within individual Kekulé valence structures leads to such quantitative Kekulé valence structures. For example, one can assign to each Kekulé valence structure as the weight the relative contribution that the particular structure makes to the molecular RE. Thus, the two nonequivalent Kekulé valence structures of naphthalene will have weights $(2R_1)/3$ and $(R_1 + R_2)/3$, respectively. To obtain numerical equivalents, all one has to do is to select numerical values for the graph theoretical parameters R_1 and R_2. For example, if we assume $R_1 = 1$ and $R_2 = 1/3$, we obtain for the relative weights of the two Kekulé structures 2/3 and 4/9, or 3:2 in the favor of the Fries Kekulé structure of naphthalene.

E. On Neglect of Local Aromaticity

We have seen that all the approaches outlined in this section on local aromaticity, starting with the work of Polansky and Derflinger and ending with graph theoretical analysis, point to differentiation of local ring characteristics that parallel suggestions implied in Clar's valence structures. In view of this overwhelming support for Clar's empirical model, it is, to say the least, difficult to understand the apparent rejection of Clar's pioneering insights into the nature of benzenoid compounds by the quantum chemistry "establishment". One wonders why skeptics preferred to ignore Clar's work on benzenoid hydrocarbons and Clar's interpretation of benzenoid structures via aromatic π-sextets instead of accepting the challenge and coming forward with their answers to the same problem from “the first principles”, if that is possible?

Let be reminded of a quotation from Max Planck:[674]

> *... the experimenter cannot afford to close his eyes to a new discovery, obtained from another point of view, which will not fit in with his own ideas, nor must he treat it as unimportant, if not incorrect...*

For this occasion, we should have replaced, as more appropriate, the term “experimenter” by “theoretician”. Since nobody has shown that Clar is wrong, we have to assume that his work was treated as unimportant — but according to Planck, theoretical chemists ought to change their attitude toward Clar. Perhaps some have hoped that, with time, this π-aromatic “headache” will fade away and disappear, but they most likely may not have heard a statement made by Sigmund Freud to the contrary:[675]

> *The voice of intellect is a soft one, but it does not rest until it has gained a hearing. Ultimately, after endless rebuffs, it succeeds. This is one of the few points in which one may be optimistic about the future of mankind.*

Theoretical chemists, who ought to lead the way in molecular modeling, have apparently failed to recognize the significance of Clar’s ideas on aromatic π-sextets, with a few exceptions. We already mention M. Orchin and H. H. Jaffe. Another “exception” is the chemical graph community, which includes A. T. Balaban, H. Hosoya, N. Trinajstić, D. J. Klein, W. C. Herndon, I. Gutman, Y. Jiang, S. El-Basil, J. Aihara, and J. R. Dias — to mention only few authors who contributed to the topic of aromaticity. Among experimentalists, there is a particularly sizable group of German chemists, including M. Zander, who was a collaborator of Clar. We should mention in particular W. Schmidt, H. Vogler, J. J. Voitländer, K. P. C. Vollhardt, and K. Müllen as the leading authorities on the chemistry of benzenoid and non-benzenoid hydrocarbons. In the special issue of *Chemical Reviews* on aromaticity, several papers, though rather briefly, mentioned conjugated circuits and Clar structures: those by Bühl and Hirsch;[676] Watson, Fechtenkötter, and Müllen;[174] Mitchell;[677] Gomes and Mallion;[644] Krygowski and Cyrański;[678] Katritzky, Jug, and Oniciu;[679] De Proft and Geerlings;[680] Schaad and Hess;[542] and Slayden and Liebman.[681] In view of the above quotation from Freud, clearly it is merely a matter of time until the ideas of Clar will become familiar to everybody and commonplace in chemistry, outside of the already indicated theoretical and experimental circles.

F. Alternative Ring Indices

Besides the already-mentioned ring indices, additional ring indices have been proposed for benzenoid (and other) hydrocarbons on the basis of different considerations. Thus, Kruszewski and Krygowski[682] considered an approach based on equalization of CC bonds. Krygowski and co-workers[682−685] considered the “harmonic oscillator model of aromaticity” (HOMA), where by using statistical analysis they were able to separate electronic and geometrical contributions to aromaticity. A close look at HOMA indices, which were reported for many benzene rings in the article by Krygowski and Cyrański in the recent *Chemical Reviews* issue on aromaticity,[678] shows regularities in their relative magnitudes similar to those displayed by the ring indices of Polansky and Derflinger outlined in this review. The harmonic oscillator model is based on bond lengths, but it differs from other geometry-based indices not only in selecting a different reference bond length but also by involving energetic considerations. It is based on a reference bond using harmonic potential and considers the energy minimum associated with the compression of CC double bonds and expansion of the length of a single bond in 1,3-butadiene.

The *C* index of aromaticity of Randić, Plavšić and Trinajstić[638] can also be viewed as an energetic index. It measures a portion of the benzene ring resonance energy that arises from the smallest conjugated circuits R_1. To a degree, the *C* index parallels the already described graph theoretical ring index, with the difference that it uses specific weights for the contributing R_1 conjugated circuits, relative to contributions arising from the larger conjugated circuits, rather than merely considering the frequency of such conjugated circuits. In Table 42 we have listed the ring codes that summarize the count of conjugated circuits for the individual rings, as well as the numerical contribution to molecular RE, for the symmetry-non-equivalent rings of the 30 smaller benzenoids shown in Figure 53. We included the results obtained when two different parametrizations were used for R_1, R_2, and R_3 in order to show that the relative magnitudes of ring RE are not very sensitive to the choice of empirical parameters.

Ring indices based on different MO calculations show some variations. Thus, ring indices based on SCF MO results, reported by Dewar and Trinajstić,[673] point to a slightly increased aromatic character of the central rings in linear acenes (anthracene, tetracene, etc.), while the calculations made by Aida and Hosoya[561] using the PPP method (the Pariser−Pople−Parr SCF calculations[41,42]) show just the opposite trend. The differences between the benzene character of these rings, which in the graph theoretical approach as well as in the approach based on the Pauling bond orders have the same ring values, are quite small, as can be seen from Figure 98, where we illustrated the “benzene characters” for the three non-equivalent benzene rings of pentacene as derived by different approaches. In order to make comparisons easier, all the ring indices have been normalized so that “the most aromatic ring” gets the ring value 1.000. On the right-hand side of the figure are shown the normalization factors. As we can see, in this respect the HMO and the PPP method calculations reported by Aida and Hosoya[561] show remarkable parallelism with the more recent accurate VB calculations reported by Li and Jiang. “*It is remarkable,*” Aida and Hosoya observed, “*how an improved MO version, PPP as compared to HMO, makes distribution of relative ring values only slight when PPP is*

Table 42. Ring Codes and Ring RE for Smaller Benzenoid Hydrocarbons (Shown in Figure 53)

molecule	ring	code	ring RE (eV)[a]	ring RE* (eV)[b]
1/53	A	2, 0, 0	0.869	0.869
2/53	A	2, 1, 0	0.657	0.611
3/53	A	2, 1, 1	0.521	0.521
	B	2, 2, 0	0.572	0.558
4/53	A	4, 1, 0	0.725	0.744
	B	2, 2, 1	0.480	0.466
5/53	A	2, 1, 1, 1	0.416	0.417
	B	2, 2, 1	0.480	0.466
6/53	A	4, 2, 1	0.579	0.581
	B	4, 3, 0	0.608	0.602
	C	2, 2, 2	0.359	0.347
	D	6, 1, 0	0.754	0.780
7/53	A	6, 2, 0	0.700	0.713
	B	4, 3, 1	0.564	0.539
8/53	A	8, 1, 0	0.770	0.800
	B	2, 3, 3, 1	0.326	0.308
9/53	A	4, 2	0.657	0.661
	B	2, 2, 2	0.418	0.405
10/53	A	2, 1, 1, 1, 1	0.347	0.347
	B	2, 2, 1	0.400	0.388
	C	2, 2, 2	0.418	0.405
11/53	A	4, 2, 2, 1	0.463	0.456
	B	4, 4, 1	0.507	0.510
	C	4, 3, 2	0.491	0.489
	D	2, 2, 2, 2, 1	0.270	0.274
	E	8, 1	0.800	0.758
12/53	A	6, 3, 1	0.606	0.591
	B	6, 4	0.620	0.610
	C	2, 2, 3, 2, 1	0.253	0.259
13/53	A	10, 2	0.765	0.730
	B	4, 4, 3, 1	0.397	0.402
	C	8, 4	0.662	0.644
14/53	A	6, 3, 2	0.560	0.548
	B	6, 5	0.586	0.582
	C	4, 3, 3, 1	0.411	0.411
	D	6, 4, 1	0.573	0.565
	E	8, 3	0.699	0.675
15/53	A	10, 3	0.725	0.697
	B	6, 5, 2	0.511	0.510
	C	8, 4, 1	0.618	0.603
16/53	A	8, 4, 1	0.618	0.604
	B	8, 5	0.630	0.618
	C	2, 3, 4, 3, 1	0.221	0.231
	D	12, 1	0.821	0.776
17/53	A	10, 4	0.691	0.668
	B	8, 5, 1	0.592	0.582
	C	4, 5, 4, 1	0.365	0.374
	D	12, 2	0.780	0.742
18/53	A	8, 3	0.699	0.675
	B	4, 4, 3	0.433	0.430
	C	2, 3, 4, 2	0.262	0.273
	D	10, 1	0.812	0.769
19/53	A	6, 2, 1	0.645	0.624
	B	4, 4, 1	0.507	0.510
	C	2, 2, 3, 2	0.281	0.288
	D	4, 3, 2	0.491	0.489
	E	6, 3	0.662	0.644
20/53	A	8, 3, 2	0.607	0.589
	B	6, 6, 1	0.523	0.525
	C	4, 3, 4, 1	0.355	0.357
21/53	A	6, 3, 1	0.606	0.591
	B	4, 4, 2	0.466	0.470
	C	2, 2, 3, 3	0.253	0.259
22/53	A	10, 4	0.691	0.668
	B	6, 5, 3	0.482	0.482
	C	8, 5, 1	0.592	0.582
	D	2, 3, 5, 4	0.213	0.223
23/53	A	20, 4	0.765	0.730
	B	8, 9, 6, 1	0.407	0.414
24/53	A	10, 7, 3	0.536	0.531
	B	4, 6, 9, 1	0.293	0.277
25/53	A	18, 2	0.807	0.764
	B	4, 6, 7, 3	0.283	0.295
	C	16, 4	0.745	0.712
26/53	A	36, 4	0.807	0.764
	B	8, 12, 13, 6, 1	0.280	0.292
	C	32, 8	0.745	0.756
27/53	A	12, 6	0.662	0.644
	B	6, 5, 5, 2	0.386	0.388
	C	8, 8, 2	0.507	0.510
28/53	A	24, 11	0.674	0.691
	B	12, 12, 11	0.414	0.420
	C	10, 11, 12, 2	0.360	0.368
29/53	A	8, 4, 4	0.521	0.724
	B	8, 8	0.558	0.559
	C	0	0	0
30/53	A	18, 8, 4	0.601	0.582
	B	14, 13, 3	0.523	0.523
	C	8, 7, 9, 6	0.319	0.323
	D	18, 10, 2	0.610	0.598
	E	8, 9, 9, 4	0.336	0.343
	F	2, 3, 6, 10, 9	0.103	0.108

[a] $R_1 = 0.869$ eV, $R_2 = 0.247$ eV, $R_3 = 0.100$ eV. [b] $R_1^* = 0.815$ eV, $R_2^* = 0.203$ eV, $R_3^* = 0.118$ eV.

compared with purely graph theoretical ring indices."[561] Aida and Hosoya conclude that, except for polyacene-like molecules, the graph theoretical ring values "*which can be obtained by hand-calculation, can be used as a rough estimation*" of ring values based on PPP.

That observation was certainly interesting and significant, yet for over 20 years it remained unrecognized! What that means, as will be elaborated later in the section on Clar's structures, is that the graph theoretical approach to local characterization of benzene rings parallels to a great degree computations based not so much on *HMO but on SCF variants of MO theory*, and even more the very accurate VB calculations made by Jiang and Li. On one hand, this then means that the empirically justified Clar's valence structures of benzenoid hydrocarbons may have a deep theoretical justification, and that there may be some quantum chemical basis for graph theoretical approach, even if we have not yet established the connection. On the other hand, it also illustrates baseless identification of the chemical graph theory with HMO theory, which was incidental in that the combinatorial and topological properties of molecules, when represented by the adjacency matrix of the molecular graph, become identical to those obtained with the HMO method. But molecules continue to have combinatorial and topological properties, even when described by the PPP method and other more advanced variants of MO theory.

We should mention that accurate VB calculations of the molecular resonance energy and the local aromaticity were recently reported by Li and Jiang[686] and Wu and Jiang[38] on medium-sized conjugated

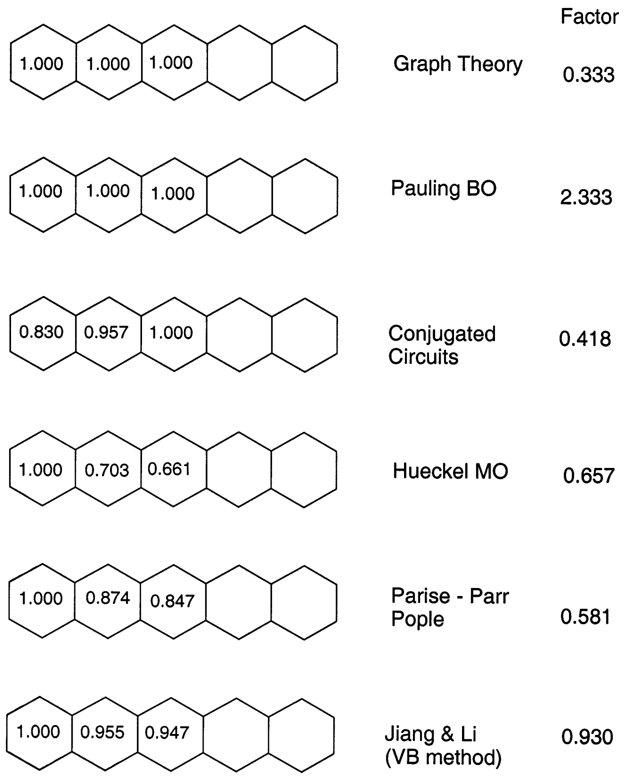


Figure 98. "Benzene characters" for the three nonequivalent benzene rings of pentacene as derived from different theoretical models.

hydrocarbons. Jiang et al. defined, similar to Herndon−Ellzey's definition of local aromaticity,[165] the local aromaticity of individual fused rings as the quotient of the local ring energy to the ground-state energy of benzene. In practice, this definition reduces to a ring index that is based on the sum of bond contributions, analogous to bond orders in MO approaches. The interpretation of the bond contributions is somewhat different: P_{ij}, according to Maynau, Said, and Malrieu,[687] represents the probability of finding a singlet arrangement between atoms i and j:

$$P_{ij} = \langle \Psi \mid {}^{1}\!/_{2}(a_i^{+} a_{\underline{j}}^{+} - a_{\underline{i}}^{+} a_j^{+})\,(a_{\underline{j}} a_i - a_j a_{\underline{i}}) \mid \Psi \rangle$$

where $a_{\underline{i}}^{+}$ and a_i are the creation operator of the spin-down electron and the annihilation operator of the spin-up electron at site i. This index allows partitioning of the VB energy into bond contributions. Jiang and Li report a good linear regression between the calculated ground-state P_{ij} and the experimental bonds, which justifies viewing P_{ij} as a bond index.

XXVI. Ring Currents

A. Ring Currents as Ring Descriptors

In their outstanding article in the recent *Chemical Reviews* issue on aromaticity, Gomes and Mallion[644] reported on aromaticity as viewed from the model of ring currents. Modeling magnetic properties and chemical shifts of benzenoid compounds on the ring current idea is a very natural "miniature" of the ideas of the classical physics described by Kirchhoff's laws. Haigh and Mallion[688] established a theoretical basis for relating the incidence of relatively "high" and "low" ring current intensities to the intuitive VB resonance theory and the "bond fixation" in conjugated compounds. This work shows how topological arguments, combined with ring current ideas, serve to reinforce Clar's rules. Here, under "Clar rules", we understand the description of benzenoid hydrocarbons by qualitative Clar's valence structures and accept the consequences of such a characterization of benzenoid hydrocarbons. In their treatment, Gomes and Mallion do not try to devise a ring current formalism that itself would be based on the VB resonance theory wave function. Instead, the philosophy that they adopted was (a) to identify and classify those specific rings in conjugated hydrocarbons which have exceptionally high and low ring currents and then (b) to use graph theoretical arguments that rely only on carbon−carbon connectivity of conjugated system to show that such rings are those in which VB computations point to "bond fixation". The bond fixation that Haigh and Mallion refer to concerns CC bonds which in all Kekulé valence structures have the same bond type, being either CC single bonds or CC double bonds. Such, for instance, are the central CC bonds in perylene that connect two naphthalene fragments and several central bonds in zethrene. Such bonds are also known as the essentially single and the essentially double CC bonds.[43]

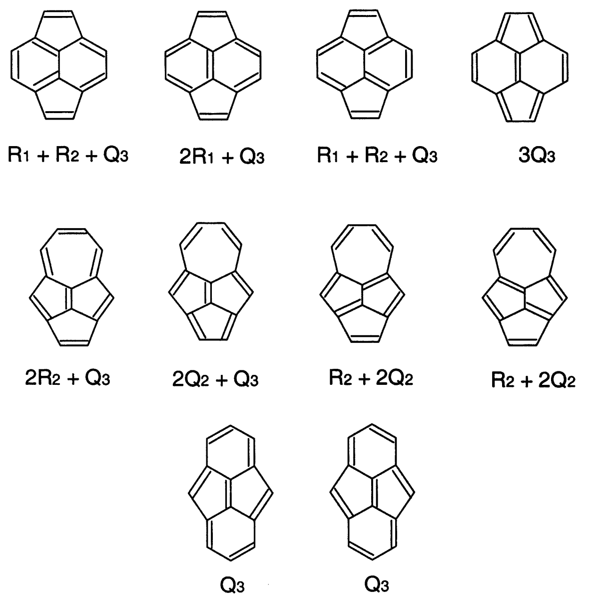


Figure 99. Decomposition of Kekulé valence structures for pyracylene and its isomers azulenopentalene and dibenzo[*cd,gh*]pentalene in $4n + 2$ and $4n$ conjugated circuits.

Let us compare the results of ring current calculations for pyracylene and its two isomers: azulenopentalene and dibenzo[*cd,gh*]pentalene, the three structures shown in Figure 99. As discussed by Gomes and Mallion,[644] there is some disagreement in the interpretation of the results reported by these authors and by Anusooya and collaborators,[689] who made more recent calculations on these systems. According to Gomes and Mallion,[644]

> ... *(Anusooya and collaborators) claimed that "the ring current results established that pyracylene can be viewed as 4n annulene system with internal vynil cross-links". However, the present authors believe that the situation is by no means that simple, and although Anusooya et al.*[689] *made reference to our work of 20 or more years ago,*[642,690] *there is no mention on their part of our detailed — and by no means straightforward — findings in ref [690] that not all three of pyracylene and its two isomers may be regarded as good models for a "perturbed[4n]-annulene" (n=3): dibenzo[cd,gh]pentalene is predicted in ref. [690] to be "very paramagnetic," while pyracylene and azulenopentalene "are marginally diamagnetic and marginally paramagnetic, respectively." Accordingly, of pyracylene and its two isomers, dibenzo[cd,gh]pentalene is the one that*[640] *"would apparently serve best as perturbed [12]-annulene in terms of the model proposed by Trost et al.*[640,641] (Reference numbers have been changed to correspond to the numbering in the current review.)

I would like to add that I tend to fully agree here with the statement of Gomes and Mallion, but that is not the reason for including the above lengthy quotation on ring calculations on pyracylene and its two isomers. The main reason for a discussion of ring properties of these molecules is to contrast the "*detailed — and by no means straightforward — findings· that not all three of pyracylene and its two isomers may be regarded as good models for a 'perturbed[4n]-annulene'* " of Gomes and Mallion with the same conclusion that follow *straightforwardly* from the model of conjugated circuits. In Figure 99 we present Kekulé valence structures for pyracylene and its two isomers, azuleneopentalene and dibenzo[*cd,gh*]pentalene. Under each valence structure is shown its decomposition in conjugated circuits, where R_1, R_2, and R_3 are $4n + 2$ conjugated circuits for $n = 1$, 2, and 3, respectively, and Q_2 and Q_3 are $4n$ conjugated circuits for $n = 2$ and 3. From the enumeration of conjugated circuits, we can obtain the expressions for their corresponding RE (vide infra). It is easy to verify that RE values of the three isomers are different:

pyracylene	$(4R_1 + 2R_2 + 6Q_3)/4$	marginally diamagnetic
azulenopentalene	$(3R_2 + R_3 + 6Q_2 + 2Q_3)/4$	marginally paramagnetic
dibenzo[*cd,gh*]-pentalene	$(2Q_2)/2$	strongly paramagnetic

Recall that $4n + 2$ conjugated circuits make positive contributions toward RE and molecular stability, with $R_1 > R_2 > R_3$, while the opposite is the case with $4n$ conjugated circuits, with $|Q_1| > |Q_2| > |Q_3|$. From the above, we immediately can see, even without resorting to numerical calculations, that among the three isomers pyracylene will have the largest RE, and that its Kekulé valence structures have the conjugated circuits with the largest $4n + 2$ components. Hence, it may be expected that pyracylene shows diamagnetic behavior. This may be "marginal", as stated by Gomes and Mallion, because of the presence of a number of anti-aromatic Q_3 conjugated circuits. On the other hand, in azulenopentalene, the contributions from the $4n + 2$ conjugated circuits have visibly decreased. On one side, there are no contributing R_1 conjugated circuits, which as a consequence means a considerable reduction of the molecular RE. At the same time, the influence of $4n$ conjugated circuits is increased by the presence of the smaller "anti-aromatic" Q_2 conjugated circuits. Thus, the conclusion that this isomer is marginally paramagnetic appears reasonable. Finally, we see that dibenzo[*cd,gh*]pentalene is devoid of any $4n + 2$ conjugated circuits, and thus it has only anti-aromatic conjugated circuits that will be associated with strong paramagnetism. Moreover, we can see from the two Kekulé valence structures that in dibenzo[*cd,gh*]pentalene the central CC bond is essentially double and the four connecting CC bonds are essentially single bonds. Thus, there is no coupling between the peripheral 12-π-electron system and the central 2 π-electrons. Dibenzo[*cd,gh*]pentalene represents prima facie case for weakly "perturbed [4*n*]annulene".

It is fitting to conclude this brief outline of the differences between pyracylene and its isomers by pointing out the potential of the conjugated circuits model to characterize conjugated benzenoid hydrocarbons. The model of conjugated circuits offers insights into structural features of conjugated systems, including some magnetic properties that otherwise may require rather sophisticated and even tedious computations. At the same time, one should point out that the conjugated circuits method well reflects molecular features connected with the molecular *resonance energy* and molecular aromaticity. It shows that molecular RE is an additive quantity in terms of conjugated circuits, and it allows one to classify conjugated hydrocarbons as fully aromatic, aromatic, less aromatic, or anti-aromatic. However, the conjugated circuits model is not a panacea: it is not a substitute for quantum chemical arguments and other theoretical studies of molecules. Chemical graph theory helps to *process* available data, but it does not, as is the case with the quantum chemistry, *generate* novel data. Hence, graph theory cannot help with questions concerning molecular geometry, molecular spectra, and molecular interactions. Graph theory cannot produce RE for anthracene and phenanthrene, as quantum chemistry can, but given these values it can forcibly argue and demonstrate why the RE of phenanthrene is greater than that of anthracene; such questions are beyond quantum chemistry, in the sense that they could not be obtained from the first principles of quantum theory.

B. Nuclear-Independent Chemical Shifts (NICS)

An alternative characterization of the local features of conjugated polycyclic hydrocarbons in terms of ring currents involves computation of the effect of ring currents on chemical shifts. It was suggested by Schleyer and collaborators[691] that the absolute mag-

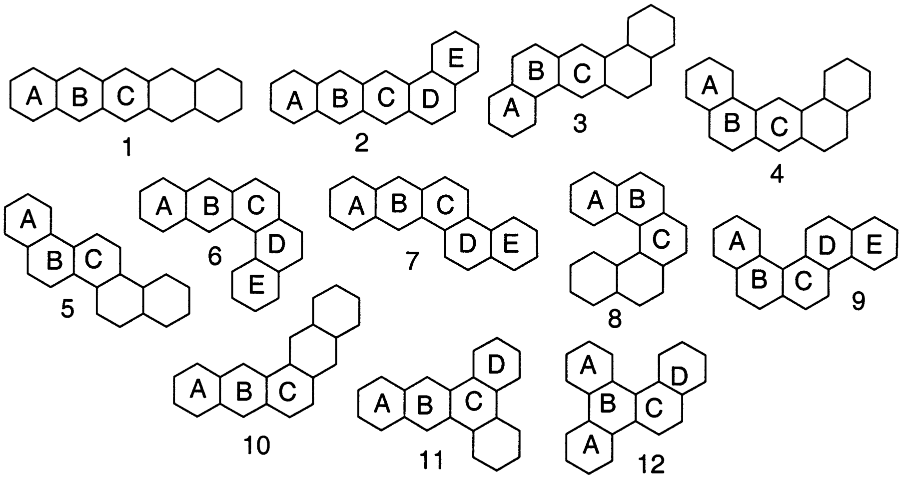


Figure 100. Pentacene isomers with labeled symmetry-non-equivalent benzene rings.

netic shielding computed at the ring center be viewed as a local index to estimate the degree of aromaticity and anti-aromaticity of a molecule. According to Schleyer, nuclear-independent chemical shift (NICS) is defined as the negative of the absolute magnetic shielding computed at the center of a ring and/or 1 Å above the center of the ring. This then gives rise to NICS(0) and NICS(1) parameters, respectively.

Gomes and Mallion[644] reproduced the relative ring currents and the relative NICS values for several conjugated hydrocarbons in their article, "Aromaticity and Ring Currents", where a detailed discussion of nuclear-independent chemical shifts is presented. There is an overall parallelism between the results of ring currents and chemical shifts at the center of a ring of conjugated hydrocarbons. Thus, the central rings in phenanthrene and triphenylene have substantially smaller ring currents and relative NICS in comparison with the peripheral rings in the same molecules. The same is true for the seven-member ring of azulene when compared to the five-member ring. On the other hand, as could have been expected, both the five-member ring in pyracylene and the four-member ring in biphenylene show strong paratropicity (i.e., negative ring current and negative NICS).

There is much more that could be written on nuclear-independent chemical shifts that is relevant for discussion of local aromaticity and deserves more attention, but there is no need to duplicate what has already been well presented elsewhere. We direct interested readers to the article by Gomes and Mallion[644] and the references cited therein for more information.

C. A Graph Theoretical View on Ring Currents

We will end this discussion of ring currents and chemical shifts by reviewing data on ring currents for a dozen isomers of pentacene $C_{22}H_{14}$, illustrated in Figure 100. The concept of ring currents, also considered by Pauling[692] over 65 years ago, is of interest for computations of chemical shifts in NMR spectroscopy. Ring currents are not observables; nevertheless, they proved useful for discussing magnetic properties of conjugated hydrocarbons. Several publications[642,688,692−698] reported the numerical values of ring currents for well over 300 rings in some 60 benzenoid systems. Although the supply of data appears satisfactory, it is worth observing *how little* was deduced from the available data concerning the regularities of ring currents for individual rings. Thus, for instance, all that Memory could conclude was "*... in general, the ratios of the individual ring currents in the pentacyclic hydrocarbons to the benzene ring current do not differ drastically from unity.*"[694] Haigh and Mallion similarly conclude "*... in polycyclic molecules, the ring currents are, in general, greater than the ring currents in benzene, but fall rapidly off with increase in condensation.*"[688] Perhaps one of the reasons that not much could be said at that time was a lack of adequate structural *vocabulary* that would allow more *precise* descriptions of different rings in different molecular environments. We will see that, with the help of graph theory and the concept of conjugated circuits in particular, considerably more could be said about the very same computational results. Aihara, who examined the diamagnetic susceptibility due to ring currents using graph theoretical terms, found that the susceptibility induced in any of the π-electron rings is roughly proportional to the contribution of the ring to the resonance energy, multiplied by a factor which depends on the ring area.[699]

In Table 43 we list the ring codes for the individual rings of the cata-condensed pentacyclic benzenoids shown in Figure 100. The entries in each code enumerate conjugated rings of different size in all Kekulé valence structures. Thus, for instance, the code 2,2,2 for the central ring of pentacene means that in the six Kekulé structures of pentacene, the central benzene ring appears twice as the conjugated circuit R_1, twice as a part of conjugated circuits R_2, and twice as a part of conjugated circuit R_3. We are not counting larger conjugated circuits R_4 and R_5, which also may be present in some Kekulé valence structures of the benzenoid hydrocarbons considered. A look at Table 43 immediately shows a number of interesting regularities in the data — well beyond "*ring currents do not differ drastically from unity*" and "*... the ring currents are, in general, greater than ring currents in benzene.*" The following are some of

Table 43. Ring Codes for Individual Rings of the Pentacyclic Benzenoids Shown in Figure 100[a]

	molecule	ring	ring code	ring current
1/100	pentacene	A	2, 1, 1, 1, 1	1.06
		B	2, 2, 1, 1	1.30
		C	2, 2, 2	1.35
2/100	benzanthracene	A	4, 2, 2, 1	1.09
		B	4, 4, 1	1.32
		C	4, 3, 2	1.35
		D	2, 2, 2, 2, 1	0.85
		E	8, 1	1.11
3/100	dibenzo[*a*,*h*]anthracene	A	10, 2	1.14
		B	4, 4, 3, 1	0.94
		C	8, 4	1.29
5/100	picene	A	10, 3	1.15
		B	6, 5, 2	1.06
		C	8, 4, 1	1.16
7/100	dibenz[*b*,*i*]phenanthrene	A	6, 3, 2	1.12
		B	6, 5	1.30
		C	4, 3, 3, 1	0.99
		D	6, 4, 1	1.08
		E	8, 3	1.15
10/100	pentaphene	A	6, 3, 1	1.11
		B	6, 4	1.23
		C	2, 2, 3, 2, 1	0.78
11/100	dibenzo[*a*,*c*]anthracene	A	8, 4, 1	1.12
		B	8, 5	1.21
		C	2, 3, 4, 3, 1	0.65
		D	12, 1	1.08
12/100	dibenzo[*a*,*c*]phenanthrene	A	12, 2	1.13
		B	4, 5, 4, 1	0.85
		C	8, 5, 1	1.09
		D	10, 4	1.10

[a] For isoconjugate structures (3, 4), (5, 8, 9), (6, 7) only one structure is listed.

the observations that follow after examination of Figure 100:[508]

(1) Within a molecule, symmetry-non-equivalent rings having the same ring code show the same ring current.
(2) Benzene rings in different molecules having the same code show the same ring current.
(3) Ring currents in rings with predominant contributions of R_1 approach the value 1.000.
(4) The smallest ring currents belong to rings with low R_1 content and "long" ring code (i.e., the presence of many large conjugated circuits).

Because individual rings are in different local environments, their ring codes depend much on the immediate neighborhood. The ring codes of Table 43 allow one to group rings of similar environments and recognize their common characterization. By looking at the table more closely, we can see additional regularities, such as an increase of the ring current in linearly fused rings as we move from the periphery toward the center. Similarly, we see that the "empty" rings of the Clar structures for the benzenoids considered have unusually small ring currents. Finally, the rings belonging to the aromatic π-sextet have larger ring currents than the adjacent rings, having fixed C═C bonds in Clar's structure of a molecule. Some points remain yet to be better understood. For instance, why does the central ring in picene have a ring current similar in magnitude to that of the terminal rings, while in 1,2:5,6-dibenzanthracene and 1,2:7,8-dibenzanthracene (the compounds **3/100** and **4/100**) the central ring has a visibly larger ring current?

It is clear from Table 43 that conjugated circuits and Clar structures play some role here in determining the relative magnitudes of the ring currents, as it is not accidental that benzene rings with the same code, i.e., the same composition of conjugated circuits, have the same ring currents. Be that as it may, it is remarkable that the simple graph theoretical approach to benzenoid hydrocarbons already provides important guidance. We can conclude from the above observations that although ring currents of benzenoid hydrocarbons were calculated independently for each ring and for each molecule, the ring currents are *transferable*, at least within cata-benzenoid hydrocarbons between rings having the same code. Caution is needed if one is to extend such considerations to peri-condensed systems, because conjugated circuits R_3, as discussed by Klein and collaborators,[533] may belong to circuits of different shapes, represented by the periphery of anthracene, phenanthrene, and pyrene. Each such R_3 conjugated circuit is likely to make a different contribution to ring current calculations as well as to other molecular properties. In particular, this will be true for conjugated circuits that encompass different areas, such as the 14 π-conjugated circuits along the perimeter of anthracene or phenanthrene and the 14 π-conjugated circuits along the perimeter of pyrene.

D. Conjugated Circuits Currents

In discussing conjugated circuits in conjugated hydrocarbons, particularly pyracylene, we already hinted in Figure 84 at a possibility that the model of conjugated circuits gives insights into variations in chemical shifts resulting from the diamagnetic and the paramagnetic contributions of ring currents. We will present here three additional examples that illustrate a connection between the ring current model and the model of conjugaed circuits. As we already know, non-benzenoid hydrocarbons may have $4n + 2$ and $4n$ conjugated circuits. We will now assume that an outside magnetic field will induce in $4n + 2$ conjugated circuits ring currents along the CC bonds of the conjugated circuits in a mathematically positive direction (that is, anti-clockwise). As a consequence, hydrogen atoms in the vicinity will experience diamagnetic shifts. On the other hand, an outside magnetic field will induce in $4n$ conjugated circuits ring currents along the CC bonds of the conjugated circuits in a mathematically negative direction (that is, clockwise). As a consequence, hydrogen atoms in the vicinity will experience paramagnetic shifts.

At the top left in Figure 101 we illustrate one of the four Kekulé valence structures for one of the isomers of pyracylene. We decomposed this valence structure into its conjugated circuits R_2, R_2, and Q_3, outlined in the center of the top row over the molecular skeleton as the peripheries of azulene (twice) and the periphery of the molecule as a whole. We assume in this qualitative representation that the two R_2 conjugated circuits will contribute a current of strength +1 in the positive (anti-clockwise) sense to each bond of the azulene periphery. On the other hand, the bonds that belong to the molecular periph-

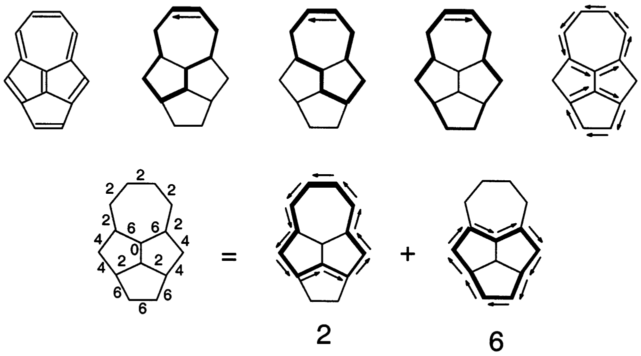


Figure 101. (Top) Decomposition of one of the Kekulé structures of azulenopentalene, for which schematic ring currents associated with $4n + 2$ and $4n$ conjugated circuits are shown. (Bottom) Resulting superposition based on the four Kekulé structures of azulenopentalene.

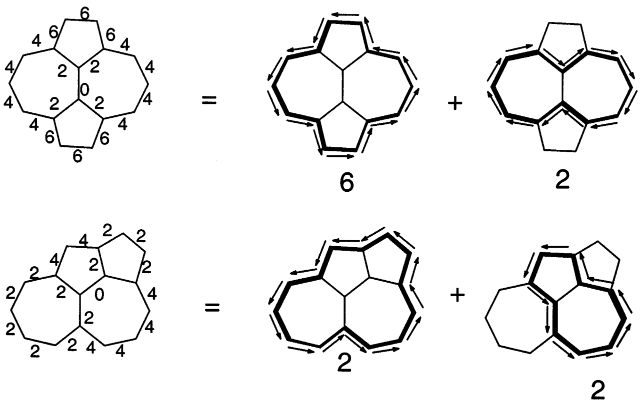


Figure 102. Ring currents resulting from the superposition of the schematic "conjugated circuit ring currents" arising from all Kekulé structures for azupyrene (top) and its isomer (bottom).

ery similarly contribute to ring currents, but in the opposite direction. As a result, for some bonds the currents will cancel and for some bonds they will add. In the right-most diagram in the top row of Figure 101, we show the result of the superposition of the three rings currents arising from conjugated circuits R_2, R_2, and Q_3. The directions of the bond contributions have to be inferred from the diagram. As we can see, the particular Kekulé valence structure of the isomer of pyracylene considered has a diamagnetic ring current in the seven-member ring and a paramagnetic ring current in the bottom five-member carbon ring. In the lower part of Figure 101, we first show the amplitudes of all bond contributions to all ring currents from all conjugated circuits in all Kekulé valence structures of pyracylene. The resultant bond currents can be shown to be a superposition of a diamagnetic current involving a seven-member ring and two adjacent five-member rings (an 11 carbon atom center) and a paramagnetic current embracing the periphery of the three five-member rings (a 9 carbon atom circuit).

In Figure 102 we show the results of a similar analysis of conjugated circuits in azupyrene and one of its isomers. Azupyrene has four Kekulé valence structures, which contribute eight R_2, two R_3, and two Q_3 conjugated circuits. It is then to be expected that the molecule will have dominant diamagnetic ring currents with minor contributions from paramagnetic currents. As we can see from Figure 102, bond current contributions split into contributions arising from the strong diamagnetic current along the molecular periphery and a weak paramagnetic current along the central heptalene periphery. The decomposition of the bond current contributions for the isomer of azupyrene is shown in the lower part of Figure 102. This molecule also has $4n + 2$ and $4n$ contributions as follows: six R_2, two R_3, two Q_2, and two Q_3. In this case, the presence of $4n$ conjugated circuits is more pronounced. Nevertheless, as we can see from Figure 102, the decomposition of the overall contributing conjugated circuits results in only diamagnetic contributions along the molecular periphery (a 14-member circuit) and along the periphery of the central azulene fragment (10-member circuit). Thus, interestingly, the presence of the $4n$ conjugated circuits in this molecule has been completely canceled by contributions from the $4n + 2$ conjugated circuits. The intensity of the diamagnetic ring currents in this isomer of azulene, though both components are diamagnetic, is smaller than the combined contributions of the diamagnetic and paramagnetic ring currents in azupyrene.

Let us end this discussion of ring currents by quoting the concluding statements from a paper in which the local aromatic properties of benzenoid hydrocarbons were discussed, as it well clarifies the distinction between the quantum chemical calculations of ring currents and the graph theoretical rationale for results so obtained on the basis of the count of conjugated circuits:[508]

> *The novel viewing of rings and ring contributions has still not resolved the issue of the relative magnitudes of ring currents in benzenoid systems. The problem has been challenge for a decade and more to quantum chemists and continue to be elusive. We are not surprised for the past lack of understanding of the relative magnitudes for ring currents. Strictly speaking the task is outside the usual scope of applied quantum mechanics since it is conceptual not computational. The concept of conjugated circuits definitely offered some guidance. To find explanation fully one needs more numerical results on additional rings and compounds. This part has to come from quantum mechanical calculations, it will not clarify the present difficulties, but may pave way to subsequent graph theoretical efforts and help in recognizing important factors. Graph theory normally does not produce new data, but hopefully can relate meaningfully the available data with a help of appropriate graph invariants. Combined quantum mechanical calculations and graph theoretical considerations are likely to further clarify the problem and possibly offer a complete understanding. The situation is a good illustration of the different character of the two important theoretical tools: quantum mechanics and graph theory.*

XXVII. Graph Theoretical Ring Resonance Energies

From the topics discussed above, we have seen that the local aromaticity index is given as a quotient in which the numerator enumerates conjugated circuits R_1 for individual rings in benzenoid hydrocarbons and the denominator is K, the number of Kekulé structures. A more complete description based on the conjugated circuits model considers ring codes derived from enumeration of *all* conjugated circuits in all Kekulé valence structures. In Tables 42 and 43 we listed ring codes for a number of smaller benzenoids illustrated in Figures 53 and 100, respectively. Immediately we see that there is a variety of ring codes: on one end the codes that show a dominance of the R_1 contribution, and on the other end the codes that show a lack of dominance of the R_1 contributions. When one compares ring codes with Clar's π-sextet formulas, one can notice that rings with the dominant R_1 contribution correspond to the rings with π-sextets, while the rings with comparable R_1 and R_2 contributions belong to the "migrating" sextets, and finally the rings that have but a minor R_1 contribution correspond to the "empty" rings.

If we multiply the triple entries of a ring code by the numerical parameters for R_1, R_2, and R_3, respectively, we obtain the ring resonance energy that is listed in the last column of Table 42. The two numerical values shown in the table were based on alternative choices for the parameters R_1, R_2, and R_3 as listed at the bottom of the table. The first set is the initial parametrization, as reported in ref 51, based on solution of the set of linear equations for benzene, naphthalene, and anthracene. The second set is based on the least-squares fitting of the expressions for RE for a collection of smaller benzenoid hydrocarbons. Clearly, by adding the RE contributions of all rings, we obtain the molecular RE, because the entries in the codes are the coefficients for the expression of molecular RE considered earlier. The derived ring RE can be viewed as an alternative (energetic) ring index. *The ring RE merely represents partitioning of molecular RE into ring contributions, just as the R_1, R_2, and R_3 contributions to individual Kekulé valence structures represent partitioning of RE into Kekulé valence structure contributions.* While such results are of considerable interest, as they clearly show the variation of local aromatic character in a benzenoid hydrocarbon, the practical importance of ring RE emerges when one wishes to calculate the RE of large benzenoids. Such molecules as a rule have large numbers of Kekulé valence structures, and a direct use of Kekulé valence structures for counting conjugated circuits becomes impractical. As we will see later on, for the case of giant benzenoids, one can obtain molecular RE for such compounds much more easily by calculating the ring RE and adding their contributions than by trying to calculate the contributions of various Kekulé valence structures.

XXVIII. The Most Aromatic Aromatic Compounds

That benzenoid hydrocarbons are aromatic is generally accepted, but we owe to Clar the enlightenment that among "equals" some are more "equal", that among aromatic benzenoids some are more aromatic than others. Clar referred to these 6n π-sextet electron systems as "fully aromatic". We will briefly examine the local aromatic properties of these, "the most aromatic aromatic compounds". In these benzenoids, the π-sextets can be distributed so that a benzene ring is represented either as an aromatic π-sextet or as an "empty" ring. The corresponding Clar's structure having n π-sextets requires a superposition of 2^n Kekulé valence structures, because each aromatic sextet is a result of superposition of two Kekulé valence structures.

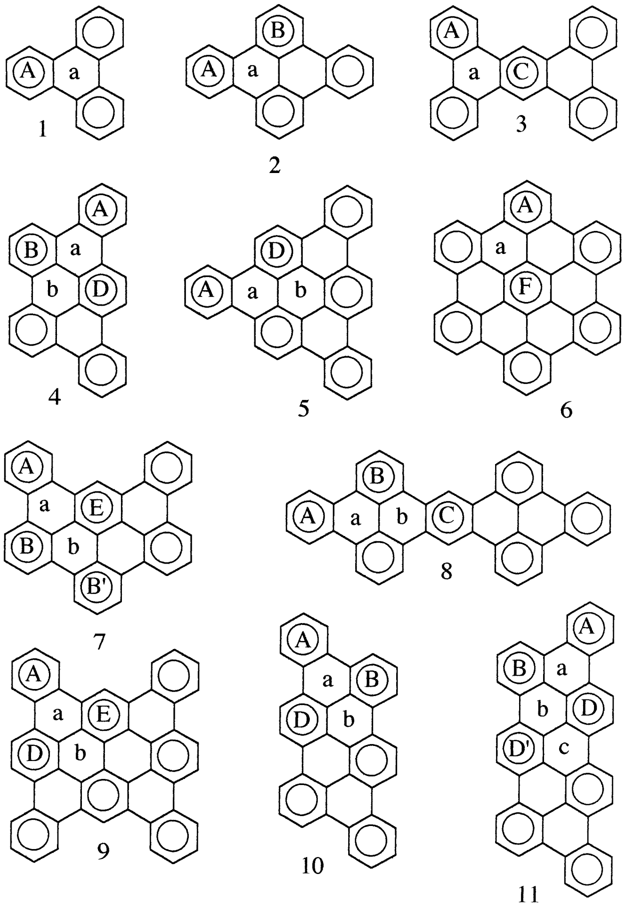


Figure 103. Clar structures for smaller fully benzenoid hydrocarbons, with symmetry-non-equivalent π-sextet rings labeled with capital letters.

A. Fully Benzenoid Hydrocarbons

In Figure 103 we show Clar structures for smaller "fully benzenoid" hydrocarbons in which we have labeled symmetry-non-equivalent π-sextet rings by capital letters and "empty" rings by small letters. In the upper part of Table 44 are the ring codes and the ring RE for the symmetry-non-equivalent rings' π-sextets listed for half a dozen of the "fully benzenoid" hydrocarbons shown in Figure 103, while in the lower part of the table are listed the codes and ring RE of the "empty" rings of the same benzenoids. As one can see from Table 44, the π-sextets at the molecular periphery have the largest ring RE, while the π-sextets situated at the inside of the molecular skeleton have the smallest ring RE. It appears that

Table 44. Ring Codes and Ring RE for π-Sextet Rings and the "Empty" Rings of Smaller Fully Benzenoid Hydrocarbons (Shown in Figure 103)

	molecule	K	ring	code	RE (eV)[a]	RE* (eV)[b]	1,1/3,1/9
			π-Sextet Rings				
1/103	triphenylene	9	A	8, 1, 0	0.758	0.800	0.926
2/103	dibenzopyrene	20	A	18, 2, 0	0.764	0.807	0.933
			B	16, 4, 0	0.712	0.744	0.867
3/103	tetrabenzanthracene	40	A	36, 4, 0	0.764	0.807	0.933
			B	32, 8, 0	0.712	0.744	0.867
4/103	tribenzoperylene	45	A	40, 5, 0	0.758	0.800	0.926
			B	36, 9, 0	0.712	0.744	0.867
			C	32, 12, 1	0.663	0.686	0.802
5/103	tribenzocoronene	103	A	90, 13, 0	0.750	0.790	0.916
			B	72, 28, 3	0.655	0.677	0.793
6/103	hexabenzocoronene	250	A	200, 50, 0	0.712	0.745	0.867
			B	128, 96, 24	0.545	0.549	0.651
7/103	tetrabenzanthanthrene	100	A	90, 10, 0	0.764	0.807	0.933
			B	80, 20, 0	0.712	0.745	0.867
			B′	80, 20, 0	0.712	0.745	0.867
			E	64, 32, 4	0.623	0.639	0.751
8/103	tetrabenzoheptacene	198	A	178, 20, 0	0.763	0.806	0.933
			B	160, 38, 0	0.716	0.750	0.872
			C	162, 36, 0	0.722	0.756	0.879
9/103	tetrabenzovalene	520	A	460, 56, 4	0.752	0.796	0.921
			D	360, 140, 20	0.684	0.672	0.786
			E	300, 168, 32	0.575	0.587	0.691
10/103	dibenzophenanthropentaphene	101	A	90, 11, 0	0.759	0.801	0.927
			B	80, 21, 0	0.708	0.740	0.861
			D	72, 27, 2	0.664	0.687	0.804
11/103	tetrabenzoterrylene	227	A	202, 25, 0	0.759	0.800	0.927
			B	180, 47, 0	0.709	0.740	0.862
			D	160, 62, 5	0.660	0.650	0.798
			D′	162, 61, 4	0.665	0.688	0.805
			"Empty" Rings				
1/103	triphenylene		a	2, 5, 1	0.362	0.341	0.420
2/103	dibenzopyrene		a	4, 6, 7	0.295	0.283	0.339
3/103	tetrabenzanthracene		a	8, 12, 12	0.289	0.278	0.333
4/103	tribenzoperylene		a	10, 14, 15	0.314	0.303	0.363
			b	8, 8, 12	0.230	0.225	0.267
5/103	tribenzocoronene		a	26, 37, 32	0.351	0.339	0.407
			b	18, 27, 48	0.277	0.263	0.314
6/103	hexabenzocoronene		a	50, 58, 41	0.252	0.248	0.296
7/103	tetrabenzanthanthrene		a	20, 28, 32	0.285	0.275	0.329
			b	20, 28, 30	0.283	0.273	0.327
8/103	tetrabenzoheptacene		a	40, 60, 69	0.297	0.285	0.342
			b	36, 54, 72	0.273	0.262	0.313
9/103	tetrabenzovalene		a	112, 156, 156	0.302	0.291	0.349
			b	112, 148, 204	0.308	0.297	0.354
10/103	dibenzophenanthropentaphene		a	22, 31, 29	0.304	0.294	0.352
			b	20, 28, 35	0.289	0.275	0.329
11/103	tetrabenzoterrylene		a	50, 70, 76	0.312	0.301	0.360
			b	44, 62, 79	0.282	0.271	0.324
			c	50, 85, 76	0.332	0.317	0.382

[a] $R_1 = 0.815$ eV, $R_2 = 0.302$ eV, $R_3 = 0.118$. [b] $R_1^* = 0.869$ eV, $R_2^* = 0.247$ eV, $R_3^* = 0.100$ eV.

minor variations in the ring RE of π-sextet rings depend on the number of CC bonds on the molecular periphery. In Figure 104 we collect the ring RE values for the π-sextets for the smaller benzenoids of Table 44 and refs 507 and 508 by grouping the results for rings in similar environments in the same column. In refs 507 and 508, a few entries were mislabeled or were in error and have been corrected here. As we can see from Figure 104, the ring RE belonging to the aromatic π-sextet is quite sensitive to the immediate ring environment. Rings with fewer peripheral CC bonds show somewhat reduced ring RE. Similar regularities have been found also for "empty" rings. The apparent constancy of the ring RE for rings in similar topological environments allows one to estimate the RE of larger "fully benzenoid" systems directly by inspecting individual ring environments, rather than following the complete analysis of their conjugated circuits.

B. Giant Benzenoids

> *Big is Beautiful.*
>
> M. D. Watson, A. Fechtenkötter,
> and K. Müllen[174]

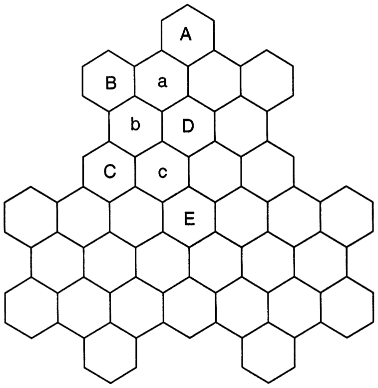
With the preparation of several extremely large polycyclic aromatic hydrocarbons derived from hexa-peri-benzocoronene, referred to as "superbenzene", Klaus Müllen and co-workers[174−177] opened a new field of chemistry: the chemistry of giant benzenoid

0.770	0.725	0.725	0.675	0.623	0.635	0.556
0.776	0.725	0.734	0.668	0.575	0.594	
0.776	0.725	0.722	0.693			
0.770	0.725		0.696			
0.763	0.727		0.671			
0.776	0.729		0.677			
0.775	0.721		0.684			
0.767	0.721		0.664			
0.771	0.712		0.660			
0.771	0.712		0.665			
0.764	0.708					
0.763	0.708					
0.752						
0.759						
0.759						

Figure 104. Summary of ring RE for π-sextets found in the smaller benzenoids shown in Figure 103.

hydrocarbons. In Figure 12 we illustrated several of the giant benzenoids described Müllen et al. Indeed, these giant benzenoids are big, are beautiful, and are exciting! First, observe that all hitherto reported giant benzenoids, the largest of which has 37 π-sextets (and 54 "empty" rings), are "fully benzenoid" hydrocarbons. As Müllen et al. report, all these hydrocarbons show unusual stability, thus fully supporting Clar's 6n π-electron rule. By having a large number of symmetry-non-equivalent rings, such systems offer insights into variations of local aromaticity with ring environment. Randić and Guo[509,700−702] examined several smaller "giants" and found, as might have been expected, that as one moves deeper into the interior of molecules, the differences between the π-sextet rings and the "empty" rings gradually decrease. The overall situation can be characterized by the word "regression", widely used in statistical analysis of data for a historical reason.[703] Hence, the interior π-sextet rings will still have a larger ring RE than the "empty" benzene rings, but not as large as the peripheral π-sextet rings. At the same time, the "empty" rings will continue to have smaller RE, but the benzene rings that are more removed from the molecular periphery will have larger ring RE than the benzene rings that are closer to the molecular periphery.

In Figure 105 we illustrate ring RE for "superphenalene", a giant benzenoid built from 34 fused benzene rings and having over half a million Kekulé valence structures.[509] In Table 45 we show the expressions for ring RE for individual benzene rings of "superphenalene". The upper part of Table 45 gives ring RE for rings carrying the π-aromatic sextet, while the lower part of the table gives ring RE for the so-called "empty" rings. We have labeled the π-sextet rings alphabetically using capital letters, starting with the ring with the highest RE, and similarly we have labeled the "empty" rings alphabetically using lowercase letters, starting with the ring having the smallest RE. As we can see from Figure 105, π-sextet rings gradually decrease their contributions to the molecular RE as we move toward the center of the molecule, while the contributions from "empty" rings increase as we move toward the center. This suggests that in the interior of graphite the distinction between π-sextet rings and "empty" rings will eventually disappear. However, judging from the differences between the aromatic π-sextet rings and the "empty" rings observed for superphenalene, the giant benzenoids so far prepared are still by far too small to suggest that we are close to approaching graphite structure in the interior parts of these molecules.



A = 0.725
B = 0.717
C = 0.603
D = 0.565
E = 0.597

a = 0.276
b = 0.271
c = 0.310

Figure 105. Variations of ring RE for the rings with π-aromatic sextets and the "empty" rings of "super-phenalene".

Table 45. Expressions for the Ring RE for Giant "Superphenalene" (Shown in Figure 105)

ring	ring RE expression
	π-Sextet Rings
A	$(432\,000R_1 + 108\,000R_2)/540\,000$
B	$(426\,000R_1 + 108\,500R_2 + 5375R_3)/540\,000$
C	$(322\,000R_1 + 171\,500R_2 + 43\,000R_3)/540\,000$
D	$(243\,000R_1 + 201\,000R_2 + R_3)/540\,000$
E	$(257\,600R_1 + 201\,600R_2 + 68\,700R_3)/540\,000$
	"Empty" Rings
a	$(109\,000R_1 + 132\,775R_2 + 146\,825R_3)/540\,000$
b	$(108\,000R_1 + 140\,200R_2 + 159\,750R_3)/540\,000$
c	$(127\,000R_1 + 139\,825R_2 + 183\,450R_3)/540\,000$

ring	ring RE expression (numerical)	ring RE (eV)[a]	ring RE* (eV)[b]
	π-Sextet Rings		
A	$0.8000R_1 + 0.2000R_2$	0.712	0.745
B	$0.7889R_1 + 0.2009R_2 + 0.0200R_3$	0.706	0.737
C	$0.5963R_1 + 0.3176R_2 + 0.0796R_3$	0.606	0.605
D	$0.4500R_1 + 0.3722R_2 + R_3$		
E	$0.4700R_1 + 0.3733R_2 + 0.1272R_3$	0.511	0.513
	"Empty" Rings		
a	$0.2019R_1 + 0.2459R_2 + 0.2719R_3$	0.269	0.263
b	$0.2000R_1 + 0.2596R_2 + 0.2958R_3$	0.287	0.268
c	$0.2352R_1 + 0.2589R_2 + 0.3397R_3$	0.310	0.302

[a] $R_1 = 0.815$ eV, $R_2 = 0.302$ eV, $R_3 = 0.118$ eV. [b] $R_1{}^* = 0.869$ eV, $R_2{}^* = 0.247$ eV, $R_3{}^* = 0.100$ eV.

As the number of Kekulé valence structures of giant benzenoids increases fast with their size and is becoming staggering, we should remember that among so many Kekulé valence structures there will be considerable variation in their importance with respect to making contributions to molecular RE. Recollect the five Kekulé structures of kekulene illustrated in Figure 65, each having a different innate degree of freedom. Hence, we should pay more attention to the hitherto not much considered "innate degree of freedom" of Kekulé valence structures. As we will see later when describing Clar's valence structures of benzenoid hydrocarbons, it follows that only Kekulé valence structures of the maximal degree of freedom are important for construction of Clar structures. For the fully benzenoid systems having n π-sextets, the number of Kekulé valence structures of the maximal degree of freedom is given by 2^n. Hence, in the case of superphenalene, of over half a million Kekulé valence structures, only 65 536 (that is, about 12%) play important roles in the representation of this giant hydrocarbon by Clar's formula.

XXIX. Clar's Aromatic Sextets

> *There is nothing more exciting than slightly unreasonable prediction.*
>
> R. Hoffmann[704]

One can view various molecular models as "predictions" of molecular structure, a theoretical prediction to be more precise. Such are Kekulé formulas for benzene, Doering's structure of bullvalene,[705,706] that was soon synthesized by Schröder and co-workers,[707,708] and Harry Kroto et al.'s spherical structure for buckminsterfullerene,[153] all exciting in their own right. Clar's aromatic sextet could be added to this class of "slightly unreasonable predictions" with the distinction that, while Kekulé's, Doering's, and Kroto's structures were recognized and immediately accepted by all chemists, Clar's model has been appreciated, enthusiastically I may add, by only a distinguished minority. So, what is so "unreasonable" about Clar's aromatic sextet that it continues not to be taken "too seriously" by so many chemists, theoretical chemists included? First, Clar speaks of partial "localization" of π-electrons, while it is fashionable to speak of total "delocalization" of π-electrons. Then Clar uses a rather simple molecular model, while fashionable molecular models are based on highly intricate numerical characterization, on molecular orbitals calculated often using double-digit precision. In addition, Clar's model is of empirical origin and lacks apparent theoretical (mathematical) formulation, which in the eyes (incorrectly) of some reduces the merits of the model. While one can understand, on one hand, that the reasons listed above may have contributed to the relative obscurity of Clar's model in some circles, on the other hand one cannot understand why Clar's $6n$ π-electron rule and Clar's postulate, that structures for which one cannot draw Kekulé valence structures cannot exist, have not attracted due attention, particularly from theoretical circles.

Be that as it may, in this section we will first outline Clar's approach to benzenoid hydrocarbons and then offer a theoretical basis for Clar's model. Finally we will show that Clar's model can be fully justified by quantum chemical calculations.

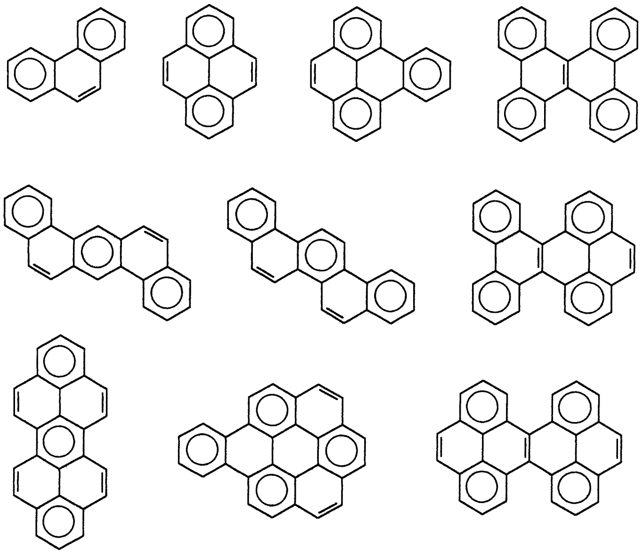


Figure 106. Smaller benzenoid hydrocarbons having a single Clar structure.

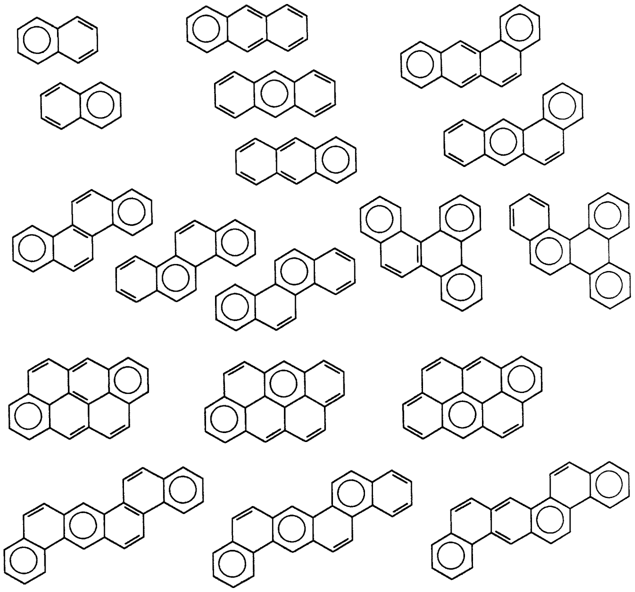


Figure 107. Smaller benzenoid hydrocarbons having several Clar valence structures.

A. Geometrical Definition of Clar's Valence Formulas

Clar's valence formulas, illustrated in Figures 103, 106, and 107 on a selection of smaller benzenoids, can be described as formulas in which π-electrons, whenever possible, tend to be localized in π-sextets within a single benzene ring. The lovely booklet by Clar,[49] *The Aromatic Sextet*, offers numerous arguments and numerous illustrations of valence structures with localized π-sextets and the "migrating" π-sextets. One can define Clar's valence structure of a benzenoid as follows:

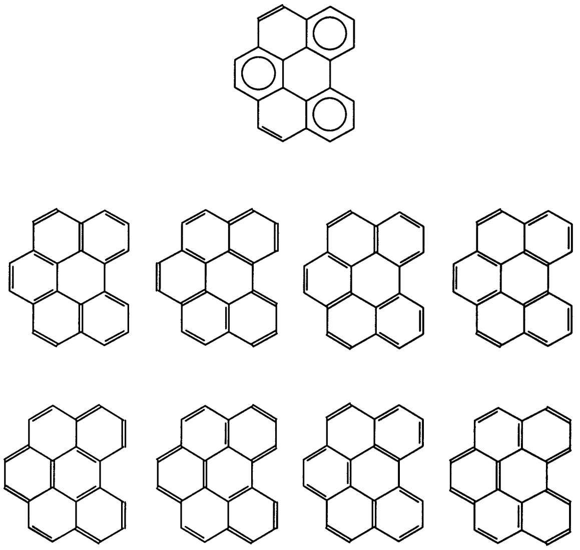


Figure 108. The eight Kekulé structures of dibenzo[*ghi*]perylene that define its Clar structure.

Definition: *Inscribe in non-adjacent benzene rings of a polycyclic benzenoid hydrocarbon the maximal number of circles (π-sextets) so that for bonds not involved in π-sextets one can complete the Kekulé valence structure.*

We may refer to this definition as "geometrical", in view of the fact that the rules allow one to draw Clar's structures on a piece of paper. In Figure 103 we have shown benzenoids with only π-sextet or "empty" rings, the benzenoids that have been referred to by Clar as "fully benzenoid" structures, and can also be called "the most aromatic aromatic compounds". In Figure 106 we show benzenoids which also have only a single Clar structure. However, in this case, in addition to the π-sextet rings and the "empty" rings, there may appear rings with a single "fixed" CC double bond. Finally, in Figure 107 we illustrate several smaller benzenoids for which one cannot draw a unique Clar structure. In order to fully represent such benzenoids, one has to draw two or more Clar's valence structures. The resultant Clar structure for these compounds should be viewed as a superposition of all possible Clar's structures. The consequence is the occurrence of "migrating" π-sextets, as Clar referred to π-sextets that are delocalized over several benzene rings, depicted by arrows that overlap several adjacent rings.

The above "geometric" definition of Clar structures suffices for construction of Clar structures for any benzenoid. So why would we need an alternative definition of Clar structures? In order to answer this and justify a search for an alternative definition of Clar structures, we have to recognize that any Clar structure can be readily decomposed into a subset of Kekulé valence structures. This is illustrated in Figure 108 again on benzo[*ghi*]perylene, which has three π-sextets. Each π-sextet in benzo[*ghi*]perylene results from a superposition of two benzene Kekulé formulas in which, except for the ring considered, all the remaining CC double bonds are in the same locations. Hence, the Clar structure of benzo[*ghi*]perylene can be obtained by the superposition of eight Kekulé formulas of benzo[*ghi*]perylene. The opposite problem, that of determining in advance which eight Kekulé structures of the possible 14 Kekulé structures contribute to the Clar structure of benzo[*ghi*]perylene, is of considerable interest and apparently was not solved until very recently. The problem asks for *characterization* of those Kekulé valence formulas that lead to Clar's structure. Looking at Figure 108, one can ask why these particular eight Kekulé structures of benzo[*ghi*]perylene make the Clar structure and not any of the remaining six structures of the 14 Kekulé valence structures. What makes these eight Kekulé structures of benzo[*ghi*]perylene more important than the others?

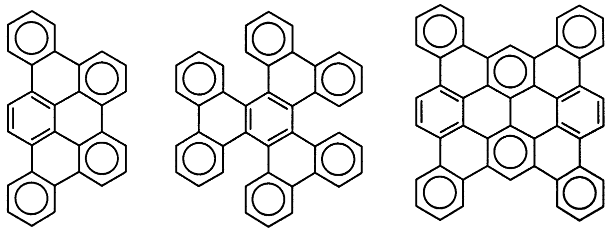


Figure 109. Valence structures that look almost like Clar structures (except for one or two rings), obtained by the minimax procedure based on Pauling bond orders.

To answer these questions, we have to solve the "inverse Clar problem". As just mentioned, the "inverse problem" of Clar's structure asks one to characterize those Kekulé valence structures that contribute to Clar's structure. If this could be solved, one would be in a position to select the Kekulé structures that make a contribution in advance — and not only after first drawing Clar's structures, as we did in Figure 108 for benzo[*ghi*]perylene. Partial progress toward solving the inverse problem was reported in 1990, when Kekulé valence structures were given weights determined by the smallest Pauling bond order for any of the CC double bonds appearing in the Kekulé structure.[207,709,710] For many smaller benzenoids, when one superimposes Kekulé valence structures having the maximal weight, one obtains their Clar structures. However, this is not the case with benzo[*ghi*]perylene. It is not difficult to see that the smallest Pauling bond order involving the 11 CC double bonds of benzo[*ghi*]perylene for four Kekulé structures in the top row equals 5/14, while for the four Kekulé structures in the bottom row it is 4/14. If we superimpose only Kekulé structures of the maximal weight, we do not get in the case of benzo[*ghi*]perylene the Clar structure. Besides benzo[*ghi*]perylene, in a few additional cases (illustrated in Figure 109) the resulting valence structures obtained by superposition of Kekulé valence structures of the maximal Pauling weights look "almost" like Clar structures, except for one or two rings, which instead of having π-sextets have "fixed" CC single and CC double bonds. Clearly, this ad hoc procedure that leads to Clar's structures for many benzenoid hydrocarbons leads in the right direction — but not always to the correct answer. Something was still missing in our characterization of Kekulé structures that yield the Clar structures!

B. Mathematical Definition of Clar's Valence Formulas

> *The first impulse towards a revision and a reconstruction of a physical theory is nearly always given by a discovery of one or more facts which cannot be fitted into the existing theory ... But it is often very difficult and complicated question to decide in what part of the theory the improvement has to be made.*
>
> Max Planck[674]

To solve the inverse problem of Clar structures we have to find, among the structural features, the "key" that characterizes a subset of Kekulé valence structures. Clearly, we need some criteria that will eliminate some Kekulé structures from consideration while retaining others. Using the weights based on the Pauling bond orders seemed a good idea — but it did not work in all cases. In science, apparently just having a "good idea" is not enough. In a later section of this review we will mention other "good" ideas, those of the "parity of Kekulé valence structures", and the "algebraic structure count", that despite being attractive have also been shown to have serious limitations. The idea of the parity of Kekulé structures was introduced in the early days of the VB theory by Dewar and Longuet-Higgins.[474] It gave good results in some applications but not in others. The same was true with the algebraic structure count used on biphenylene derivatives, in which by following some rules one associates positive and negative numbers with valence structures. In such situations, often it is best to abandon these approaches and try with a new start.

Obviously, some ideas and models may lead to "good results", while others lead to a "dead end". Sometimes a "good idea" that has been proposed in relation to a particular problem may be recognized as being important in problems that are apparently unrelated. This is what happened with solving the inverse problem of Clar's structures. We have already outlined the "innate degree of freedom" of Kekulé valence structures, a "good idea" that had limited application.[217,218] However, if we superimpose Kekulé valence structures of *the maximal innate degree of freedom*, we may be surprised that we always obtain the Clar structure for the benzenoid considered. Hence, we have the following mathematical definition for Clar structures:[86,87]

Definition: *The Clar structure of a benzenoid hydrocarbon is given by a superposition of Kekulé valence structures of the maximal degree of freedom.*

In practical terms, the geometrical approach to construction of Clar's structures is clearly simple enough and simpler than drawing all Kekulé valence structures of a benzenoid and investigating their degrees of freedom. However, when it comes to computer manipulations of Kekulé valence structures, the mathematical definition has some advantages. We should add that by solving the inverse problem we obtained an insight into the structural factors that play a role in Clar's model of benzenoid hydrocarbons. Most importantly, however, is that now, with a mathematical definition of Clar structures, we can *extend the concept of Clar π-sextets to non-benzenoid hydrocarbons, including fullerenes*, which was until now not possible.

XXX. Quantum Chemical Justification for Clar's Structures

By having a "mathematical" definition of Clar's formulas, we can appreciate the intuition of Clar, who had no theoretical basis for justifying his valence structures. Clar knew nothing of the innate degrees of freedom of Kekulé valence structures, yet he arrived at a description of benzenoids in which the innate degrees of freedom of Kekulé valence structures play the dominant role! Clar's intuitive approach may have agitated skeptics who continued to be reserved, and possibly "alarmed" critics that, in this age of quantum chemistry, some "amateurs" look the other way and seek truth, apparently disregarding the "deep" truth of quantum theory. But one should be reminded here of a statement recorded by Werner Heisenberg, attributed to Niels Bohr:[711]

> *If you have a correct statement, then the opposite of a correct statement is of course an incorrect statement, a wrong statement. But when you have a deep truth, then the opposite of the deep truth may again be deep truth.*

Hence, one should differentiate the fact that the approach of Clar apparently lacks a tangible connection to quantum chemistry from assumptions that it contradicts quantum chemistry — as it does not!

One could turn the question around and ask why the believers in the "ultimate theory" should totally ignore facts, the empirical approaches such as Clar's approach. The experimental arguments that support Clar's model were outlined, besides in the research of Clar,[49,50] by Zander,[712] Voigtländer and co-workers,[713−715] Glidewell and Lloyd,[580,581] and others.[716−718] Anyway, now that we found the missing link between Clar's formulas and the corresponding graph theoretical model, a quantum chemical justification of Clar's approach is possible. The approach to be shortly outlined can be viewed as a "reversal" of the pioneering approach of Polansky and Derflinger,[582] who interpreted quantum chemical results (HMO calculations on benzenoids) in terms of graph theoretical concepts (like partitioning of MO's into ring components), which in itself can be viewed as a quantum chemical justification of Clar's formulas. Now just the opposite will be the case: The well-established graph theoretical scheme of local aromaticity characterization will be interpreted in terms of quantum chemical quantities.

In order to see if Clar structures have quantum chemical justification, we will make a careful analysis of the benzenoids depicted in Figure 110, where in the case that there are several Clar structures, only one was shown. In particular, we will make a comparison between characterizations of various benzene rings of these structures as suggested by their Clar structures and as based on quantum chemically computed contributions of their rings to

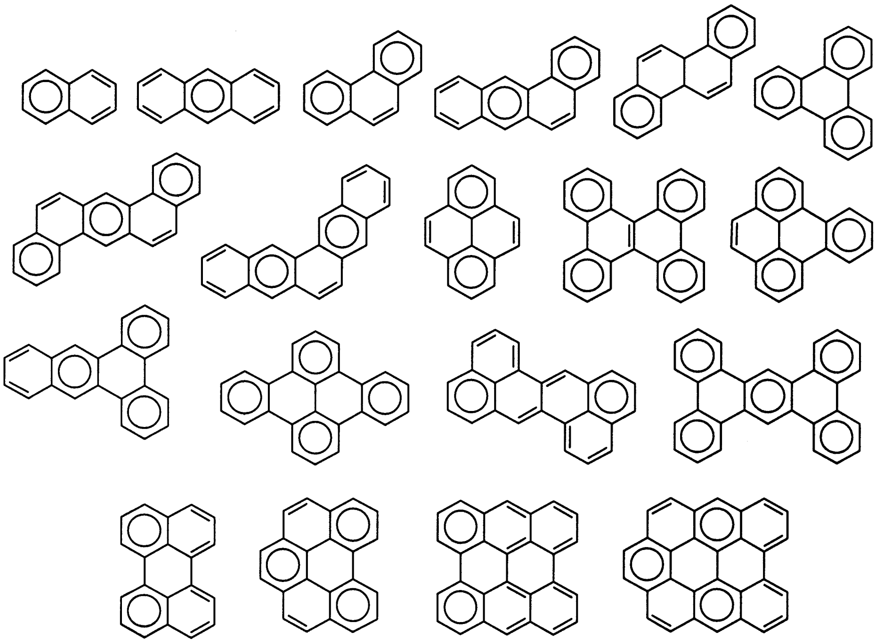


Figure 110. Smaller benzenoids selected for comparison of ring RE. (In cases of molecules having more than one Clar structure, only one Clar structure is shown.)

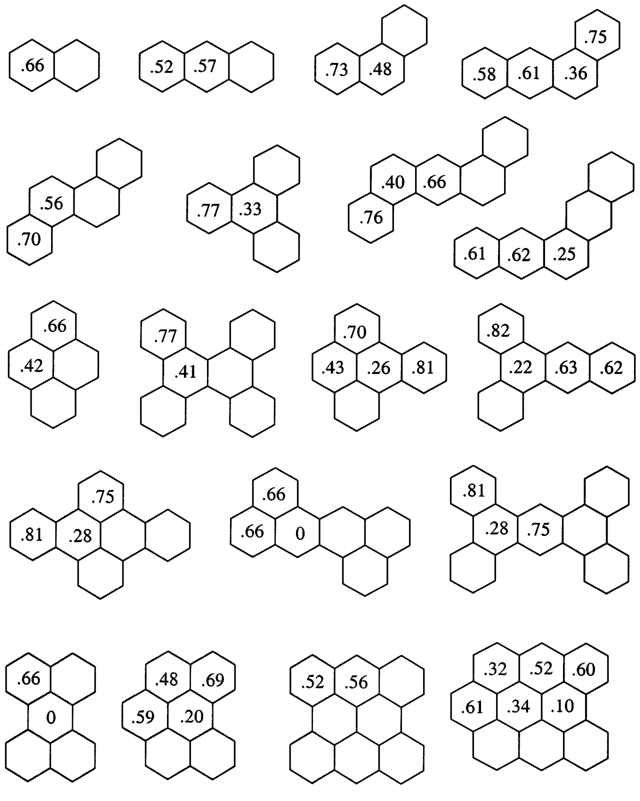


Figure 111. Quantum-chemically computed ring contributions to molecular RE for the smaller benzenoids shown in Figure 110.

the molecular RE. We gave in Figure 96 the graph theoretical ring indices for these benzenoids. In Figure 111 we show quantum chemically evaluated ring RE contributions to the molecular resonance energy RE for the same set of benzenoids. If we can find a strong correlation between the numbers in Figure 96, which are of graph theoretical origin, and the numbers in Figure 111, which are of quantum chemical origin, we would establish the missing connection between Clar's π-model and quantum chemistry, even though regression between quantities does not imply a causal relationship.

The ring RE is determined by multiplying the ring codes by R_1, R_2, and R_3 in their RE expressions, i.e., by 0.815, 0.302, and 0.118 eV, respectively. Recall that these numbers represent the contribution of conjugated circuits of different size to the molecular RE, as based on SCF MO parametrization of R_1, R_2, and R_3. The ring numbers of Figure 111 can be viewed as quantum chemically derived quantities that have "nothing to do" neither with Kekulé valence structures nor with Clar valence structures, because they merely represent a *partitioning* of a computed molecular property, RE, to molecular components, here taken to be fragments representing individual benzene rings. One could, if one so desires, partition RE into components, which could be individual Kekulé valence formulas, in which case one would obtain some indication of the relative importance of an individual Kekulé valence structure according to RE calculations. In fact, most earlier calculations of the molecular RE via conjugated circuits were completed by calculating the contributions of the individual Kekulé valence structures, which is very practical if the number of Kekulé structures is not excessive.

Let us now consider the numerical Clar valence structures shown in Figure 96, in which the reported ring indices result from a pure graph theoretical analysis, counting the occurrence of Kekulé benzene rings in a particular location in a molecule. One can characterize this activity as something that has "nothing to do" with the quantum chemistry or the quantum mechanics. When indices derived in this way (that are normalized to the number of Kekulé valence structure) are plotted against the ring RE, we obtain the correlation shown in Figure 112. Support for our claim that quantum chemically

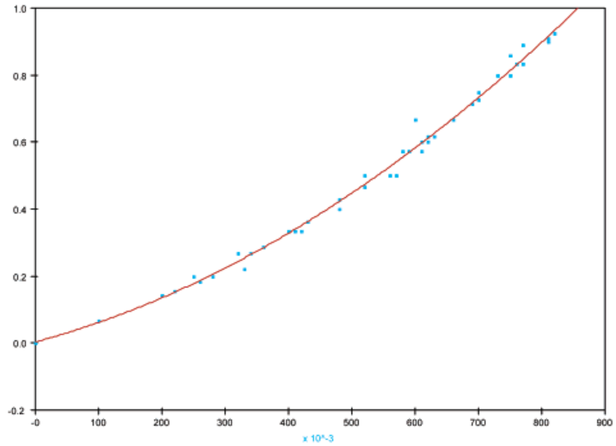


Figure 112. Plot of the graph theoretical ring RE and the quantum chemical ring RE for the benzenoids shown in Figure 110.

computed RE values support Clar's structures follows from Figure 112, in which we show a correlation between the two sets of indices for which there was no a priori rationale to expect correlation, the least strong correlation. The correlation between the two sets of rings supports Clar's qualitative representation of benzenoid hydrocarbons by π-electron sextets. Skeptics may not be willing to accept our arguments on two counts: (1) We did not perform any quantum chemical calculations, but rather based our partitioning of molecular RE on parameters of the calculations of Dewar and de Llano.[39] (2) We have not offered any *rigorous* mathematical justification for the validity of Clar structures, but "only" established correlation using statistical analysis. It is well known that a correlation, even of very high quality, does not necessarily imply a cause−effect relationship; that is, it has no connotation of "causality".

Concerning the first point, recall that the values chosen for R_1, R_2, and R_3 are of quantum chemical origin. One can, just as Herndon did in his resonance theory,[164] define these quantities as quantum chemical interaction integrals, which can be computed if necessary. The resonance theory of Herndon, just as conjugated circuits calculations, represents mathematical models, except that one is cast in the terminology of quantum chemistry and the other in the terminology of graph theory. Herndon,[540] along with Schaad and Hess,[541] was first to point out that, under certain conditions, the two models are mathematically fully equivalent. They differ in the conceptual frame and the computational procedures, particularly when it comes to calculations on large systems. Let us clarify this on buckminsterfullerene, C_{60}, which has 12 500 Kekulé valence structures.[155]

According to Klein and co-workers,[481] one can enumerate not only the Kekulé valence structures but also conjugated circuits of different size using the transfer matrix approach[481−486] (briefly mentioned in the introductory part of this review). In the case of C_{60}, the expression for the RE is[155]

$$\mathrm{RE} = (83\,160\ R_1 + 59\,760\ R_2 + 44\,760\ R_3 + 50\,880\ Q_3)/12\,500$$

or

$$\mathrm{RE} = 6.6528R_1 + 4.7808R_2 + 3.5808R_3 + 4.0704Q_3$$

Assuming that the contributions from R_3 and Q_3 approximately cancel each other, we obtain an estimate for the RE of buckminsterfullerene of 6.866 eV, or 0.114 REPE. This is comparable with the values for many conjugated hydrocarbons.

More serious appears the objection of skeptics concerning the lack of a causal relationship between Clar structures and quantum chemistry. According to one reviewer:

> *I read this section with much interest, but it is a shame that, in the end, the "missing connection" in the Clar idea, that Professor Randić refers to, turn out to be just a statistical correlation, rather than something that displays a necessary causative connection. I thus found the argument for Clar's idea to be disappointingly qualitative — I should like to see a nice, rigorous mathematical justification.*

Well, I could start with the reply, *I would also like to see a nice, rigorous mathematical justification.* However, rigorous mathematical justifications can be put forward to prove *equivalence* of apparently dissimilar theories or models, as was the case with the early matrix mechanics described by Heisenberg and the wave mechanics of Schrödinger, or on a much smaller scale, the case of Herndon's resonance theory and the conjugated circuits model described by this author. We also mentioned earlier the *equivalence* of the spectral theory of graphs and the Hückel Molecular orbital method, the importance of which turned out to be in part the main cause for the prolonged confusion of the chemical graph theory with the HMO method that persisted for quite a time. But we are here addressing a different issue, the issue of *representation* of molecular structure. Molecules can be represented in very many different ways, each having some advantage for a particular use. In particular, we have been concerned with Clar's representations of benzenoid hydrocarbons and were exploring their use for describing molecules and their properties. Formally, Clar structures are purely notational devices that may turn out to be useful, awkward, useless, unnecessary, misleading, etc. What we have tried to show is not only that Clar structures are a useful notational novelty (if one can speak of something over 75 years old as a novelty!), but also that they are more than a notational device.

That selection of a notation is of greater importance in science than some may think is well illustrated by the history of the origin of calculus. It is generally believed that Newton and Leibniz independently developed calculus. Apparently, after the deaths of Newton and Leibniz, the followers of Newton in England and the followers of Leibniz in continental Europe were bitterly engaged in the "dispute" over the priority in the discovery of calculus. It has been said that England was behind in the development of calculus by about 100 years. This can be attributed in part to a lack of flexibility of the notation used by Newton as compared with the notation developed by Leibniz. English mathematicians favored Newton and followed Newton's notation, while in continental Europe mathematicians followed Leibniz notation, which was superior. Leibniz's notation was "operational"; that is, it allowed one to separate the sign for derivative df/dx into df, dx, d/dx, etc., each of which has its own meaning. Incidentally, it was the English mathematician Cayley, who made the first enumeration in graph theory followed by enumeration of chemical isomers in 1875, who is responsible for "resurrecting" Leibniz's notation in English mathematical circles.

Over the years, Clar's structures could have been found inadequate, improper, fallacious, etc. — but they were not. Now, suppose that at the end of our comparison of the numerically represented Clar structures and quantum chemically computed ring RE we found no correlation at all, the two set of ring indices not being correlated at all — we would then have to conclude that Clar's notion of π-aromatic sextets is not sound! This would be a valid conclusion because partitioning of RE into ring contributions is a legitimate computational process — and hence ring RE values are valid structural descriptors (like bond orders and such, that are generally accepted). That would be the end of Clar — but as we can see from Figure 112, the outcome of the partitioning of the quantum chemically computed RE parallels the expectations that Clar structures suggest! Hence, this is a new beginning for Clar structures, if I may say so — not an end.

As is well known, statistics can be used and misused, and not used! Arguments that statistics is less reliable, not causative, and such may turn some away. That some scientists have reservations about arguments based on statistics is well reflected in the quotation from Ernest Rutherford (1871–1937): *"If your experiment needs statistics, you ought to have done a better experiment."* But for us the choice is not to do an experiment or not to do one, but to use statistics or not to use them. Without statistics our arguments would be *qualitative*; with statistics they become *quantitative*. The correlation between the ring RE and the graph theoretical descriptor R_1/K, illustrated in Figure 112, is characterized by the following statistical parameters:

$$r = 0.9961; \quad s = 0.019; \quad F = 4883$$

where r is the correlation coefficient, s the standard error, and F the Fisher ratio. The regression is of such good quality that it allows one not only to compute ring RE and total RE with sufficient accuracy, but also to make such computations "on the back of an envelope". Instead, to consider all Kekulé valence structures and count all conjugated circuits, it suffices to examine the Clar structure and assign to its ring corresponding fractions that give the frequency of Kekulé benzene rings in different locations. Computations "on the back of an envelope" in themselves are of no such importance today as they would have been in the time of Clar, but more important is the fact that such "on the back of an envelope" calculations often give better *insights* into the underlying structural features of the model which are lost or never attained in piles and piles of numerical data that fast computers generate. In order to see the advantage of modeling, we will address in the next section some questions relating to analysis of data in general and RE of benzenoid hydrocarbons in particular.

XXXI. On Interpretation of Molecular Resonance Energy

As has already been said more than once, graph theory does not give, on its own, any molecular property — it needs input either from experiments or from theoretical computations. Data obtained in this way could then indicate numerical values for the parameters used, like here the relative contributions of the conjugated circuits R_1, R_2, and R_3. Hence, the question is not whether we should calculate RE by advanced quantum chemical methods or by relatively simple graph theoretical schemes. When it comes to molecular RE, clearly ab initio MO theory and accurate VB theory can obtain the necessary numerical results. However, neither MO nor VB theory can tell us why benzo[*a*]pentaphene has larger RE than dibenzo[*a*,*c*]naphthacene, both of which have the same number of Kekulé valence structures, or why benzo[*i*]pentahelicene and dibenzo[*f*,*k*]tetraphene both have the same RE? Clar's model and the conjugated circuits expressions for RE here give answers that clearly cannot be obtained without resorting to concepts that are outside quantum chemistry.

For the most part, much of the debate in the past between MO and VB theories versus graph theory has illustrated *misconceptions* about chemical graph theory. The two theoretical methodologies, quantum chemical and graph theoretical, consider somewhat different questions or different aspects of the same problem and are thus *complementary* to one another rather than competitive. So while MO and VB theories are, and will remain, about "the nature of the chemical bond", we can say that Clar's model and chemical graph theory are, and will remain, about "the nature of the chemical structure". Clearly, we need both the quantum chemical tool and the graph theoretical ideas to be combined in order to advance our understanding of complex chemical systems.

XXXII. Other Points

> *It is unusual for only one model to be compatible with experimental observations. Often data are not sufficiently extensive to discriminate among rival models and new experiments must be designed to answer the outstanding questions. The statistical, graph theoretical, and sensitivity analysis methods ... can identify the areas for further investigation that are likely to produce significant new results.*
>
> M. C. Kohn[719]

In this section we will first revisit benzenoid hydrocarbons and examine the possibility of discriminating between various Kekulé valence structures.

Table 46. Expressions for RE for the Smaller Benzenoids (Shown in Figure 53) Based Solely on Kekulé Structures of the Maximal *df*[a]

molecule	RE expression based on maximal df	RE	difference	
1/53	$(2R_1)/2$	0.3376	−0.0341	*
2/53	$(4R_1 + 2R_2)/3$	0.4791	−0.0272	*
3/53	$(6R_1 + 4R_2 + 2R_3)/4$	0.6037	−0.0272	*
4/53	$(9R_1 + 2R_2 + R_3)/4$	0.6678	−0.0275	
5/53	$(8R_1 + 6R_2 + 4R_3 + 2R_4)/5$	0.6784	0.0199	*
6/53	$(15R_1 + 6R_2 + 2R_3 + R_4)/6$	0.7829	−0.0066	
7/53	$(20R_1 + 10R_2 + 2R_3)/8$	0.8023	0.0145	*
8/53	$(25R_1 + 3R_2 + 3R_3 + R_4)/8$	0.8395	0.0154	*
9/53	$(10R_1 + 4R_2 + 2R_3)/4$	0.8008	−0.0771	
10/53	$(10R_1 + 8R_2 + 6R_3 + 4R_4 + 2R_5)/6$	0.7283	0.0924	*
11/53	$(21R_1 + 10R_2 + 6R_3 + 2R_4)/8$	0.8808	0.0202	
12/53	$(25R_1 + 14R_2 + 3R_3)/9$	0.9008	0.0149	
13/53	$(28R_1 + 8R_2 + 4R_3)/8$	0.9980	−0.0257	
14/53	$(30R_1 + 18R_2 + 6R_3 + R_4)/11$	0.9229	0.0300	
15/53	$(28R_1 + 10R_2 + 2R_3)/8$	0.9995	0.0009	
16/53	$(41R_1 + 12R_2 + 3R_3 + 4R_4)/12$	0.9546	0.0434	
17/53	$(42R_1 + 13R_2 + 4R_3 + R_4)/13$	0.9242	0.1000	
18/53	$(27R_1 + 7R_2 + 5R_3 + R_4)/8$	0.9726	−0.0325	
19/53	$(21R_1 + 11R_2 + 5R_3 + 3R_4)/8$	0.8816	0.0074	
20/53	$(36R_1 + 24R_2 + 14R_3)/13$	1.0122	0.0397	*
21/53	$(22R_1 + 14R_2 + 9R_3 + 3R_4)/8$	1.0027	−0.0389	
22/53	$(29R_1 + 11R_2 + 7R_3 + R_4)/8$	1.1057	−0.0588	
23/53	$(70R_1 + 14R_2 + 12R_3)/16$	1.1832	0.0421	
24/53	$(48R_1 + 28R_2 + 11R_3 + R_4)/13$	1.2044	−0.0173	
25/53	$(68R_1 + 12R_2 + 12R_3 + 4R_4)/16$	1.1444	0.0116	
26/53	$(168R_1 + 24R_2 + 24R_3 + 8R_4)/32$	1.2044	−0.0173	
27/53	$(32R_1 + 16R_2 + 8R_3)/8$	1.2641	−0.0795	
28/53	$(88R_1 + 21R_2 + 19R_3)/16$	n/a[b]		
29/53	$(48R_1 + 32R_2 + 16R_3)/16$	outlier		*
30/53	$(85R_1 + 54R_2 + 32R_3 + 12R_4 + 4R_5)/21$	n/a		

[a] Asterisk indicates cases in which all Kekulé structures have the maximal df. [b] n/a = not available.

Although, as we will see, discrimination between contributing Kekulé valence structures will produce alternative quantitative characterization of molecules, it does not result in a dramatic change of the picture of benzenoid hydrocarbons. Extension of such considerations to biphenylene and closely related [n]-phenylenes, however, as we will see, has a more dramatic effect. What we propose to do is to exclude from considerations as “undesirable” Kekulé valence structures of a lesser degree of freedom. We will find then that the bent [n]phenylenes became stable, in agreement with their successful experimental syntheses. We will also re-examine the concept of superaromaticity, evoked by Clar, and will see, following the arguments of Aihara, that notion of superaromaticity, though it may look attractive, is not valid. The findings of Aihara agree fully with the model of conjugated circuits, which also does not support such a notion. We will then outline generalizations of Clar structures as pioneered by Hosoya, Herndon, and their collaborators. Finally, we will very briefly refer to the aromaticity of fullerenes, particularly from the point of view of the conjugated circuits model. A more detailed account of the valence bond view of fullerene can be found in a chapter by Schmalz[720] in the recent book on VB theory, and in papers by Schmalz, Klein, and Lui.[721,722] We will end with a description of the Clar structures of buckminsterfullerene.

A. Benzenoid Hydrocarbons Revisited

> *How often have I said to you that when you have eliminated the impossible, whatever remains, however improbable, must be the truth?*
>
> Conan Doyle[723]

We will only briefly outline the characterization of benzenoid hydrocarbons when we restrict attention solely to Kekulé valence structures of the highest degree of freedom. This is tantamount to describing benzenoid hydrocarbons only by Clar structures. In Table 46 we have collected the expressions for RE for smaller benzenoids based solely on Kekulé structures of the maximal df. In the last column of Table 46, we have indicated by an asterisk the compounds for which all Kekulé valence structures have the same df— hence, benzenoids for which the expression for RE has not changed when comparison is made with similar expressions for RE in Table 15 based on the use of all Kekulé valence structures. These cases include all acenes (linearly fused benzenoids like naphthalene, anthracene, tetracene, etc., with $df = 1$) as well as all even-ring fibonaccenes (chrysene, fulminene, etc., with $df = 2$). In passing, let us mention that the label “fibonaccenes” for families of benzenoid hydrocarbons for which K_{n+1} is given by $K_n + K_{n-1}$, where subscripts n+1, n, and $n-1$ relate to successive members of the family, each having one benzene ring less, apparently appeared for the first time in the mathematical literature![724]

In order to obtain a novel numerical value for RE based only on Kekulé structures of maximal *df*, we have to reparametrize the values for R_1, R_2, and R_3. The least-squares linear multi-regression yields (in units of *J*):

$$R_1 = 0.1972 \qquad R_2 = 0.1137 \qquad R_3 = 0.1077$$

with the statistical parameters $r = 0.9803$, $s = 0.047$, and $F = 180$ (where *r* is the coefficient of regression, *s* the standard error, and *F* the Fisher ratio). The above can be compared to the corresponding parameters obtained when all Kekulé valence structures are considered:

$$R_1 = 0.2277 \qquad R_2 = 0.0841 \qquad R_3 = 0.1497$$

with the statistical parameters $r = 0.9939$, $s = 0.026$, and $F = 599$. As we can see, the regression based on RE expressions using all Kekulé valence structures gives better statistical parameters. However, at the same time, the regression based on RE expressions using only Kekulé valence structures of the highest degree of freedom is similarly accompanied by satisfactory statistical parameters. In order to choose between the two, we have to consider additional factors. Observe that the relative magnitudes of the conjugated circuits contributions, R_1 and R_2, have not changed dramatically between the two alternative approaches for determining the contributions of conjugated circuits of different size, but the value of R_3 decreased from 0.1497 to 0.1077 *J* when only Kekulé structures of the maximal degree of freedom were used. This is very desirable, because within the conjugated circuits models the contributions of R_3 ought to be smaller than those of R_2.

That R_3 is now smaller than R_2 is an important result. Unexpectedly, we may view this result as an independent *argument* in favor of Clar's model for benzenoid hydrocarbons. Recall that the condition $R_1 > R_2 > R_3$ was evoked as a test of the internal consistency of various semi-empirical quantum chemical calculations. Here we use the same arguments not to discredit the VB calculations of Jiang and Li, which we assumed to be correct, but rather to discredit an assumption that *all* the Kekulé valence structures within a molecule play equally important roles. When we assume that only Kekulé structures of the highest degree of freedom are relevant for calculation of the molecular RE, which is tantamount to assuming Clar's aromatic π-sextet model for benzenoid hydrocarbons, we see that we do satisfy the condition $R_1 > R_2 > R_3$, which is not the case when R_1, R_2, and R_3 were obtained by using all Kekulé valence structures.

The "revised" expressions for RE have in the denominator an effective K^*, the number of Kekulé valence structures that contribute to Clar structures. Benzenoid hydrocarbons having a single Clar structure necessarily have $K = 2, 4, 8, 16, 32$, etc., while if $K^* \neq 2^k$ ($k = 1, 2, 3, ...$) we have benzenoid hydrocarbons with a migrating π-aromatic sextet. We have listed in Table 46 the revised graph theoretical RE values (in units of the exchange integral *J*) and the difference between the graph theoretical values and the quantum chemically calculated values. As we can see the agreement between the quantum chemical calculations and the graph theoretical ones is quite satisfactory, except for bisanthene (**29/53**). For that reason bisanthene was excluded as an outlier and its RE was not used in the calculation of R_1, R_2 and R_3 so that it does not influence numerical values for parameters of R_1, R_2 and R_3 to be used for other molecules. For bisanthene Jiang and Li calculated RE as 1.2445 *J*, which is about 0.10 *J* above the value of two molecules of anthracene RE (1.1530 *J*). Because the central rings in bisanthene have essentially single CC bonds the central rings do not participate in delocalization of π-electrons, just as is the case with the central ring in perylene. In the case of perylene Jiang and Li obtained for RE 0.8920 *J*, which is very close to the value for two molecules of naphthalene (0.9037 *J*). So apparently bisanthene does not parallel the expectation that its RE is approximately twice of that of anthracene. This may be some artifacts of the calculations of RE, such as caused by selection of the reference molecule or some numerical error.

We should have mentioned that the multi-linear regressions cited above are associated with a relatively sizable constant term, which was 0.1404 and 0.0946 *J* for the Clar model and the model using all Kekulé valence structures, respectively. The constant terms of a regression affect the origin on the RE energy scale. If we force the constants to be zero instead of the already listed R_1, R_2, and R_3 parameters, we obtain the following (in units of *J*):

$$R_1 = 0.2304 \qquad R_2 = 0.1499 \qquad R_3 = 0.0982$$

(with $r = 0.9647$, $s = 0.063$, and $F = 98$) when only Kekulé structures of the maximal *df* are used. These are to be compared to the parameters obtained when all Kekulé valence structures are used:

$$R_1 = 0.2544 \qquad R_2 = 0.1033 \qquad R_3 = 0.1459$$

(with $r = 0.9875$, $s = 0.038$, and $F = 288$). Again, the statistical parameters are somewhat better when all Kekulé valence structures are considered in the evaluation of RE, but unacceptable values for the relative magnitude of R_2 and R_3 are obtained. In contrast, when we limit the calculation of RE to the Kekulé valence structures of the maximum degree of freedom, as we can see, the relative values for contributions of 6-member, 10-member, and 14-member conjugated circuits are even somewhat "improved" (making R_3 appreciably smaller than R_2.

In Table 47 we have collected RE and REPE values obtained by the ambitious VB calculations of Wu and Jiang,[38] and those of Alexander and Schmalz,[39] to be compared to the RE values calculated by the simple Hückel MO method. Both VB calculations used the graphical unitary group technique that have produced highly efficient methods for ab initio calculations, the so-called graphical unitary group approach (GUGA), in which only the non-zero matrix elements are computed.[182−190,725,726] One should recall that the

Table 47. RE and REPE Values Calculated by Ambitious VB Calculations of Wu and Jiang,[38] and Alexander and Schmalz,[39] Compared to Hückel MO RE and REPE

	Wu and Jiang		Alexander and Schmalz		HMO	
molecule	RE	REPE	RE	REPE	RE	REPE
1/53	0.304	0.0507	1.1055	0.1843	2.0000	0.3333
2/43	0.452	0.0452	2.0399	0.2040	3.6832	0.3683
3/53	0.577	0.0412	2.9505	0.2108	5.3137	0.3796
4/53	0.641	0.0458	3.0255	0.2159	5.4483	0.3892
5/53	0.699	0.0388	3.8582	0.2143	6.9308	0.3850
6/53	0.777	0.0432	3.9445	0.2191	7.1013	0.3945
7/53	0.817	0.0454	3.9931	0.2218	7.1875	0.3993
8/53	0.855	0.0475	4.0394	0.2244	7.2745	0.4041
9/53	0.724	0.0453	3.6326	0.2270	6.5055	0.4066
10/53	0.821	0.0373	4.7665	0.2167	8.5440	0.3884
15/53	1.001	0.0455	4.9708	0.2259	8.9432	0.4065
18/53	0.941	0.0471	4.6513	0.2326	8.3361	0.4168
19/53	0.899	0.0450	4.5920	0.2296	8.2220	0.4111
21/53	0.964	0.0438	5.1935	0.2361	9.2529	0.4206
22/53	1.047	0.0476	5.2848	0.2402	9.4251	0.4284
24/53	–	–	5.9510	0.2480	10.5718	0.4405
25/53	1.156	0.0482	5.6688	0.2362	10.1644	0.4235

number of singlet valence bond states increases very fast, as indicated below by the Catalan numbers for benzenoids having 1–12 fused benzene rings:

1	2	3	4	5	6	7	8	9	10	11	12	13	14
1,	2,	5,	14,	42,	132,	429,	1430,	4862,	16,796,	58,786,	208,012,	742,900,	2,674,440

Because of the fast growth, the exact VB ground-state energies as of today have been calculated for systems up to eight rings or 28 π-electrons, which includes molecules such as bisanthene, which has 4×10^7 configurations. The two exact VB calculations, those of Wu and Jiang and those of Alexander and Schmalz, reported the energies of the lowest state as the molecular RE shown in Table 47, expressed in units of the integral J (Wu and Jiang) and $\Delta E/J$ (Alexander and Schmalz). The Hückel RE values are expressed, as usual, in units of the β integral.

From Table 47 we can observe some discrepancies between the RE and REPE values calculated by different VB approaches and by the HMO method. The first thing to notice is that REPE values, in the calculations of Alexander and Schmalz and the HMO method, increase with the size of the molecules, leaving the smallest value for the benzene REPE. This is not the case with the calculations of Wu and Jiang and with graph theoretically calculated REPE. Since the calculations of both Wu and Jiang on one side and Alexander and Schmalz on the other side are exact, we have to attribute the disagreement between the two VB calculations to differences in extracting the RE from the total energy of molecules by the two groups of investigators. Despite these differences, both calculations show similar trends in molecular RE for some molecules. Thus, for example, the two pyrene derivatives **18/53** and **19/53** show that benzo[*e*]pyrene has a greater REPE than benzo[*a*]pyrene, which is expected from the Clar models for these benzenoids. Benzo[*e*]pyrene has a single Clar structure with three π-aromatic sextets and can be viewed as closely related to triphenylene; thus, it is not surprising that it has higher RE and REPE. In contrast, benzo[*a*]pyrene has several Clar structures, implying migrating π-sextets, and consequently lower RE. This case well illustrates the distinction between the quantum chemical approaches to molecular RE and the graph theoretical approaches to RE. Quantum chemical calculations can produce RE. In addition, one should not overlook the fact that quantum chemical calculations give the total molecular energy and the total molecular wave function, which allows calculations of several other molecular properties. However, quantum chemistry can tell nothing about why, for instance, the RE in benzo[*e*]pyrene is bigger than the RE in benzo[*a*]pyrene. Graph theory does not produce numerical results on its own, but it allows analysis of results of exact quantum chemical calculations and may offer an interpretation of such results. Graph theory can, among *apparently unrelated* data, *discern patterns*, like the additivity of the RE in terms of the conjugated circuits.

Alexander and Schmalz made a comparison between their RE values and those obtained by the simple Hückel MO method and found that the RE values predicted by VB theory correlate well with the results of the Hückel theory, "*in spite of the very different assumptions underlying the two methods*."[39] This correlation, in our view, may be an artifact of the definition for RE adopted by Alexander and Schmalz, who defined the VB resonance energy to be the negative of the difference between the calculated VB energy of a molecule and the energy expectation value for a single Kekulé structure. Each Kekulé valence structure represents a covalent spin-pairing in which each π-electron is singlet-paired to an electron on a nearest-neighbor site. However, different Kekulé valence structures will produce different VB energies – thus possibly causing variation in computed RE values. In the case of the Hückel MO method, one can define RE unambiguously as the total energy found by assigning electrons to the lowest available MO's minus 2β for each isolated CC double bond.[39] That HMO theory does not properly reflect the benzenoid character of hydrocarbons is visible from the fact that the two fully benzenoid hydrocarbons in Table 47, triphenylene (**8/53**) and dibenzopyrene (**25/53**), which should have the largest REPE values among the benzenoids shown in Figure 53, do not have the largest REPE values.

Before leaving this topic, we should comment once again on the "testing" of various semi-empirical methods using the condition for the relative contributions of conjugated circuits of different sizes: $R_1 > R_2 > R_3$. With the hindsight that we have now, one should re-examine some of those approaches that failed the test – because as we have seen here, it is possible that methods that would have passed the test at the time recognized the fact that not all Kekulé valence structures participate necessarily in characterization of benzenoid hydrocarbons, as suggested by Clar's model of benzenoid hydrocarbons. We leave the task of re-testing semi-empirical methods to those interested in it as an exercise, in view of the fact that most of these semi-empirical methods are currently of limited interest, while the authors of such methods have the benefit of doubt that their approach may, after all, not have failed the test.

B. Biphenylenes Revisited

As we have seen, Clar structures as strictly defined hold for benzenoid hydrocarbons. Can the notion of Clar's structures for benzenoids be extended to non-benzenoids? Can they be extended to biphenylenes? From a theoretical point of view, biphenylene is an intriguing structure built formally by fusion of six-member and four-member rings. The central question is whether it should be viewed as a doubly connected pair of benzene rings, in an analogy with diphenyl, which represents a singly connected pair of benzene rings, or does the conjugation within four-member ring make a substantial (anti-aromatic) contribution?

1. Parity of Kekulé Valence Structures

To account for specific properties of biphenylene and structurally related non-benzenoids, the notion of parity of Kekulé valence structures has been considered. It has been recognized for a long time that biphenylene is not as aromatic as phenanthrene, although both have five Kekulé valence structures. This contradicts the simple empirical finding that holds for benzenoid hydrocarbons, that the resonance energy, the aromaticity, and the stability increase with K, the number of Kekulé valence structures. The empirical relation described by Swinborne-Sheldrake et al.[432] has shown that, to a high degree, RE is proportional to log K. Dewar and Longuet-Higgins[474] tried to resolve the difficulty of biphenylene versus phenanthrene by introducing the concept of the *parity* of a Kekulé valence structure, which holds only for alternant hydrocarbons. Alternant hydrocarbons are defined as follows:

Definition: *An alternant hydrocarbon is any polycyclic conjugated hydrocarbon having only even-member rings.*

Hence, naphthalene, phenanthrene, pyrene, and biphenylene are alternant hydrocarbons, while azulene, pyracylene, and its isomers are non-alternant conjugated hydrocarbons. The idea of classification of hydrocarbons as alternant and non-alternant goes back to Coulson and Longuet-Higgins and the early days of HMO theory. An important property of alternant hydrocarbons, as opposed to non-alternant, is that for alternant systems all HMO eigenvalues come in pairs $\pm\lambda_i$, while this is not the case for non-alternant systems. It is interesting to mention that this particular mathematical property of alternant hydrocarbons was known to theoretical chemists before it was re-discovered by mathematicians.

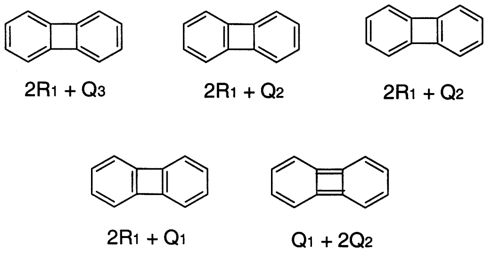


Figure 113. Decomposition of the five Kekulé structures of biphenylene into $4n + 2$ and $4n$ conjugated circuits.

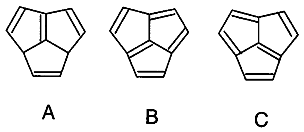


Figure 114. Tricyclic structure contradicting the parity concept that is valid for alternant systems.[740]

Parity is defined for individual Kekulé valence structures of alternant benzenoids. We will illustrate the concept and the definition on the Kekulé structures of biphenylene. In Figure 113 we depict the five Kekulé structures of biphenylene. Parity is a relative quantity defined for a pair of Kekulé valence structures. One can determine the parity of a Kekulé structure by examining its superposition with a Kekulé valence structure of known parity by the following:

Definition: *If superposition of two Kekulé structures gives* $4n + 2$ *conjugated circuits, the two Kekulé valence structures are of the same parity. If superposition results in 4n conjugated circuits, the two Kekulé valence structures are of the opposite parity.*

We can assume, without loss of generality, that the first Kekulé structure of biphenylene in Figure 113 has positive parity. The concept of parity assigns to an individual Kekulé valence structure an algebraic sign. As a result, the count of Kekulé structures is modified accordingly and is given by adding positive and negative contributions: ASC $= K^+ - K^-$, where K^+ is the number of Kekulé valence structures of positive parity and K^- is the number of Kekulé structures of negative parity, respectively. The resulting count of valence structures has been referred to as the algebraic structure count (ASC),[727,728] or the "corrected structure count".[462,464] According to Wilcox, "*algebraic number of structures of a molecule containing any number of non-fused 4n-membered rings is the number of structures remaining after all structures having 2n cyclic double bonds within any of the (4n)-membered rings have been deleted.*" [727]

Hence, while for biphenylene $K = 5$, the ASC $= 3$ because we have $K^+ = 4$ and $K^- = 1$. Cancellation of contributions of structures of opposite parity in the algebraic count of Kekulé valence structures can explain the difference between biphenylene and phenanthrene. The notion of parity of Kekulé valence structures attracted a fair interest.[727-739] Among its limitations, if one may say so, is the fact that, as Gutman, Randić, and Trinajstić[740] pointed out, the notion of parity cannot be extended to peri-condensed systems, in which three odd rings have a common carbon atom. True, as defined by Dewar and Longuet-Higgins, the concept strictly holds for *alternant* hydrocarbons. When three *odd* rings are fused with a common carbon atom (Figure 114), parity assignment leads to a contradiction requiring that the pairs of structures (A,B), (A,C), and (B,C) have opposite parity, but if (A,B) and (A,C) have opposite parity, then the pair (B,C) has to be of the same parity, thus contradicting the initial parity assignments.

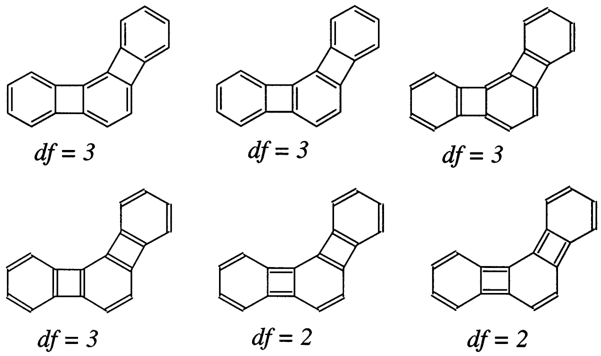
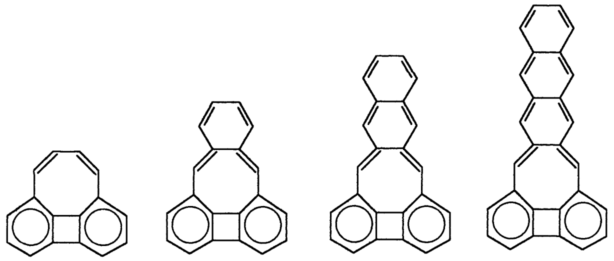


Figure 115. Several Kekulé valence structures of bent [3]-phenylene and their degrees of freedom.

We brought up the discussion of the notion of parity of Kekulé valence structures for several reasons. It serves as an illustration of a concept that seemingly appears elegant, worthy of attention: a notion that is mathematically rigorous (within its domain of definition), but at a same time a notion that is introduced in an ad hoc manner and without enough theoretical justification. At the same time, one can show that the notion of parity may lead to misleading conclusions concerning the chemical description of conjugated hydrocarbons. In order to illustrate a serious deficiency of the parity concept, consider bent [3]phenylene, the biphenylene derivative shown in Figure 115 having two cyclobutadiene rings. The molecule has 13 Kekulé valence structures, 6 of which are shown in Figure 115. It is a simple exercise to construct and examine the 13 Kekulé valence structures of bent [3]phenylene and find that $K^+ = 9$ and $K^- = 5$, and hence ASC = 5. It is also clear that Kekulé structures of negative parity (two of which are shown in the second row of Figure 115) have “unacceptable” CC double bonds in the four-member ring, and hence ought to be rejected and not included in the calculation of molecular RE, just as they have been in the case of biphenylene. But the problem with this parity approach is that the last Kekulé valence structure shown in Figure 115, which if this argument on additivity of contributions from the local structural features holds, should be rejected even twice as “strongly”, because it has *two* unfavorable four-member rings with bridging C=C bonds. Yet, the last Kekulé structure shown in Figure 115 has the *same* parity as the first, very favorable, Kekulé valence structure!

Dias[728] considered Wilcox’s hydrocarbons[741] shown in Figure 116 and pointed out some inconsistencies with the ASC approach. According to Dias, consistent results could be obtained if ASC could assume not only positive but also negative values. At the bottom of Figure 116 we give for Wilcox hydrocarbons the count of Kekulé structures of positive parity, K^+, and those of negative K^- parity, and the count of Kekulé structures (K). In addition, we also indicated the fraction of Kekulé structures having the maximal degree of freedom df, designated as DF. As we can see, DF is constant along the homologous series of Wilcox hydrocarbons.



ACS = 2	ACS = 1	ACS = 0	ACS = -1
$K^+ = 4$	$K^+ = 4$	$K^+ = 4$	$K^+ = 4$
$K^- = 2$	$K^- = 3$	$K^- = 4$	$K^- = 5$
K = 6	K = 7	K = 8	K = 9
DF = 4	DF = 4	DF = 4	DF = 4

Figure 116. Cycloocta[*def*]biphenylene and related structures studied by Wilcox.[741]

2. Degrees of Freedom of Kekulé Valence Structures of Non-benzenoids

If we apply to Wilcox hydrocarbons the arguments that characterize Clar structure, that is, if we consider only Kekulé valence structures of the highest innate degree of freedom, we no longer have difficulties with either biphenylene or biphenylene derivatives. It is not difficult to see that, of the five Kekulé valence structures of biphenylene shown in Figure 113, four have $df = 2$ and only one Kekulé valence structure has $df = 1$. Rather than considering the difference in the number of Kekulé structures of different degree of freedom analogous to ASC, we will consider as the effective number of Kekulé valence structures the number of structures contributing to the Clar structure of the conjugated hydrocarbon, DF. Hence, in the case of biphenylene, $DF = 4$. In the case of bent [3]phenylene, we find that eight Kekulé structures have $df = 3$, and six Kekulé structures have $df = 2$. The difference with ASC is that now, besides the five structures of negative parity, also the last Kekulé structure, which has positive parity, has $df = 2$. Thus, for bent [3]phenylene, $DF = 8$. In Figure 117 we show for several biphenylene derivatives Kekulé valence structures of low df value.

The approach based on discrimination of Kekulé valence structures of different degree of freedom and selection of only those Kekulé valences structures that have the maximum innate degree of freedom automatically extends the idea of Clar structures from benzenoid hydrocarbons to non-benzenoid hydrocarbons, and even fullerenes. In Table 48 we show RE values calculated using only Kekulé valence structures of maximal degree of freedom for a selection of biphenylene derivatives. When we restrict the contributions to molecular RE only to Kekulé valence structures of maximal degree of freedom, we obtain higher RE values than previously calculated. That the “corrected” RE will increase can be easily understood, because in summing the contributions from different Kekulé valence structures, we have discarded the contributions from Kekulé valence structures that make substantially smaller contributions

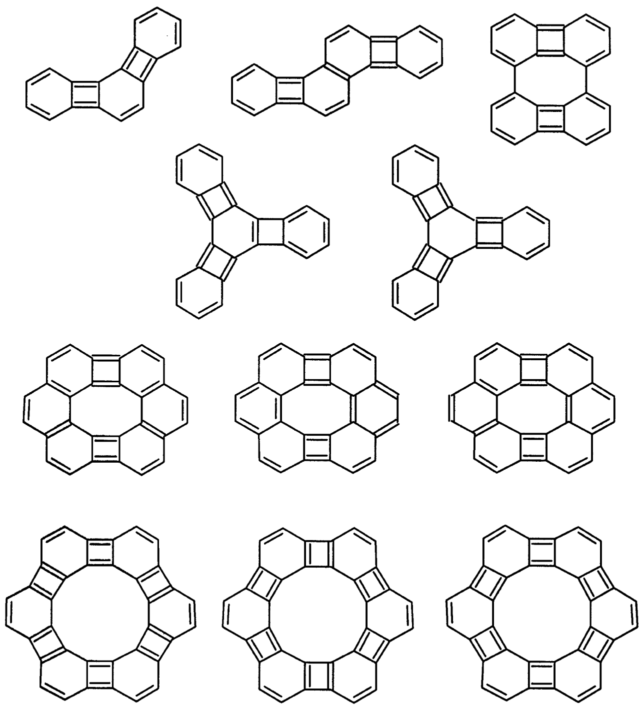


Figure 117. Kekulé valence structures of low *df* for a collection of derivatives of biphenylene.

to the RE, and in this way the contributions of the remaining Kekulé valence structures to RE have increased. In the last column in Table 48 are shown RE values based on the use of all Kekulé valence structures. As we can see, the model based on *all* Kekulé valence structures predicts instability for bent cyclobutadiene derivatives —contrary to experimental results.

C. Dilemma: Kekulé Structures or Clar Structures?

> *To be, or not to be: that is the question.*
>
> W. Shakespeare, *Hamlet*

"To use all Kekulé valence structures, or only Kekulé structures of maximal degree of freedom: that is the question." The failure of the concept of parity, which did not offer satisfactory identification in non-benzenoid hydrocarbons of Kekulé structures that may be important for the description of such molecules, has been resolved by discriminating Kekulé structures using the "degree of freedom" of Kekulé as the underlying basic concept. These attempts toward better understanding of factors that are critical for characterization of non-benzenoid hydrocarbons have led to the central dilemma: for description of conjugated polycyclic hydrocarbons, should one use the *complete set* of Kekulé valence structures or a *subset* of Kekulé valence structures involved in characterization of Clar structures? Briefly: Should we use Kekulé structures or Clar structures to describe polycyclic conjugated hydrocarbons?

For calculation of molecular RE, both approaches require decomposition of Kekulé valence structures into conjugated circuits. The outcomes of such enumeration will differ somewhat, and further theoretical as well as experimental arguments and facts can assist us in resolving the dilemma. Both alternatives are conceptually acceptable; that is, formally both are equally legitimate and both can be viewed, in the words of Niels Bohr, as "deep truth". They do not contradict each other — but one may be a "deeper truth" than the other. Which? It is instructive here to recall the discussion of bond orders as derived from HMO and PPP models. The HMO calculations *start* by assuming that all CC bond lengths are equal, but at the *end* we find that they are not! Hence, we have an innate inconsistency of the model (that is typical also of other computational models and that can be ameliorated by an iterative procedure until internal consistency is reached). The results of PPP calculations of CC bond lengths can be interpreted as suggesting that some Kekulé valence structures have greater weight than others. Thus, besides the empirical rule of Fries that signaled that some Kekulé valence structures are more important than others, a similar message was contained in PPP calculations. Finally, with the development of the conjugated circuits model, it was found that not all Kekulé valence structures make an equal contribution to RE. However, it was Clar's ideas of π-aromatic sextets that required that some Kekulé structures be included and some excluded from the pool of structures that characterize benzenoid hydrocarbons. Hence, it is either—or, a characterization by a discrete set of valence structures, rather than use of continuos weights based on real numbers. So we have to make a choice:

(1) Should our models of benzenoid and non-benzenoid hydrocarbons be based on characterization based on the use of *all* Kekulé valence structures; or

(2) Should our models of benzenoid and non-benzenoid hydrocarbons be based on characterization based on use of a *subset* of Kekulé valence structures that are implied by Clar structures of molecules?

Briefly: Kekulé valence structures or Clar valence structures?

Table 48. RE Values Calculated for the Smaller Non-benzenoids Shown in Figure 66 Using Only Kekulé Valence Structures of Maximal Degree of Freedom[a]

molecule	only Kekulé structures of maximal *df*	RE(only)	RE/sextet	RE(all)
1/66	$(8 R_1 + Q_1 + 2Q_2 + Q_3)/4$	1.390	0.695	0.878
7/66	$(24R_1 + 4Q_1 + 8Q_2 + 4Q_3)/8$	1.938	0.646	1.238
8/66	$(24R_1 + 4Q_1 + 8Q_2 + 4Q_3)/8$	1.938	0.646	0.837
9/66	$(64R_1 + 12Q_1 + 24Q_2 + 12Q_3)/16$	2.487	0.622	1.501
11/66	$(64R_1 + 12Q_1 + 24Q_2 + 12Q_3)/16$	2.487	0.622	0.840
13/66	$(64R_1 + 12Q_1 + 24Q_2 + 12Q_3)/16$	2.487	0.622	0.734
14/66	$(160R_1 + 32Q_1 + 64Q_2 + 32Q_3)/32$	3.035	0.607	

[a] $R_1 = 0.841$ eV, $R_2 = 0.336$ eV. $Q_1 = -0.650$ eV, $Q_2 = -0.260$ eV.

If we choose Kekulé structures, we should use them for characterization of not only benzenoid hydrocarbons but also non-benzenoid hydrocarbons. If we choose Clar structures, we should use them for characterization of not only benzenoid hydrocarbons but also non-benzenoid hydrocarbons. So far, we have found the following arguments against Kekulé valence structures (i.e., against use of all Kekulé valence structures):

(1) Inconsistent parameters for some exact VB calculations that do not satisfy the inequality $R_1 > R_2 > R_3$.

(2) Stability of bent [*n*]phenalenes.

Both of these inconsistencies are fully eliminated when we use only those Kekulé valence structures that contribute to the Clar structure for the description of molecules. Observe that the dilemma is not to use or not to use conjugated circuits, but whether to use all Kekulé valence structures or only some. Thus, if someone finds that bent [3]phenalene is as stable as linear [3]phenylene (although the RE calculated by the conjugated circuits model based on all Kekulé valence structures does not support this), it does not necessarily mean that "the primitive graph theoretical approach based on conjugated circuits model fails completely", but perhaps that the assumption that all Kekulé valence structures make the same contributions to molecular RE "fails completely". As we will see, this is indeed the case, despite an attempt by some to place the blame for the prediction of unstable bent [*n*]phenalenes on "conjugated circuits model" instead of on the underlying assumptions of alternative VB descriptions of [*n*]-phenalenes.

Hence, it is of considerable interest to see what happens with [3]phenylene and [4]phenylene isomers when they are described by a subset of Kekulé structures. By revisiting linear and angular isomers, and including in the case of [4]phenylene the branched isomer, we find that isomers have the same resonance energy if only the Kekulé valence structures of the highest degree of freedom are used for calculation of RE. Hence, unexpectedly, [*n*]phenylenes became a testing ground for determining the validity of the Clar model in general, and its extension to non-benzenoid hydrocarbons in particular. Babić and Trinajstić[742] have examined RE for *cis*-bent [*n*]phenylenes using several approaches, including the conjugated circuits model, and found that with the conjugated circuits model the RE is fairly constant among [*n*]phenylenes, which is also visible from Table 48. In contrast, we can see that RE for linearly fused [*n*]phenylenes increases with the molecular size. This then clearly points out what has been already said, that in contrast with linearly fused benzenoid hydrocarbons, which become less and less stable as the number of fused rings increases, this is not the case with biphenylene derivatives. Observe that in linear acenes all Kekulé valence structures have the same *df* and are therefore included in the model based on calculation of molecular stability when we restrict the selection of Kekulé structures to those of the maximal df, which is not the case with [*n*]phenalenes. According to the calculations of Kovaček, Margetić, and Maksić, who at about the same time applied semiemprical AM1 calculations to a selection of biphenylene derivatives, including linear and bent [3]-phenylene, bent [3]phenalene is found stable: "*that bent [3]phenylene has a lower total energy in spite of the fact that it is more localized system than the linear isomer.*"[743] They continue: "*The primitive graph-theoretical approach based on the "conjugated circuits" model fails completely in this respect.*"

Let us assume that the semiemprical AM1 calculations are trustworthy and indeed that bent "*[3]-phenylene has a lower total energy... than the linear isomer.*" How can this contradict the results of the "primitive" graph theoretical analysis of molecular *resonance energies* using conjugated circuits in biphenylene derivatives? Kovaček et al. were not calculating RE at all. They were interested in contributions of strained CC bonds associated with four-member rings and were focusing on the difference in stability in angular and linear [3]phenylene associated with re-hybridization and interaction of σ- and π-electrons. The conjugated circuits model, whether one refers to it as "primitive" or by other derogative labels, has noting to do with calculations of the overall molecular stability, with re-hybridization of σ-electrons, with interactions of σ- and π-electrons, with the notion of concertedness of σ- and π-electrons, and such. All that it shows is that molecular RE is circuit-additive, and more specifically additive in terms of conjugated circuits. Molecular RE is, of course, non-observable, but as long as it is used in chemistry, it is useful to know that it is an additive quantity in terms of conjugated circuits. There is no doubt that quantum chemists can calculate the RE of many conjugated benzenoid hydrocarbons, and calculate it with respectable precision, as Dewar and De Llano did with their MINDO calculations. The result of such efforts is a list of numbers, the RE values, for a list of compounds. Now, whether it is a "primitive" discovery or a "prime" discovery that a set of apparently unrelated quantities, RE values, are out of "nowhere" found to be inter-related is for readers to judge.

We decided to include this "Biphenylenes Revisited" section in this review article on aromaticity for two reasons: (1) to draw attention to the inadequacy of the concept of parity of Kekulé valence structures and the inconsistencies of the approaches based on the "algebraic count" of Kekulé structures for discussion of conjugated polycyclic hydrocarbons, which is still practiced; and (2) to raise awareness in theoretical circles of a need for reliable computations of the molecular energy and RE of non-benzenoid conjugated hydrocarbons. This is desirable not only so that we can obtain better sets of parameters needed for calculation of the resonance energies of non-benzenoid hydrocarbons but also so that we can get better insight into the roles of various Kekulé valence structures in representation of molecules and find out to what extent the ideas of Clar can be extended to non-benzenoid systems. If we find out that indeed only Kekulé valence structures of maximal degree of

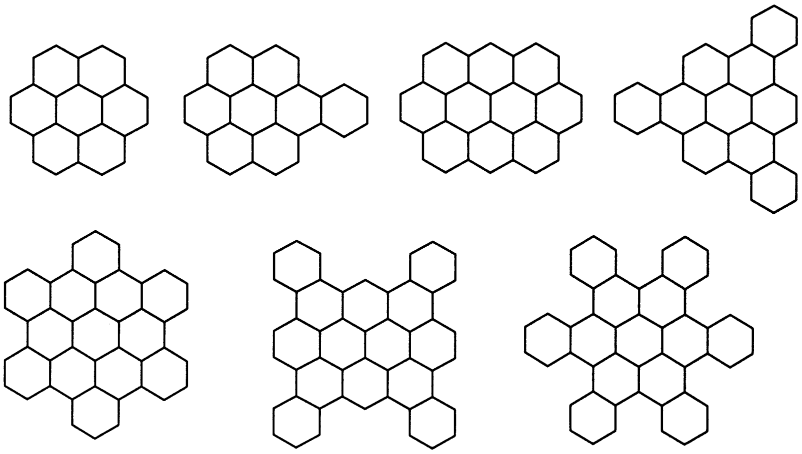


Figure 118. Coronene and related benzenoids that have been thought to give rise to "super-aromaticity".

freedom are relevant for representation of nonbenzenoid hydrocarbons, then synthesis of anti-kekulene should not be necessarily coupled with unusual difficulties. The RE of anti-kekulene would then be relatively large, and its RE/sextet would be comparable in magnitude to the RE/sextet for structurally related [*n*]phenylenes, several of which were successfully synthesized.[744-746] If all Kekulé valence structures play a similar role, then the RE of anti-kekulene would be of the same magnitude as the RE in other bent [*n*]phenylenes, and consequently the RE/sextet would decrease and suggest a lack of stability.

Incidentally, the trivial name "anti-kekulene" for the cyclic [6]phenylene $C_{36}H_{12}$ was introduced by Diercks and Vollhardt.[745]

D. On Kekulene and Superaromaticity

Chemists have recognized for some time that some Kekulé valence structures are simply "unacceptable". Such are the Kekulé structures shown in Figure 16, the Kekulé valence structures of low degree of freedom shown for kekulene in the lower part of Figure 64, and the valence structures of biphenylene derivatives shown in Figure 117, which have been successfully synthesized by Staab and co-workers.[613,614] The question is whether such Kekulé structures can be completely ignored, which would suggest extension of the notion of Clar's aromatic π-sextet to non-benzenoid hydrocarbons, or whether they play some visible role in the overall calculation of the molecular stability and molecular RE. Others have also recognized the limited use of some Kekulé valence structures. For example, Balaban characterized the valence structure of kekulene with $df = 3$ as "incorrect", in the sense that it is not important. If that is the case, then even more "incorrect" would be the last valence structure shown in Figure 65 with $df = 2$, which has been rejected, as discussed in the literature, because it is not consistent with NMR data nor with molecular geometry. In some respects kekulene is somewhat special, if not unique. For kekulene there are 200 Kekulé valence structures, while Clar's structure of kekulene requires only contributions from 64 Kekulé valence structures having $df = 6$. Usually the number of Kekulé valence structures of the maximal *df* is relatively large or at least comparable to the number of Kekulé structures of lower *df*. The expression for molecular RE based on $K = 200$ and the corresponding expression based on $K^* = 64$ are respectively

$$\mathrm{RE} = (1188R_1 + 696R_2 + 174R_3)/200 \qquad \text{or}$$
$$\mathrm{RE} = (5.94R_1 + 3.48R_2 + 0.87R_3)$$

$$\mathrm{RE} = (480R_1 + 192R_2 + 96R_3)/64 \qquad \text{or}$$
$$\mathrm{RE} = (7.50R_1 + 3.00R_2 + 1.50R_3)$$

The numerical values for RE are 6.112 and 7.320 eV, respectively. As we can see from the above, Clar's model enhances the RE by not considering Kekulé valence structures of low priority (low *df* values), which have fewer contributions from R_1. Later we will mention a somewhat similar situation with buckminsterfullerene, for which Klein et al. have shown that less than 50% of Kekulé valence structures contribute over 99.8% toward molecular RE.

In the case of kekulene and benzenoids having coronene substructure illustrated in Figure 118, the possibility of "extra" aromaticity, referred to as "super-aromaticity", due to the presence of conjugation involving the cyclic periphery of several fused benzene rings has been raised. Clar[49] has evoked the notion of "super-aromaticity" when considering migrating sextets of coronene, which is the smallest benzenoid having a "super" ring made from the 18 carbon atoms on its periphery.

The idea of super-aromaticity (just as was the case with the notion of parity of Kekulé valence structures) attracted attention.[745-748] However, the presence of large conjugated circuits makes a small contribution, if any, to molecular RE. So the question can be raised: Is super-aromaticity a fact or an artifact? In fact this question has been raised by Aihara in an article entitled, "Is Superaromaticity a Fact or an Artifact? The Kekulene Problem."[747] Aihara has examined the kekulene problem on the basis of several theoretical approaches, such as the method of additive nodal increments of Cioslowski,[749,750] the method of conjugated circuits, the topological resonance energy, and the circuit resonance energies, and concluded the following:[747]

> *Graph-theoretical analysis have clarified that super-conjugation resulting from the cyclic array of benzene rings does not yield appreciable super-aromatic energetic effects. Decisive evidence for the lack of super-aromaticity in kekulene was given simply by calculating the energy difference between true kekulene and super-antiaromatic kekulene. The total π-electron energy of true kekulene is very close to that of super-antiaromatic kekulene, hence, there is no reason to believe that annulenoid conjugation contributes much to the thermodynamic stability of kekulene. Kekulene is a regular benzenoid hydrocarbon in all aspects.*

As Aihara points out, "*This approach is general and applicable to any macrocyclic conjugated systems with an inner cavity*." Thus, the myth of super-aromaticity, just as has been the case with the myth of parity, has been demoted if not ended.

Finally, we should add that contributions from large conjugated circuits should not be totally ruled out as totally unimportant. It may depend on what molecular property one considers. If we speak of molecular stability and the molecular resonance energy, then large conjugated circuits make negligible contributions. But, if we look at [18]annulene, as discussed by Sondheimer and Wolovsky,[93] as being planar, we have to attribute some role to the presence of conjugation through conjugated circuits having 18 carbon atoms. It was believed by some that there is a critical size beyond which conjugation accompanied with equalization of CC bond lengths stop and alternation of CC double and CC single bonds sets in, and that may well be the case for conjugated $4n + 2$ rings with $n = 5$. This belief has been given a death blow by Gossauer and Rexhauser of Berlin Technical University,[645] who succeeded in synthesizing a 22-π-electron system by enlarging a naturally occurring porphyrin ring, which has 18 π-electrons. For a popular account of this by no means small synthetic achievement, see an article in *New Scientist*.[751]

XXXIII. Clar Structures Revisited

> *Nothing is more interesting to the true theorist than a fact which directly contradicts a theory generally accepted up to that time ... But it is often very difficult and complicated question to decide in what part of the theory the improvement has to be made.*
>
> M. Planck[674]

A. Exceptions to the Rule

In discussing the properties of benzocoronene,[699] Clar has evoked a π-sextet structure (shown in Figure 119 at the top left) which has one sextet less than the maximal number of possible aromatic sextets for benzocoronene, that defines Clar's structure (shown in Figure 119 at the top right). The "lesser" Clar structure was introduced in order to account for some apparent features of benzocoronene that parallel those of coronene, in which there are migrating sextets and, as Clar believed, "super-aromaticity".

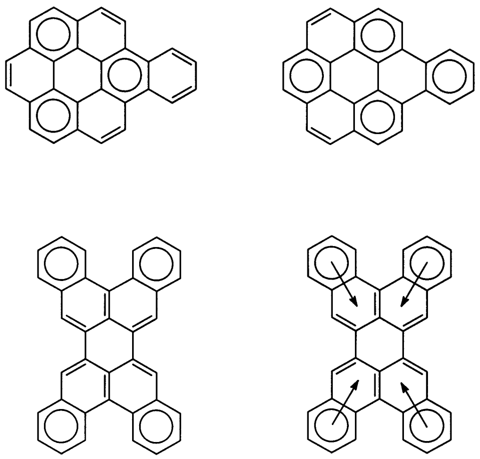


Figure 119. Modified Clar structures of benzocoronene (top left) and tetrabenzoperylene (bottom left) having one sextet less than the corresponding Clar structures (right) having the maximal number of aromatic sextets.

Another somewhat related anomaly concerns tetrabenzoperylene, for which Clar proposed the structure shown at the bottom left of Figure 119.[752] Clar argued that in this structure all the CC double bonds and all the four π-aromatic sextets are fixed, while according to the generally outlined π-aromatic sextet model, tetrabenzoperylene should have migrating sextets, similar to those in benzo[*c*]phenanthrene, which constitutes a fragment of tetrabenzoperylene. It is not clear from the theoretical point of view why, among several possible Clar structures, the one with exocyclic CC double bonds to the central ring should be preferred. But the "bay" protons show a chemical shift at 872 Hz, indicative of π-electrons causing a ring current in the central ring.[753,754] In comparison, the bay protons in perylene, which has an "empty" ring, are at 805 Hz, and the bay protons of phenanthrene are at 850 Hz. This suggests compellingly that the central ring in tetrabenzoperylene is more similar to the central ring of phenanthrene (which has a fixed CC double bond in Clar's structure) than to that of perylene. It is interesting that the valence structure of tetrabenzoperylene, for which Clar proposed the structure shown at the bottom left of Figure 119 and which involves exocyclic CC double bonds to the central ring, is obtained as the result when instead of using *df* for selecting Kekulé valence structures to be combined into the Clar structure, we resort to the weights given by the smallest Pauling bond order for any of the CC double bonds in a Kekulé valence structure. In Figure 120 are shown Kekulé valence structures of benzo[*c*]phenanthrene and their weights based on the smallest Pauling bond order for any of the CC double bonds in a Kekulé structure. So, it may be that the weights given by Pauling bond order may be used to discriminate among Kekulé valence structures having the same *df*.

Anomalies like those pointed out may have stimulated interest in the description of selected benzenoids with additional Clar structures, which led to the notion of generalized Clar structures.

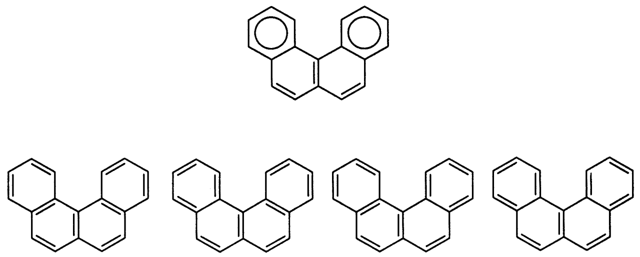


Figure 120. The four Kekulé valence structures of benzo[*c*]phenanthrene, having the maximal weight based on the smallest Pauling bond of CC double bonds.

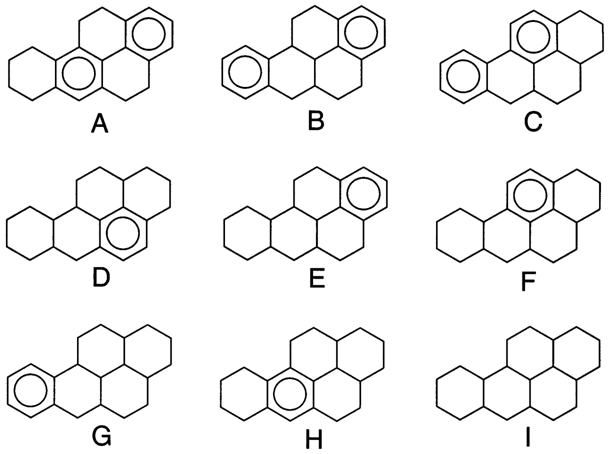


Figure 121. The nine generalized Clar structures for benzo[*a*]pyrene, described by Hosoya and Yamaguchi.[755]

B. Generalized Clar Structures

It was not until 1975 that Hosoya and Yamaguchi[755,756] introduced generalized Clar structures, which are defined as follows:

Definition: *A generalized Clar structure of a polycyclic benzenoid hydrocarbon is a valence formula in which one or more aromatic π-sextets are inscribed in non-adjacent benzene rings such that the remaining part of the structure, obtained by deletion of benzene rings with sextets, must have a Kekulé valence structure.*

Hence, the generalized Clar structure can always be obtained from a Clar structure by erasing one or more aromatic sextets. The set of generalized Clar structures includes on one side the Clar structure (that has the maximum number of sextets) and also, by definition, the molecular graph without any sextet. In Figure 121 we show the nine generalized Clar structures for benzo[*a*]pyrene. Hosoya and Yamaguchi observed that the number of generalized Clar structures equals the number of Kekulé valence structures. Later Hosoya and Ohkami[757,758] were able to show that indeed there is a formal one-to-one mapping between Kekulé valence structures and generalized Clar structures. He and He have also studied a one-to-one correspondence between Kekulé structures and sextet patterns.[759,760] This is an intriguing correspondence in that Clar structures imply inclusion of at least two Kekulé valence structures, and yet here we have a one-to-one relationship between Clar structures with π-sextets and Kekulé valence structures. To discern the correspondence between the two, one has to focus attention on the "vertical" CC double bonds in any of the Kekulé valence structure. If a benzene ring has a "vertical" CC double bond on the left side, it is called "left", and if it has a "vertical" CC bond on the right side, it is called "right", as shown in the middle of Figure 122). Hence, first one differentiates between the "left" (L) and the "right" (R) Kekulé valence structures of fused benzene rings and then replaces each L ring by a sextet circle, while ignoring rings without vertical CC bonds and all R rings. It is not difficult to verify that the nine Kekulé valence structures shown in the lower part of Figure 122 have been ordered so as to correspond to the nine generalized Clar structures in Figure 121. Because of the one-to-one correspondence, it appears that the generalized Clar structures offer an alternative representation of benzenoid hydrocarbons.

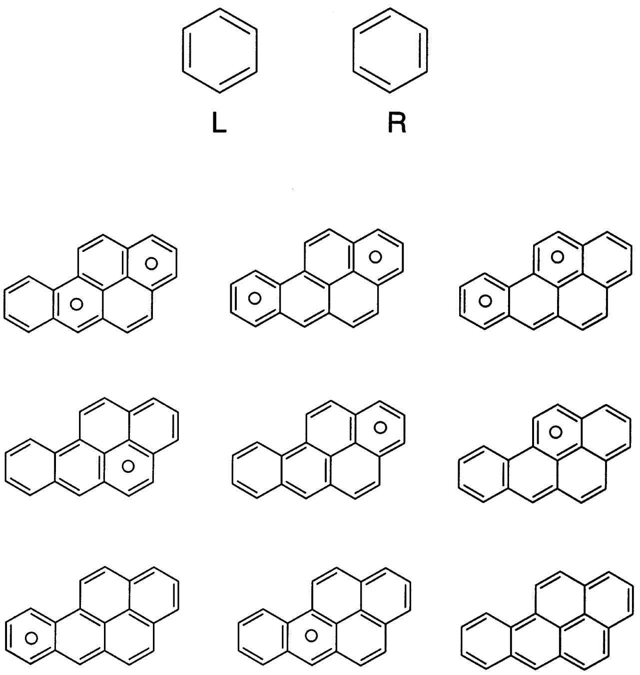


Figure 122. "Left" (L) and "right" (R) Kekulé valence structures of benzene. The "left" structure (indicated by a small circle) was used to illustrate the correspondence between the number of Kekulé valence structures and the number of generalized Clar structures.

The above relationship between generalized Clar structures and Kekulé valence structures holds for classes of benzenoids that have no coronene sub-unit, such as cata-condensed benzenoid hydrocarbons, for which Gutman, Hosoya, and co-workers[761] gave a proof. Zhang and Chen[762] have shown that, in the case of coronene, and structures having coronene sub-units, if a "super-ring" that involves 18 carbon atoms on the molecular periphery is included as an "aromatic π-n-sextet", again a one-to-one correspondence between Kekulé structures and generalized Clar structures is established. The "missing" structure for the one-to-one correspondence of the super-aromatic-ring sextet of Zhang and Chen corresponds to the disjoint conjugated circuits illustrated in Figure 21. For more on global and local properties of Clar π-electron sextets and a quantitative approach to Clar's sextet model, consult ref 219.

Table 49. Sextet Polynomials for a Collection of Smaller Benzenoid Hydrocarbons (As Reported by Hosoya and Yamaguchi[755])

molecule	$S(x)$	$S'(x)$	$S(1)$	$S'(1)$
benzene	$1 + x$	1	2	1
naphthalene	$1 + 2x$	2	3	2
anthracene	$1 + 3x$	3	4	3
phenanthrene	$1 + 3x + x^2$	$3 + 2x$	5	5
tetracene	$1 + 4x$	4	5	4
benzanthracene	$1 + 4x + 2x^2$	$4 + 4x$	7	8
chrysene	$1 + 4x + 3x^2$	$4 + 4x$	8	10
benz[*c*]phenanthrene	$1 + 4x + 3x^2$	$4 + 9x$	9	13
triphenylene	$1 + 4x + 3x^2 + x^3$	$4 + 6x + 3x^2$	6	6
pyrene	$1 + 4x + x^2$	$4 + 2x$	6	5
pentacene	$1 + 5x$	5	9	11
benztetracene	$1 + 5x + 3x^2$	$5 + 6x$	10	13
pentaphene	$1 + 5x + 4x^2$	$5 + 8x$	11	15
benzo[*b*]chrysene	$1 + 5x + 5x^2$	$5 + 10x$	12	18
dibenzo[*a*,*h*]anthracene	$1 + 5x + 5x^2 + x^3$	$5 + 10x + 3x^2$	13	20
picene	$1 + 5x + 6x^2 + x^3$	$5 + 12x + 3x^2$	13	21
benzo[*b*]triphenylene	$1 + 5x + 5x^2 + 2x^3$	$5 + 10x + 6x^2$	14	23
benzo[*g*]chrysene	$1 + 5x + 6x^2 + 2x^3$	$5 + 12x + 6x^2$	9	11
benzo[*a*]pyrene	$1 + 5x + 3x^2$	$5 + 6x$	9	12
perylene	$1 + 4x + 4x^2$	$4 + 8x$	11	16
benzo[*d*]pyrene	$1 + 5x + 4x^2 + x^3$	$5 + 8x + 3x^2$	19	31
coronene*	$1 + 8x + 9x^2 + 2x^3$	$8 + 18x + 6x^2$	20	32

C. Sextet Polynomial

Hosoya and Yamaguchi have introduced the sextet polynomial as a book-keeping device for different types of structures that occur in the generalized Clar polynomial. By definition, the constant term of the polynomial is equal to one (and corresponds to the molecular graph of the benzenoid considered). The coefficients of various powers of x that constitute the polynomial count the number of structures having different number of π-sextets, and the coefficient of the term x^k tells how many k sextets are in the molecule. For example, for benzo[*a*]pyrene the sextet polynomial is $S(x) = 1 + 5x + 3x^2$, which means that there are three structures with two sextets, five with one sextet, and one structure with no sextet. In Table 49 we have listed sextet polynomials for a collection of smaller benzenoid hydrocarbons, as reported by Hosoya and Yamaguchi.[755] The coefficients of the sextet polynomials have been referred to as the "resonant sextet number", that is, the number of ways in which k mutually resonant sextets can be selected in a benzenoid structure.

Sextet polynomials have several interesting mathematical properties that allow one to use recursion formulas to derive sextet polynomials for larger benzenoid hydrocarbons.[761] As Hosoya and Yamaguchi[755] and Knop and Trinajstić[764] pointed out, one can derive from the sextet polynomial useful structural invariants of benzenoids. By setting $x = 1$, we have $S(1) = K$, the number of Kekulé valence structures of the benzenoid. This may appear a trivial result, but the fact that one can construct sextet polynomials, at least for structurally related families of graphs by recursion, allows one to find K in some large benzenoids without actually using any typical counting algorithms. It is also easy to evaluate the derivatives of the sextet polynomial, $\mathrm{d}S/\mathrm{d}x$, which graphically corresponds to the collection of subgraphs of the graph G of the benzenoid considered, obtained by erasing one ring and all adjacent edges at a time. If we set $x = 1$ in $\mathrm{d}S/\mathrm{d}x$ (that is, in the notation of Newton, $S'(1)$), we obtain, as Knop and Trinajstić pointed out, the number of integrals γ_1 which enter into Herndon's resonance theory. Alternatively, this is the number of edges in the resonance graphs depicted in Figures 69–71, and twice $\mathrm{d}S/\mathrm{d}x$ for $x = 1$ gives the number of conjugated circuits R_1.

By knowing $S(1)$ and $S'(1)$, we can construct the quotient $S'(1)/S(1)$, which is a measure of the total aromaticity of a benzenoid, as outlined by this author in an early paper on conjugated circuits.[765,766]

D. Canonical Clar Structures

Herndon and Hosoya[539] re-examined the concept of generalized Clar structures and suggested the use of only a subset of generalized Clar structures which satisfy the condition that once circles representing aromatic sextet are inscribed, the remaining part of a structure should have a unique assignment of CC double and CC single bonds. They referred to this subset as the canonical set of Clar structures. In Figure 123 we have illustrated the five structures that form the canonical set of Clar structures for benzo[*ghi*]perylene. Using the canonical set as a basis, Herndon and Hosoya outlined an empirical VB

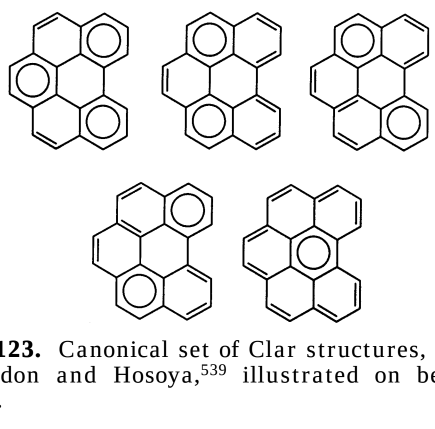


Figure 123. Canonical set of Clar structures, described by Herndon and Hosoya,[539] illustrated on benzo[*ghi*]perylene.

Table 50. Resonance Energies for a Set of Benzenoid Hydrocarbons Based on the Canonical Set of Clar Structures (As Reported by Herndon and Hosoya[539])

compound	Clar	Kekulé	RE(SCF)	RE(VB)	difference
benzene	1	2	0.869	0.859	0.010
naphthalene	2	3	1.323	1.325	−0.002
anthracene	3	4	1.600	1.606	−0.006
tetracene	4	5	1.822	1.819	0.003
pentacene	5	6	2.004	2.004	0.000
perylene	6	9	2.619	2.651	−0.032
zethrene	4	9	2.694	2.651	0.043
quarterrylene	4	81	5.309	5.302	0.007
acenaphthylene	16	3	1.335	1.325	0.010
fluoranthene	2	6	2.141	2.184	−0.043
phenanthrene	2	5	1.933	1.924	0.009
pyrene	3	6	2.098*	2.099*	−0.001
benzo[*c*]phenanthrene	3	8	2.478	2.477	0.001
benz[*a*]anthracene	3	7	2.291	2.313	−0.022
chrysene	3	8	2.483	2.477	0.006
triphenylene	2	9	2.654	2.652	0.002
dibenz[*a*,*c*]anthracene	3	13	3.058	3.076	−0.018
dibenz[*a*,*h*]anthracene	3	12	2.948	2.958	−0.010
dibenz[*a*,*j*]anthracene	3	12	2.948	2.958	−0.010
benzo[*a*]pyrene	4	9	2.594*	2.579*	0.005
benzo[*d*]pyrene	3	11	2.853*	2.842*	0.011
benzo[*ghi*]perylene	5	14	3.128	3.098	0.030
coronene	7	20	3.524	3.516	0.008
benzo[1,4]bisanthene	11	30	3.862	3.902	−0.040
ovalene	15	50	4.539	4.526	0.013
biphenyl	1	4	1.699	1.718	−0.019
styrene	1	2	0.858	0.859	−0.001
trans-stilbene	1	4	1.712	1.718	−0.006

calculation of RE. The total RE was obtained by solving the secular equation of an effective Hamiltonian:

$$\mathrm{Det}\,|\,\mathbf{Q} - x\mathbf{I}\,| = 0$$

where **I** is the $N \times N$ unit matrix (having all elements zero except those on the main diagonal, which are equal to one), and the **Q** matrix involves interaction terms which can be obtained by counting the aromatic sextets and CC double bonds involved in π-sextet migrations following the rules outlined in their paper. In Table 50 we show the resonance energies for a set of benzenoid hydrocarbons as reported by Hosoya and Herndon based on the parameters $a = 0.8590$, $b = 0.0744$, and $k = 0.3176$, determined from a linear regression of the SCF MO resonance energies obtained by Dewar and de Llano on 10 smaller benzenoids when using the canonical Clar structures. Here, a refers to a Coulomb-type integral for the aromatic sextet, b is a Coulomb-type integral for CC double bonds, and k represents the VB exchange integral associated with resonance between two Clar structures associated with a single migrating π-sextet. In practice, a and b represent the counts of π-sextets and CC double bonds. Observe the very good agreement between the RE(SCF) and RE(VB) based on the canonical Clar formulas. Herndon and Hosoya used the corrected values for RE for pyrene, benzo[*a*]pyrene, and benzo[*e*]pyrene, the compounds that apparently were in error as reported in the initial work of Dewar and de Llano. The very good agreement between the calculated RE(SCF) and RE(VB) may be viewed as an additional argument in favor of Clar's description of benzenoid hydrocarbons.

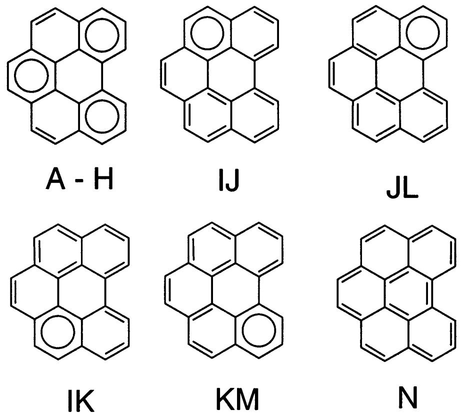


Figure 124. "Resonance Clar structures" for benzo[*ghi*]perylene, obtained by restricting the superposition of Kekulé structures to valence structures having the same degree of freedom.[86,87]

E. Resonant Clar Structures

This author has suggested[87] another subset of generalized Clar structures as potentially interesting for characterization of benzenoid hydrocarbons, illustrated for benzo[*ghi*]perylene in Figure 124. These structures are constructed by allowing *only* superposition of the Kekulé valence structures of the same degree of freedom. In the case of benzo[*ghi*]perylene, as one can see by comparing Figures 123 and 124, only the first structure, which is the "classical" Clar structure for benzo[*ghi*]perylene, is the same. Under each structure in Figure 124 we have indicated with letters A−N the Kekulé valence structures of benzo[*ghi*]perylene involved in the superposition using the labels A−N already shown in Figure 15. The first novel Clar structure involved superposition of eight Kekulé valence structures having the maximal degree of freedom, $df = 3$. The next four structures result from superposition of Kekulé valence structures having $df = 2$. Finally, as we can see, the last structure is the Kekulé valence structure having $df = 1$, which is the only structure with $df = 1$, and hence cannot participate in superimposition with other structures. We may refer to this novel canonical set of Clar structures as resonant Clar structures, or "R-Clar" structures, to avoid confusion with Herndon and Hosoya's canonical Clar structures, which may be referred to as "HH-Clar" structures, leaving the symbol "HY-Clar" structures for the generalized Clar structures of Hosoya and Yamaguchi.

Construction of HY-Clar structures is rather straightforward. The selection of the subset of HH-Clar structures requires some caution, but can be accomplished also for smaller benzenoids by trial and error. Construction of R-Clar structures also requires considerable care, as it presumes a prior determination of df for individual Kekulé valence structures. However, as outlined in ref 87, R-Clar structures can be constructed from HH-Clar structures by identification of the "vulnerable" π-sextets, which are the sextets obtained by a superposition of Kekulé valence structures having *different* degrees of freedom.

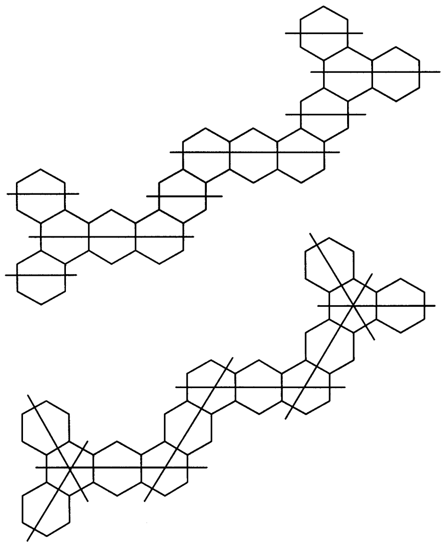


Figure 125. Graphical method of Klavžar, Žigert, and Gutman[767] for determining the number of π-aromatic sextets in cata-condensed benzenoids (top) and an alternative proposal by this author[768] that indicates rings involving π-aromatic sextets (bottom).

F. Graphical Construction of Clar Structures

We will end this discussion of generalized Clar structures by briefly outlining a graphical construction of Clar structures that has been recently reported by Klavžar, Žigert, and Gutman.[767] Clar structures are drawn by inscribing circles signifying the aromatic π-sextets in individual benzene rings such that the structure has the maximal number of rings, providing that no circles appear in adjacent rings, and that all CC bonds not involved in aromatic sextets are either CC double or CC single bonds. The number of π-aromatic sextets in a benzenoid hydrocarbon is an important structural invariant, which is not readily available for larger benzenoid systems, including large cata-condensed benzenoids. The graphical approach of Klavžar et al. allows determination of the number of π-aromatic sextets. It is illustrated in Figure 125 (top) on one of the benzenoids which they considered. According to these authors, the smallest number of line segments required to cross all benzene hexagons gives the number of π-aromatic sextets.

The linearly fused benzenoids naphthalene, anthracene, tetracene, and so on are the only benzenoids for which there is but one way of drawing the line that crosses all the fused rings. For other benzenoids there are more than two ways in which the "crossing" lines can be drawn. Rather than choosing the crossing lines arbitrarily, which suffices to determine the number of π-aromatic sextets, we advocate[768] drawing the "crossing" lines so that they result in the *maximal number of crossings* of the line segments. This is the case with the diagram shown on the bottom in Figure 125. From Figure 125 we can see that, for this particular benzenoid, the eight lines allow a maximum of five crossings of the line segments, and as we will see, the number of crossings corresponds to the number of "empty" rings in the Clar structure for the benzenoid considered.

Let us point out that benzenoid isomers that differ only in the orientation of linear branches at the "kink" rings (i.e., the ring angularity fused to a linear fragment) have the same sextet "crossing" numbers. The smallest such case is that of chrysene and benzphenanthrene, both of which are "covered" by two non-crossing line segments. By not having "crossing" of line segments, we immediately know that benzphenanthrene has no "empty" rings. Benzenoid isomers that differ only in the orientation of linear branches at the "kink" rings have been referred to as isoconjugate, or iso-Kekuléan, because there is a one-to-one correspondence between their Kekulé valence structures, which differ in spatial orientation but have the same conjugated circuits count. Balaban and Tomescu,[769] in a paper on deriving algebraic expressions for the number of Kekulé structures of cata-condensed benzenoids, referred to these isomers as isoarithmic. Such polycyclic hydrocarbons have necessarily the same count of conjugated circuits not only for a molecule as a whole, but also for individual Kekulé valence structures. Živković, Klein, and Schmalz[770] define two molecular species as isoresonant if both have like numbers of the same type of bonds and there is an isomorphism between the superposition of pairs of Kekulé structures giving equivalent interaction patterns.

The reason that line segments should be drawn so that the number of crossings of lines is maximal follows from an observation that a benzene ring at which line segments are crossing cannot be the site of an aromatic π-sextet in a Clar structural formula. This is evident from the fact that each benzene ring along the line segment represents a possible site for an aromatic π-sextet. When we place aromatic π-sextets on those parts of two (or more) lines that do not cross, we achieve the maximal number of aromatic π-sextets. If we were to put aromatic π-sextets at the benzene rings where two lines cross, we would place one sextet on two lines, that is, one sextet less than would be otherwise possible, thus violating the requirements for the maximal number of aromatic π-sextets imposed by Clar. It follows, then, that benzene rings, which are the sites of crossing of lines, are either the so-called "empty" rings or the rings with fixed CC double bond assignment. Thus, once we have drawn the diagrams with the smallest number of lines that intersect every benzene ring and have the maximal number of crossings, we in fact have an alternative diagram for Clar structures of benzenoids. All that one has to do is to place an aromatic π-sextet in any of the rings that have no crossing of lines (subject to the requirement that no aromatic π-sextets can appear in adjacent rings). It is also immediately clear that not only will benzenoids without crossing of line segments necessarily have "migrating" sextets, but the migrating sextet can occur in every benzene ring of a molecule. Migrating sextets will also appear in those benzenoids having crossing of lines segments but also having two or more linearly fused benzene rings adjacent to any of the "crossed" ring. All this holds for benzenoids having a unique Clar structure and benzenoids having a unique "crossing" pattern. However, there are benzenoids that have two optimal drawings. The smallest such case is that of picene (five zigzag fused benzene rings) and the corresponding iso-Kekuléan structures. In such cases, a benzene ring that is the site of crossing in either of the two structures should be considered "forbidden" for the site of the aromatic π-sextets.

XXXIV. Fullerenes

A short review of fullerenes is in order, in view of the underlying common structural features of all-carbon and hydrocarbon compounds. Formally, by disregarding the geometrical features of fullerenes as 3-D cages, the main distinction between hydrocarbons and fullerenes is that the former have apparent 2-D "peripheral" features with hydrogens playing an important role, while the latter, being of closed polyhedral geometry, have no such 2-D periphery. If we focus attention to the interior parts of both classes of compounds, then we find similar structural elements making similar contributions.

The term "fullerene" was coined by H. Kroto[771] for families of unsaturated carbon compounds having a polyhedral carbon skeleton consisting of 12 pentagons and additional ($n/2-10$) hexagonal faces for which one can draw Kekulé valence structures. For the smallest structure satisfying the above conditions, a regular dodecahedron, $n = 20$, which thus has no hexagons. Grünbaum[772] has pointed out that polyhedra satisfying the above condition exist for $n \geq 20$, except for $n = 22$. Enumerations of fullerenes have shown that the number of possible isomers grows fast with n.[721] Recently, Schmalz[720] presented a valence bond view of fullerenes in which he outlined the resonance theoretic model of Herndon and the conjugated circuits approach as resonance models for fullerenes. When one consider fullerenes, in view of the enormous number of Kekulé valence structures that these systems have, it is important immediately to stress the necessity for novel and efficient graph theoretical computational schemes for enumeration not only of Kekulé valence structures (K) but also of conjugated circuits of different size. Without such an efficient tool, extension of the conjugated circuits model to fullerenes would be not possible. Fortunately, Klein and Liu[516] have shown how one can extract K and the number of conjugated circuits without difficulty from a few minors of the adjacency matrix of a molecular graph of fullerene. Thus, perhaps quite unexpectedly, the adjacency matrix, which played the central role in the HMO method, again comes to the center of attention, this time in relation to fullerenes! Thus, the conjugated circuits model requires as input for computations only information on carbon−carbon connectivity − the same information that defines HMO computations. According to Schmalz, the conjugated circuits computations "*... are therefore an attractive complement to Hückel calculations since, though also highly approximate, they approach the solution from the opposite, highly correlated, valence bond limit.*"[720]

We almost fully agree with this characterization, except for the somewhat ambiguous label of "also highly approximate". Most chemists will agree that Hückel MO calculations are highly approximate, but an empirical approach such as the conjugated circuits model is *as much approximate as is the source* method on the basis of which the empirical parameters are calculated. If one is to label Dewar and de Llano's SCF MO calculations of the PPP type and the Jiang and Li VB calculations as "very approximate", then surely the same label describes the corresponding results derived from the conjugated circuits model. However, the calculations of Dewar and de Llano, as well as the more recent calculations of Jiang and Li, would be more correctly described as "advanced" (particularly in comparison to the HMO method), and hence less approximate. In fact, all calculations are approximate, including ab initio calculations, such as those using the Gaussian computational package, but some are less approximate than others. Among the less approximate calculations we find the VB calculations of Jiang and co-workers and other exact GUGA VB calculations.

In contrast, the conjugated circuits method gives expressions for molecular resonance energy, and these expressions can be postulated as representing the definition of RE. Thus, there is nothing approximate, at the least "very approximate", about the conjugated circuits model, just as there is nothing approximate, or very approximate, about the Schrödinger equation, which has been postulated as the basic equation of quantum theory. Of course, solutions of the Schrödinger equation will be approximate or very approximate, depending on the choice of computational methodology, just as RE derived from the expressions based on the count of conjugated circuits will be approximate or very approximate, depending on the choice of empirical parameters. While thus, in a way, the Schrödinger equation and the conjugated circuits model are on the same footing, one should keep in mind that the conjugated circuits model *serves* to help interpretation of some details of the calculations of the Schrödinger equation when applied to conjugated hydrocarbons! Hence, the Schrödinger equation is the *master*, and the conjugated circuits model is at best a *servant*. Our effort in this review on the aromaticity of conjugated hydrocarbons is to show that, when it comes to the aromaticity of conjugated hydrocarbons, the conjugated circuits model is not only a very good servant, but is also a master-servant.

The chemistry of fullerenes appears to continue to grow steadily. The aromaticity of fullerenes has been reviewed in the recent issue of *Chemical Reviews* on aromaticity in an article by M. Bühl and A. Hirsch, entitled "Spherical Aromaticity of Fullerenes".[676] The title immediately sends a message of unsuspected novelty that has opened with the recognition of buckminsterfullerene's spherical structure, which as Kroto suggested could be "*the first example of a spherical aromatic molecule.*"[771] We will only supplement this review by reporting on some aspects of fullerene aromaticity as described by the conjugated circuits model, as reflected in the works of Klein, Schmalz, and co-workers.[774−776] They performed conjugated circuits calculations on all isomers of buckminsterfullerene C_{60}, a total of 1812 isomers. The largest RE belongs to buckminsterfullerene, which is the only experimentally detected isomer. What is unique among the 1812 isomers is that buckminsterfullerene is the only isomer in which 12 pentagonal faces are disjoint, and it is also the smallest fullerene with "isolated" pentagons. In all other isomers, one or more pentagonal faces are adjacent. This has led Schmalz et al.[777,778] to propose the "isolated pentagon rule", which states that preferable fullerenes avoid geometrical forms in which pentagonal faces are adjacent, the so-called "abutting pentagons". Kroto[771] has also pointed out that polyhedra with abutting pentagons cause greater strain on the σ CC bonds. The "isolated pentagon rule" [777−779] was proposed "*in light of the conjugated circuit analysis of resonance energy, which shows that destabilizing conjugated eight circuits develop around the periphery of any two pentagons which have an edge.*" [779] Hence, adjacent pentagons are favored neither by σ bonding nor by π bonding. In fact, ab initio calculations performed by Cioslowski[780] suggested that each pentagon−pentagon contact decreases the stability by approximately 1.5 eV (which is about twice the stabilization produced due to the presence of an additional conjugated circuit R_1). Hence, it is not surprising to see that fullerenes with abutted pentagons are difficult to find, even though Pistoti et al.[781] have reported such in C_{36} fullerene.

Another interesting result of the analysis of fullerenes via the conjugated circuits model by Liu, Klein, and Schmalz[518] concerns fullerenes having from 60 to 100 carbon atoms, all having disjoint pentagonal faces. The article contains results for 1812 "isolated pentagon" rule fullerenes of 180 atoms, each a *leap-frog* of one of the 1812 C_{60} fullerenes. The leap-frog transformation, in its chemical context as a way of expanding fullerene frameworks to yield larger cages with specific electronic structure, was introduced by Folwer.[782] Before we define the leap-frog transformation, we will describe it on a transformation of dodecahedron to buckminsterfullerene. We start with a regular dodecahedron having 20 vertices which is built from 12 pentagons. We place at the center of each pentagon a vertex and connect it to the five vertices of the pentagonal face. In this way we introduced 12 vertices of degree 5, while the 20 initial vertices of dodecahedron, instead of being of degree 3, are now of degree 6. This operation is referred to as *capping*, and when it is applied to *all faces* of a polyhedron, it is referred to as *omnicapping*. The resulting polyhedron, all faces of which are triangles, is referred to as a *deltahedron*. Deltahedra are of considerable interest in the chemistry of polyhedral boranes and related molecules and graph theoretical characterization of possible three-dimensional aromaticity in boranes.[783−787] The omnicapping has transformed a dodecahedron having 12 faces to a deltahedron which has 60 triangular faces. A *dual* of this deltahedron produces the carbon skeleton of buckminsterfullerene with 60 vertices, 12 pentagonal faces (around vertices of degree 5), and 20 hexagonal faces (around vertices of degree 6). Hence, by successive application of (1) *omnicapping* and (2) *dualing*, we obtained from dodecahedron a polyhedron having 3 times more vertices. The process can be repeated over and over again, which creates from a fullerene having n vertices the next fullerene having $3n$ vertices. This process is referred to as leap-frog transformation, being reminiscent of children's play of hopping one over another. Hence, leap-frogging can be defined as follows:

Definition: *A leap-frog transformation represents omnicapping of a polyhedron followed by dualing, which results in a novel polyhedron having 3 times more vertices.*

Thus, from buckminsterfullerene we obtain fullerene having 180 vertices, then by repeating the process we obtain fullerene having 540 vertices, and so on.

Despite a scatter of computed RE values for fullerenes that did not offer a simple pattern Liu, Klein, and Schmalz[518] noticed that some fullerenes appear to have visibly higher RE than others. Upon inspection, they were able to characterize these somewhat "unusually" stable fullerenes as those structures for which one can draw Kekulé valence structure such that every benzene ring has three CC double bonds. In the case of benzenoid hydrocarbons, this was the case with compounds having a dominant (Fries) Kekulé valence structure, as shown in Figure 74 (except for benzo[*a*]pyrene and benzo[*e*]pyrene, for which it is not possible to have all rings shown as benzene Kekulé structures). Moreover, when one excises the carbon atoms of the 12 pentagonal faces, one obtains a collection of benzenoid fragments, all of which would classify as "fully benzenoid" hydrocarbons in the terminology of Clar. Liu, Klein, and Schmalz[518] refer to these unusually stable fullerenes as the "Clar sextet fullerenes". However, one should not confuse "Clar sextet fullerenes" with Clar structures of fullerenes, to be discussed in the next section.

The smallest of the Clar sextet fullerenes is C_{60} buckminsterfullerene, which when all 12 pentagons are removed leaves no fragments. As Schmalz pointed out, C_{60} buckminsterfullerene can be viewed as the first member of a family of the "Clar sextet fullerenes" having $(60 + 6n)$ carbon atoms, with $n = 2, 3, 4, ...$. It is interesting to observe the appearance of Clar's $6n$ π-electron rule in somewhat modified form. However, as Schmalz indicated, strain associated with σ CC bonds also is important for the stability of higher fullerenes, but the calculation of this strain apparently remains unsolved. Actually, curvature matching tells about this to a certain extent.[721,722] Thus, any speculation on the possible stability of higher fullerenes based solely on structural features resulting from interacting π-electrons will remain for a while — just an educated speculation.

Clar Structures of Buckminsterfullerene.

> *You know my methods. Apply them.*
>
> Conan Doyle[723]

Construction of Clar structures for fullerenes requires one to identify locations of aromatic π-sextets in a polycyclic structures having, besides benzene rings, additional pentagonal non-benzene rings. Clearly, only benzene rings could be the site of aromatic π-sextets. In buckminsterfullerene C_{60},

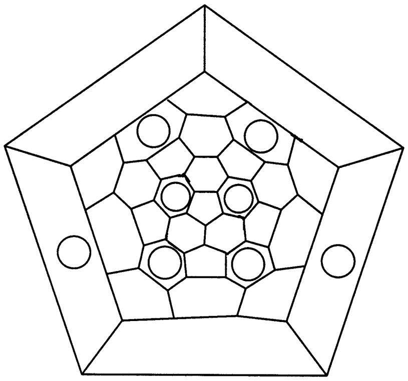


Figure 126. Clar's structure of buckminsterfullerene C_{60}, having eight (the maximal number) disjoint π-aromatic sextets.

there are 20 hexagonal rings, and as Figure 126 shows, we can place over the Schlegel diagram of C_{60} at most eight π-sextets. Observe that this optimal arrangement of aromatic π-sextets separates the sextets by naphthalene groups. If one tries to place sextets closer to each other to form locally the Clar formula of triphenylene, one finds that such a distribution would result in seven, not eight, π-sextets. Each local group of four π-sextets forms Clar structure for 1.2,7.8-dibenzochrysene, with the central CC bond as double. The Clar structure shown in Figure 126 is one of five possible symmetry-related Clar structures of C_{60}; thus, all π-sextets in buckminsterfullerene are in fact the migrating π-sextets. However, in contrast to most migrating π-sextets, which can "move" independently, all eight π-sextets of C_{60} have to move synchronously, just as has been the case with the three π-sextets of coronene.

A Clar structure with eight π-sextets requires 2^8, or 256, Kekulé valence structures. Five such structures therefore require at most 5 times more, that is, 1280. However, it is not difficult to see that each of the five symmetry-related Clar structures will contain, among those 256 valence structures, the unique Fries structure of C_{60} in which all CC bonds exocyclic to pentagonal faces are CC double bonds. This reduces the number of participating Kekulé valence structures to 1276 out of a possible 12 500 Kekulé structures of C_{60}, that is, just slightly above 1%.

Flocke, Schmalz, and Klein[788,789] reported on a variational resonance valence bond study on the ground state of C_{60} using the Heisenberg model. The Heisenberg model represents a valence bond method for π-electrons which includes electron correlation, which can be solved on the basis of Kekulé valence structures. This model, which consistently yields about 90% of the exact ground-state energy, is suitable for calculations on fullerenes. What is of considerable interest is that these authors found that, from the 12 500 Kekulé valence structures of buckminsterfullerene, a smaller set of 5828 valence structures already gives 99.82% of the energy of the full set of Kekulé structures. Hence, over half of all Kekulé valence structures of C_{60} contribute about 0.18% toward molecular energy!

The subset of 5828 structures that formed the basis for simplified calculations was selected by considering benzene rings of the Fries structure of C_{60} shown on the left in Figure 127 (which has 20 rings with Kekulé valence structure) and Kekulé structures obtained by rotating Kekulé benzene rings in disjoint hexagons in all possible combinations. Recall that this procedure in benzenoid hydrocarbons, as shown by Gutman and Randić,[209] would generate all Kekulé valence structures, but only if all conjugated circuits of different size were also considered. In the case of C_{60}, one obtains in this way only those Kekulé structures of C_{60} which have in their rings either three CC double bonds or two CC double bonds separated by a single CC bond. For instance, one cannot obtain in this way the anti-Fries structure of C_{60} shown in Figure 127 on the right, in which there are no hexagonal rings with three CC double bonds. Observe that in this structure the innermost pentagon and the outermost pentagon are the only pentagons with five exocyclic CC double bonds. Hence, there being 12 pentagons in C_{60}, the anti-Fries structure of buckminsterfullerene shown on the right in Figure 127 is one of six such symmetry-equivalent anti-Fries structures. Similarly, by rotation of CC double bonds within various hexagons of the Fries structure of buckminsterfullerene, one cannot obtain Kekulé structures of C_{60} with two CC double bonds separated by *two* CC single bonds, nor Kekulé structures with hexagonal rings with a single CC double bond or Kekulé structures with hexagonal rings without a single CC double bond, that is, hexagons with six exocyclic double CC bonds. The number of these structures that cannot be obtained by rotation of bonds within individual hexagons of the Fries structure of C_{60} is apparently 6672.

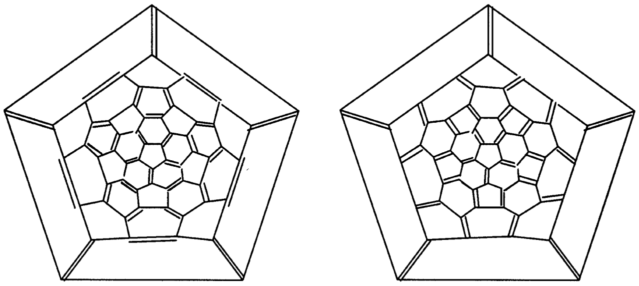


Figure 127. Fries and anti-Fries Kekulé valence structures of C_{60}.

The count of Kekulé structures which qualify as contributing significantly to the computation of the energy, as outlined by Klein et al.,[788] can be simplified by constructing a reduced dual of buckminsterfullerene structure in which only the 20 hexagonal rings are considered as vertices of a dual. In this dual, each hexagon is represented by a vertex placed in the center of the hexagon, and vertices belonging to adjacent hexagons are connected. As a result, we obtain the graph of dodecahedron (shown in Figure 128). The reduction of buckminsterfullerene to dodecahedron can be viewed as an "anti" leap-frog transformation, being the opposite (inverse) of the leap-frog transformation. The count of structures generated by simultaneously rotating *m* benzene rings of nonadjacent hexagons (where $m = 0, 1, 2, ..., 8$) is tantamount to the count of possible ways of selecting *m* vertices in dodecahedron so that no two are

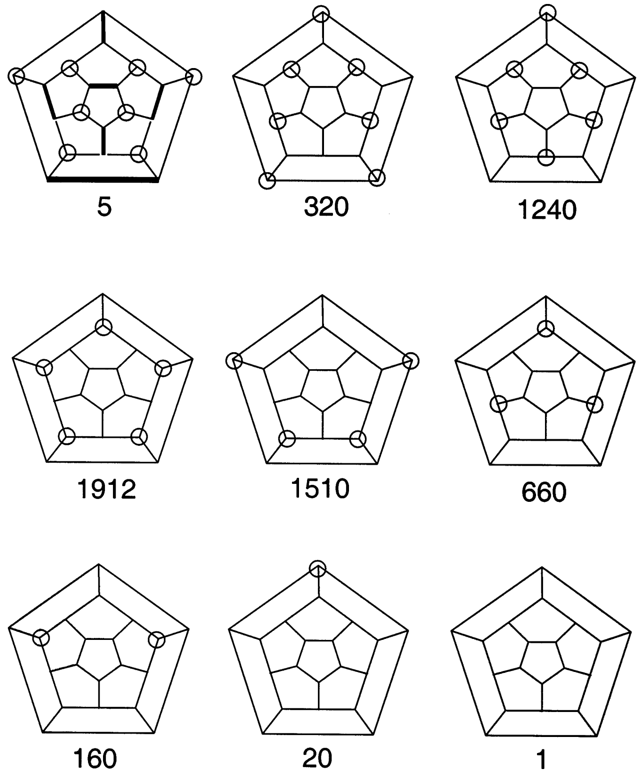


Figure 128. The dual of the hexagonal faces of the buckminsterfullerene structure and the count of Kekulé structures obtained by rotation of the CC double and CC single bonds within a single benzene ring of the Fries structure of C_{60} shown in Figure 127.

adjacent. In Figure 128 we have indicated these possibilities starting with the first dodecahedron that corresponds to five possible Clar structures of buckminsterfullerne. When all the numbers in Figure 128 are added, we obtain 5828, the subset of Kekulé structures which form the basis for the simplified calculations of Klein et al.[788]

In graph theory, a subset of disjoint vertices is known as an independent set of vertices:

Definition: *A subset S of vertices V of a graph is called an independent set of graph G if no two vertices of S are adjacent in G.*

Hence, Figure 128 at the same time illustrates for all possible values of *m* a single independent set, while the numbers under the dodecahedra give the total number of independent sets for dodecahedron. Thus, the construction and the count of independent sets represents an alternative approach to selecting the most important Kekulé valence structures of C_{60}. We may add that Gutman and El-Basil[790,791] were the first to recognize the relevance of independent sets for the theory of generalized Clar structures.

As already mentioned, finding all Clar structures in larger benzenoids,[792-795] such as the benzenoids of Müllen and co-workers, as well as fullerenes, requires some effort. A procedure for constructing such Clar structures for large benzenoids has been outlined[792] and is illustrated in Figure 129 on hexabenzocoronene. It starts with a single Clar structure, like the first Clar structure shown in Figure 129, and considers all possible "moves" for π-sextets on the "board" of fused hexagons representing the carbon skeleton of the benzenoid. We have shown only symmetry-non-equivalent patterns of π-sextets.

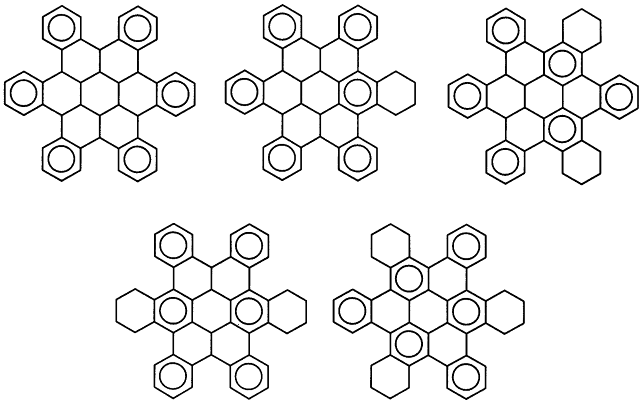


Figure 129. The five symmetry-unrelated Clar structures of hexabenzocoronene.

Flocke et al. have pointed out that, in the terminology of VB calculations, the subset of 5828 Kekulé structures "*has the important property that each Kekulé function in it may be chosen with a sign such that it has positive overlap with all other functions*" of the subset.[788] In this way the selected Kekulé structures enter the ground-state wave function with positive coefficients. This can always be done for alternants, but need not follow for non-alternants, "*and indeed cannot be done for the full set K of C_{60}.*" [788] Flocke et al. summarized their result by stating that the Kekulé basis of C_{60} could be separated naturally into two sets, the dominant set of 5828 Kekulé structures and the not so important set of 6672 Kekulé structures, suggesting that the resonance theoretic ideas developed for organic hydrocarbons could work for fullerenes as well. In simple language, this indicates that the concept of the aromatic sextet plays an important role in C_{60}. In view of this important classification of Kekulé structures of fullerenes (and other non-alternant conjugated systems) into major and minor groups, it seems fitting to give to these two groups appropriate names, and we suggest that the first be referred to as the "generalized Clar structures" of fullerenes, while the second group can be referred to, in analogy with anti-Fries structures of benzenoids, as the "anti-Clar structures" of fullerenes, and in general non-alternant non-benzenoids.

It is clear that by rotating CC double and single bonds within the benzene hexagons of the Fries structure, the number of aromatic π-sextets remains the same, but the number of R_1 conjugated circuits, which in the case of the Fries structure of C_{60} is 20, may vary considerably among different Kekulé structures. By rotating CC bonds in a single hexagon of the Fries structure of C_{60}, the number of R_1 conjugated circuits is already reduced by 3. The calculations made by Flocke et al.[788] on buckminsterfullerene, which have shown that not all Kekulé structures make an important contribution to molecular energy, suggest that the next VB study of interest may be one in which calculations of contributions to the molecular energy are restricted solely to Clar structure (those 1276 structures), a subset of the subset of generalized Clar structures. Clar structures may not suffice to give satisfactory molecular energy but are expected to give satisfactory resonance energy, which is the quantity of interest in characterization of the degree of aromaticity of organic compounds. Accurate VB calculations, such as those of Klein et al. based on the Heisenberg Hamiltonian framework, and also those calculations of Jiang and collaborators mentioned earlier, may offer some insights into the role of Clar structures and generalized Clar structures, that is, the Clar structures with the lesser number of aromatic π-sextets, in the estimation of molecular RE. Equally, it seems of interest to revisit benzenoid hydrocarbons and apply the same methodology to the subset of Kekulé valence structures defined by the procedure that starts with the Fries structure and considers rotations of CC bonds within different sextet rings analogous to those described by Flocke et al. on C_{60}.

We have presented so far the Clar structure for a single fullerene, C_{60}, which as we have seen is not unique, there being five symmetry-equivalent such structures. A fullerene that has a unique Clar structure in which all carbon atoms are spanned by π-sextets has been referred to as "a perfect Clar structure" by Fowler and Pisanski.[796] Hence, "perfect Clar structure" for polyhedral graphs is one in which all carbon atoms belong to one of numerous π-aromatic sextets, no two aromatic π-sextets are adjacent, and no CC bonds appear as C=C double bonds. For fullerenes this means that all pentagonal faces are necessarily "empty" faces, and in addition a number of hexagonal faces are also "empty", analogous to the case of the "fully benzenoid" hydrocarbons of Clar. According to a theorem of Folwer and Pisanski, "*A trivalent polyhedral graph has perfect Clar structure if and only if it has a Fries structure.*"[796]

This theorem is interesting in that it combines the almost forgotten Fries structures with the leap-frog transformation in extending characterization of larger fullerenes on the basis of smaller ones. As Dias has shown,[797] leap-frogging, although initially designed as an operation on fullerenes, can also be applied to benzenoid hydrocarbons. In such cases, only the internal faces are capped and instead of duals, only the so-called inner dual is considered (which excludes the exterior of the benzenoid to be viewed as a face). Leap-frogging of a benzenoid in this way always generates "fully benzenoid" hydrocarbons, but the reverse need not hold: not every fully benzenoid hydrocarbon is a leap-frog. According to Fowler and Pisanski, in the case of fullerenes, all Clar fullerenes are leap-frogs. These authors came up with a number of interesting propositions concerning fullerenes and more general Clar type polyhedra (or maps), which are defined as a collection of faces whose boundaries form a 2-factor of a map. This means that one can select a set of faces which are disjoint and which cover all vertices of the map. For such polyhedra the following propositions (or theorems) are true:

Proposition 1: *A trivalent polyhedral graph has a perfect Clar structure if and only if it has Fries structure.*

Proposition 2: *If a trivalent map has perfect Clar structure, then all odd faces belong to it.*

Proposition 3: *Each trivalent map with odd faces has at most one perfect Clar structure.*

Proposition 4: *For a trivalent map, any two perfect Clar structures either completely coincide or have no face in common.*

Proposition 5: *If a trivalent map has two odd faces sharing an edge, then such a map does not have a perfect Clar structure.*

The main reason to mention perfect Clar structures is to draw the attention of readers to *different* definitions used here by Fowler and Pisanski, *different* classifications of Clar cages by Flocke, Schmalz, and Klein,[788,789] and *different* definitions of Clar structures of fullerenes as we have outlined at the beginning of this section. Upon closer examination, we expect readers to agree that our approach is the only one that truly extends the spirit of the π-aromatic sextets of Clar from benzenoid hydrocarbons to fullerenes. That does not make the alternative approaches, which are equally legitimate, less worthy, as each of them serves its own purposes — but readers should be alerted in advance and should be spared possible confusion due to use and promotion of the name of Clar in several different conceptual connections. Observe that in our definition of the Clar structure of fullerene, only hexagonal faces can be the site of aromatic π-sextets, but that is not the case in the approach of Fowler and Pisanski, where pentagonal faces play a role similar to that of hexagonal faces.

XXXV. Challenges and Unsolved Problems

> *... the discovery by Thiele in 1900 of the cyclopentadienide anion was a remarkable seed, the descendants of which continue to produce good crop .... The remarkable stability of the $C_5H_5^-$ ion with its six π-electrons has been abundantly considered one of the large blocks supporting the theory.*
>
> W. von E. Doering[798] (See ref 200 in this review for a citation of Thiele's work.)

If a reader got an impression after coming to the end of this review that concerning aromaticity, at least in the case of polycyclic conjugated hydrocarbons, things have now been settled, then I must have failed in not sufficiently emphatically stressing numerous challenges, theoretically unsettled topics, and open problems.

A. Challenges

(1) We have considered here only neutral conjugated hydrocarbons, leaving out charged polycyclic conjugated ions as well as heterocyclic conjugated cyclic and polycyclic compounds. Charged polycyclic conjugated ions and heterocyclic conjugated compounds are beyond the scope of this review. If one were to extend the present considerations to such systems with a desire to arrive at quantitative rather than merely qualitative results, one would need good-quality quantum chemical results for numerous compounds which are currently not available. Aro-

maticity of charged polycyclic conjugated ions and heterocyclic conjugated cyclic and polycyclic compounds presents a challenge that should be taken up. Let us only mention that some exploratory graph theoretical studies[799−804] have been reported on charged polycyclic conjugated ions and heterocyclic conjugated cyclic compounds, polycyclic compounds, and radicals.

In comparison with calculations on benzenoids and a selection of non-benzenoids, the major disadvantage of extending the approach of conjugated circuits to charged molecules is the occurrence of a large number of “ionic” Kekulé structures that need to be analyzed. For example, the cation described by M. S. Newman,[805] having 20 π-electrons, of which 14 form a peripheral ring and 6 contribute to the π-electron inner ring, has 90 ionic Kekulé valence structures. [799] This can be compared with the number of Kekulé valence structures of neutral benzenoids of a similar size, which is at most 20 (e.g., coronene). In addition, it is needless to say that such extensions would require their own (reliable) parametrization in order to produce acceptable RE values, and we may add that no such reliable parametrization is available today.

(2) A relatively reliable estimate of RE for non-benzenoid compounds is needed. One way to arrive at such an estimate is to perform quantum chemical calculations of higher quality (not necessarily of ab initio type) for two dozen non-benzenoid compounds. The challenge here for theoretical chemistry is not so much in making quantum chemical calculations as such, but in being able to *extract* from such calculations an inherently consistent non-observable, known as RE. This would then facilitate parametrization of contributions of 4*n* conjugated circuits. Individual calculations, especially made on a few molecules and with different assumptions, as we have seen already in the case of benzenoid systems when using conjugated circuits for diagnostic purposes, may yield internally inconsistent parametrization.

(3) We consider it a challenge to extend the approach of Polansky and Derflinger[582] to obtain contributions of MO’s in different conjugated circuits. The first stage of this problem could be just to consider benzene rings (i.e., conjugated circuits R_1) and then make some analogy with the work of Ham, Ruedenberg, and Platt[171−173] when relating Coulson MO bond orders with Pauling bond orders. For example, following Polansky and Derflinger,[582] one obtains MO contributions to individual benzene rings of polycyclic systems by using the corresponding benzene orbitals instead of atomic orbitals. If one would divide such contributions by the orbital eigenvalue, one may get a VB equivalent of Polansky and Derflinger’s MO ring indices.

(4) Finding conjugated circuits and enumerating linearly independent conjugated circuits in benzenoid hydrocarbons is not so difficult, but this need not be the case with non-benzenoid hydrocarbons. Consider, for example, the two non-benzenoids structures **9/89** and **10/89** shown in Figure 85, which have only 9 and 14 Kekulé structures, respectively. While finding all Kekulé structures is rather simple, finding all conjugated circuits (8 in the case of **9/89** and 13 in the case of **10/89**) requires some attention, and finally finding which conjugated circuits make a linearly independent set is even harder. We illustrate in Figure 130 decomposition of one of the 14 Kekulé structures of **10/89** into conjugated circuits, which we labeled A−M. We know that among the 13 diagrams there are 9 linearly independent conjugated circuits, but it may take some effort to establish the combinations that produce, upon superposition, the same conjugated circuits. It is apparent that L = A + B and M = C + D, but we also have E + F = C + G and J + K = M + L, which is not necessarily so readily visible. To find an efficient algorithm that will search among possible combinations of circuits, those that are linearly dependent combinations may present a challenge, though advantage may be gained here by adopting some techniques known in chemical documentation relating to SSSR (the search for the smallest set of smallest rings).

(5) Following the work of Klein and collaborators on “preferred” Kekulé valence structures in fullerenes, which has shown that about 50% of well-selected Kekulé valence structures can account for approximately 99% of the molecular energy, it seems very desirable to extend such calculations to benzenoid as well as non-benzenoid hydrocarbons in order to find if similar results could be obtained. The “preferred” structures (which can be generated from the Fries structures of such molecules) appear to represent a model that is “half-way” between the standard use of all Kekulé valence structures and Clar’s π-aromatic sextet model.

B. Unsolved Problems

(1) While there are several standard quantum chemical methodologies to obtain reasonably accurate wave functions and total molecular energy, there is no standard scheme available yet to obtain molecular resonance energy (RE). For characterization of aromaticity, it is essential to obtain a reasonably accurate ansatz for RE. For example, there is no doubt that the VB calculations of Alexander and Schmalz[39] and Jiang and co-workers[37,38] are of high accuracy concerning the total molecular energy, but the same calculations may, at least in some molecules, lead to different RE values if different scheme for calculation of RE are considered. Is there a preferred scheme, and if so, what is it?

(2) Can more elaborate VB calculations (those that are above the resonance theory of Herndon in the diagram shown in Figure 50, which represents the hierarchical relationship between different VB models according to Klein et al.[7,534]) be cast in an alternative but mathematically equivalent formalism based on the decomposition of Kekulé valence structures in conjugated circuits, rather than using Kekulé valence structures?

(3) As outlined by this author and collaborators,[806] one can consider and enumerate conjugated circuits in valence structures of “higher degree of excitation” (as referred to by G. Wheland[129]) for polycyclic conjugated hydrocarbons. Besides the fact that such enumerations are rather tedious and error prone when made by examination of individual excited

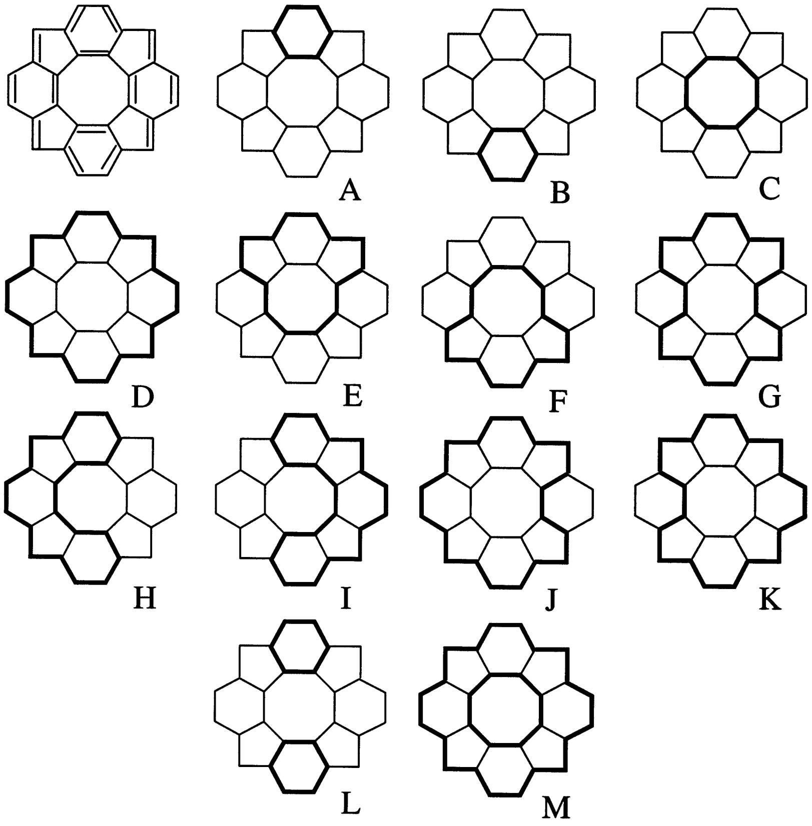


Figure 130. Decomposition of a Kekulé structure of a larger non-benzenoid into conjugated circuits.

valence structures, the number of excited structures is given by Catalan numbers and increases fast (as mentioned earlier in the sections Valence Bond Theory Versus Molecular Orbital Theory and Benzenoid Hydrocarbons Revisited and in GUGA accurate VB calculations). However, currently there is no known algorithm that would make it possible to delegate enumeration of conjugated circles in excited structures to computers, which would be very desirable.

(4) Construction of Kekulé valence structures for non-benzenoid hydrocarbons is straightforward, as it can be performed by using or modifying the existing algorithms that are valid for polycyclic benzenoid systems. However, enumeration of conjugated circuits in such systems is already more demanding. Even more tedious is finding combinations of conjugated circuits that are linearly dependent. Theoretically, this can be accomplished by using the exclusive/or command that has been useful in finding the set of smallest independent rings in polycyclic systems, but a procedure that would implant this specifically for conjugated circuits remains yet to be proposed. A related and possibly even more difficult task is to find a procedure to establish the degree of freedom of individual Kekulé valence structures in larger non-benzenoid polycyclic conjugated compounds. Solving this problem will, for example, facilitate construction of Clar sextet structures for fullerenes. In the case of benzenoids, we have seen that *df* is given by the largest number of disjoint conjugated circuits. This is, however, not the case for non-benzenoids. For example, the Kekulé structure shown in Figure 130 has at most two disjoint conjugated circuits but $df = 3$.

(5) As mentioned in the text, on a few occasions it is desirable to obtain better values for graph theoretical parameters R_n and Q_n, corresponding to the contributions of $4n + 2$ and $4n$ conjugated circuits toward molecular RE, respectively. Equally it is desirable to obtain values for graph theoretical parameters R_n* and Q_n*, corresponding to the contributions of $4n + 2$ and $4n$ conjugated circuits toward molecular RE when only Kekulé valence structures of the maximal degree of freedom are used as the basis for evaluating molecular RE.

XXXVI. Concluding Remarks

> *... a new scientific truth does not triumph by convincing its opponents and making them see the light, but rather because its opponents eventually die, and a new generation grows up that is familiar with it ...*
>
> Max Planck[674]

Extension of the conjugated circuits model to both ions and heteroconjugated systems has to await calculations from other sources. The challenge, hence, is presented to theoretical quantum chemists to rise to the occasion and offer very reliable computations on molecules of interest that could serve as standards for parametrization of various graph theoretical quantities. Assuming that such calculations are available (and some have been available), the challenge is in *partitioning* computed quantities and arriving at RE in a way analogous to the earlier work of Dewar and de Llano. Such work will no doubt bring again discussions of how to extract from computed data a non-observable quantity such as RE. But theoretical chemists have in the past manipulated various non-observables (e.g., bond orders, bond dipoles, atomic charges, atom−bond polarizabilities, etc.), so there is no reason not to re-examine alternative routes to RE.

Indeed, we have been consumed in this review with hydrocarbons, as if other kinds of molecules do not exist. But to repeat what was stated at the beginning, the reason for such “limited” concern is the belief that *unless and until we all agree on what is aromaticity for hydrocarbons, we are not likely to agree on more complex systems*, such as conjugated ions and heteroconjugated systems. It is not that this author and others involved in the development of graph theoretical approaches to chemistry have been so much infatuated with hydrocarbons, but one may say that hydrocarbons offer enough diversity and enough material where one can test new “tools”. This “preoccupation” with hydrocarbons may have led to an impression that chemical graph theory is limited to hydrocarbons and cannot be extended beyond hydrocarbons. This is not correct, even though occasionally we in chemical graph theory were “accused” of giving preference to hydrocarbons, which comprise hardly 1% of chemistry. What has been overlooked is that chemical graph theory has made and is making important *conceptual* advances in tracing structural factors responsible for specific molecular properties.

In summary, one can say that chemical graph theory has an outstanding past, a rich present, and a promising future, despite past, present, and possibly future misunderstanding. As E. B. Wilson pointed out, concerning “novel” disciplines:[208]

> *The most rewarding work is usually to explore a hitherto untouched field. These are not easy to find today. However, every once in a while some new theory or new experimental method or apparatus makes it possible to enter a new domain. Sometimes it is obvious to all that this opportunity has arisen, but in other cases recognition of the opportunity requires more imagination.*

Chemical graph theory, strictly speaking, is not *a hitherto untouched field*, but there have been too few willing to travel its uncharted paths. On this note, which implies that advances in *computational chemistry* alone are not enough for progress, not only in chemistry but also in theoretical chemistry, and that *conceptual* aspects of modeling are at least as important, we end this provocative review on aromaticity expecting anger and pleasure to be mixed in the minds of readers, hopefully more pleasure than anger.

XXXVII. Epilogue

> *If a man does not keep a pace with his companions, perhaps it is because he hears a different drummer. Let him step to the music he hears, however measured or far away.*
>
> Henry D. Thoreau[807]

We started this review with a brief discussion of some apparent dilemmas that we face in chemistry: qualitative versus quantitative approaches, observables versus non-observables, structural criteria versus properties as criteria for characterization of aromaticity, chemical graph theory versus quantum chemistry, Clar $6n$ rule versus Hückel $4n + 2$ rule, and hydrocarbons versus heteroatomic systems. As we have seen, most of the mentioned dilemmas are man-made and reflect inbred biases of different circles of chemists. It is not uncommon to come across critics with strong opinions and weak arguments, and it would be a waste of time to try to point out to them “the other side of the coin”. Max Planck apparently experienced difficult times before his quantum constant was accepted, as is reflected in the following quotations:[674]

> *A new truth always has to contend with many difficulties; if it were not so, it would have been discovered much sooner.*

> *... a new scientific truth does not triumph by convincing its opponents and making them see the light, but rather because its opponents eventually die, and a new generation grows up that is familiar with it ...*

As we have seen, Planck has been vindicated. It is my expectation that Clar’s views will be similarly vindicated. It is not that Clar does not have followers, because as we have seen he does. The criticism is more directed to theoretical chemists, and to be more precise to theoretical quantum chemists, rather than to experimentalists. Appalling is the *indifference* that theoretical chemists have shown toward Clar’s empirical ideas on some aspects of the structure of benzenoid hydrocarbons. If Clar is wrong, the why do we not see arguments that show that this is the case? If Clar is not wrong, then why we do not see arguments that support his “case”?

We have arguments based on theoretical considerations that support Clar’s π-aromatic sextet model, such as those based on computed ring RE. An additional argument followed from the analysis of computer RE by Jiang and Li. Finally, an examination of biphenylene derivatives strongly supports that Clar’s model can be extended to non-benzenoids. However, there are additional experimental data that strongly support Clar’s model. The fact that bent [n]-phenylenes are stable is one such strong argument. In addition, we may mention data on the triplet zero-field-splitting parameters for aromatic hydrocarbons which have been successfully interpreted in terms of local benzenoid characteristics by Voitländer, Bräuchle, and co-workers.[808,809]

Apparently, there is yet another dilemma that confronts chemistry: modeling versus non-modeling. Models are, by definition, based on selective approximations, while in contrast non-modeling in our context is represented by ab initio calculations. That ab initio calculations have merits is well known. See Table 51 for an overview of the evolution of Gaussian computations as advertised in the mid-1990s by Gaussian, Inc. (Pittsburgh, PA). Even a laic who may not appreciate the high level of computations will be impressed. But there is also "the other side of the coin" that is worth observing. Because few have the courage to look in the "wrong" direction, to hear a different tune, it is not surprising that many theoretical chemists are not aware that numerous *concepts* used in quantum chemistry are in fact of graph theoretical origin. That is, they are fully defined solely from considerations of topological and combinatorial properties of molecules!

A. Quantum Chemical and Graph Theoretical Analysis of [*n*]Phenylenes

> *To calculate a molecule is not to understand a molecule.*
>
> R. G. Parr[810]

> *From much empirical experience, a little simple theory, chemists have gained much intuitive knowledge of the what, how, and why molecules hold together. To put it provocatively as I can, our physicist friends know better than we how to calculate the electronic structure of a molecule or solid, but often they do not understand it as well as we do ...*
>
> R. Hoffmann[811]

The other illustration that we would like to cite concerns properties of biphenylene and several structurally related compounds. By using a semi-empirical AM1 approach, Kovaček and collaborators[743] included naphthalene as a reference molecule in their study. We would like to comment briefly on their discussion of naphthalene and bent [3]phenylene. Their calculation of CC bonds in naphthalene agrees well with available experimental data reported by Brock and Dunitz[812] that show slightly increased CC double bond character for bond 1,2. This is how the authors comment on that:[743]

> *It is interesting to note that naphthalene can be considered as a fused system composed of two annelated benzenes. Since the bond angles are very close to 120°, there is no significant angular strain involved in this molecule. Hence the distance variations in* **1** *[naphthalene] is entirely due to interactions between π-electrons. If one benzene is considered as the original π-electron aromatic sextet, then perturbation exerted by the additional four electrons results in shifting the π-density to a peripheral part of benzene thus forming a cis-1,3-butadiene-like fragment as evidenced by the π-bond orders. The choice of one ring as benzene and the other as perturbation caused by annelation is of course arbitrary and one could do it the other way round. Consequently, the whole picture is symmetric relative to the mirror plane passing through the central atoms ...*

The reason for citing this lengthy section on naphthalene is to point out that all that is said above could be said in a much shorter way by simply presenting the Clar structure of naphthalene, which has a single π-aromatic sextet, that can "migrate" from one ring to another. But there is no mention of Clar in this work, even though the concept of the π-sextet has been explicitly referred to! There is also no mention of Fries structure, even though it was depicted. Finally, there is no mention of Pauling bond orders, which account for the major aspects of variations of CC bonds in naphthalene. This all could be deliberate or accidental, but it illustrates a lack of familiarity among some theoretical chemists with the basic ideas of chemical graph theory. The Clar structures, the Fries structure, and the Pauling bond orders are all intimately connected to combinatorial and topological properties of molecules — and can be thus obtained from molecular graphs without AM1 computations! The results of the particular calculations are nevertheless useful beyond the apparent intentions of the authors, because the agreement of AM1 calculations on naphthalene with the characterization of naphthalene as given by graph theoretical analysis clearly points to the ability of the AM1 method of Dewar to correctly account for some combinatorial and topological properties of benzenoid hydrocarbons. We have seen earlier in this review that a number of semi-empirical MO theories *failed* in this respect (see Table 31).

There is one additional point to be raised in connection with this paper, in which, after naphthalene, biphenylene and [3]phenylenes were studied. After a detailed analysis of the strain and rehybridization caused by the presence of fused four-member rings in biphenylenes, the authors found bent [3]phenylene was slightly more stable than linear [3]phenylenes. The decomposition of these compounds in conjugated circuits (Table 35) shows that RE (when based on all Kekulé valence structures) is larger for linearly fused [*n*]phenylenes in comparison with angularly fused isomers. This "disagreement" between the two approaches is thus characterized:[743]

> *Competitive interactions between the increase in aromaticity and the decrease in angular strain and antiaromaticity in fused planar systems provide an interesting challenge for future investigations.*
>
> *As a corollary one can reiterate once again a caveat against the uncritical use of graph-theoretical indices in estimating aromaticity in general and the application of the "conjugated circuit" model in particular. The latter yields incorrect results even for π-electrons in planar systems involving fused six- and four-membered rings and the important role of the σ-electrons is completely neglected.*

One may wonder who is being uncritical, who is using graph theoretical models uncritically. Those who are trying to find contributions to RE due to π-electron interactions? Or those who are extending graph theoretical concepts to situations for which they were not intended? Surely, the overall stability of strained structures will depend among others also on the *strain* energy, whether it is cyclopropane, biphenylene derivatives, or fullerenes. An estimate of strain energy, molecular geometry, bond lengths, and bond angles is within the realm of quantum chemistry. Numerical calculations of molecular en-

Table 51. Development of Computational Capabilities of the ab Initio Commercial Computer Package Gaussian from 1980 to 1994[a]

Gaussian 80	**Gaussian 82**	**Gaussian 86**	**Gaussian 88**
numerical SCF SCF minima MP2 + MP3 + CI HF stability	analytic SCF numeric MP2 MP4	IR and Raman intensities polarization hyperpolarization	multiple moments electron density direct SCF energies and gradients
Gaussian 90	**Gaussian 92**	**Gaussian 94**	
excited states reaction paths direct SCF frequencies direct MP2 energies	Onsager solvent effects 3-D electrostatic potential semi-direct MP4	Kohn−Sham stabilities MNR shielding tensors electron affinities cavity solvent effects analytic excited states	

[a] The Gaussian programs are produced by Gaussian Inc., Pittsburgh, PA.

ergy are also in the domain of quantum chemistry. But calculations of molecular RE are always model-dependent. Conjugated circuits offer for polycyclic conjugated compounds one such model based on *additive* properties of RE that has been totally unknown to quantum chemists, a model that is clearly beyond the first principles of quantum mechanics. This model is suitable for VB calculations but is not the only graph theoretical model for calculation of RE. TRE described by Trinajstić and Aihara is related to calculations of RE from MO calculations. What models for RE are available from quantum chemistry circles? Graph theoretical considerations have led to the additivity of RE in terms of conjugated circuits − a concept unknown in traditional quantum chemistry. In this connection it may be mentioned that the Pauling bond orders, although first found in the early quantum chemical calculations, nevertheless are conceptually pure graph theoretical quantities. This is one of many facts pertaining to graph theory that many quantum chemists are not aware of. Hence, the dilemma is not quantum chemistry *or* graph theory, as some would like to simplistically ask in considering occasional disagreements in the predictions of different models, but the answer is quantum chemistry *and* graph theory. The disagreements between different models should not be overlooked but should properly be *interpreted* within the particular molecular models. The finding by Kovaček et al.[743] that the conjugated circuits model failed to proper predict the relative stability of linear and bent [3]phenylenes may indicate either (1) that *additional* structural factors beyond graph theory are responsible for the stability in these molecules or (2) that not all Kekulé structures used in computation of RE make equal contributions.

Kovaček *et al.* may have been successful in pointing out that re-hybridization and the strain associated with the presence of the four-member rings are such important factors. However, their concluding remark, "*The oversimplified graph-theoretical approach based on 'conjugated circuits' fails completely*" in reproducing the relative stability of linear and bent [3]-phenelyne, is not in order. Resonance energy makes but a contribution to the stability of [*n*]phenylenes. Hence, the prediction that bent [3]phenylene is more stable than linear [3]phenylene, if this indeed is the case, does not reflect limitations of the conjugated circuits model. It rather illustrates a failure of those making such claims to keep track of the basic premises of distinct mathematical models of chemical structure. Kovaček et al. failed to recognize that graph theory is concerned with *topological* and *combinatorial* properties of molecular structure. Molecular resonance energy, as the model of conjugated circuits has shown, has combinatorial and topological origin, and hence regularities in RE can thus be illuminated by the conjugated circuits approach. Variations in hybridization and variations in molecular geometry are sensitive to molecular overall energy, and as such are *outside* the domain of chemical graph theory.

Trying to blame a model for not achieving a goal that is outside its domain is, according to Damer,[91] a reflection of "faulty reasoning". As Damer has pointed out, "neglect of relevant evidence" and "assignment of irrelevant goals" are among frequent errors in reasoning. The first usually appears in arguments that ignore the importance of evidence unfavorable to one's position. The second appears as a "criticism" of a program because it does not achieve goals that it was not designed to achieve. To view graph theoretical models as "oversimplified" or "primitive" reflects rather an unfamiliarity of some chemists with the complexities accompanying combinatorial and topological properties of chemical structures. It may also reflect ignorance and a lack of the imagination that is required if one is to bridge the gap between "traditional" and "innovative" modeling in chemistry. Recall the quotation of Wilson:[208]

> *... every once in a while some new theory- ... makes it possible to enter a new domain. Sometimes it is obvious to all that this opportunity has arisen, but in other cases recognition of the opportunity requires more imagination.*

It is fitting to end these misunderstandings about the role of graph theory in chemistry by citing a statement made by the late Professor Hirschfelder,[813] found in his book entitled *My Adventures in Theoretical Chemistry*:

> *Unfortunately, now there are too few theoretical chemists with sufficient vision to take a giant step of exploring completely new techniques. Instead, scientists in the 1980s get so immersed in a maze of computational detail that they lose sight of the simple, elegant theories.*

B. Clar Structures for Non-benzenoid Hydrocarbons

> *Too often scientists ignore the work of others.*
>
> R. G. Parr[810]

Here we will briefly advocate extension of Clar formulas to biphenylene derivatives. However, we ought to point out that Clar himself already viewed biphenylene as a non-benzenoid with two aromatic π-sextets.[814] He also briefly discussed linear and bent derivatives of biphenylene, compounds 2−6 illustrated in Figure 66, in which there are migrating π-sextets within annealed naphthalene moieties. According to Clar,[814] "*the central four-membered ring is not completely void of p-electrons. There are indications of a weak ring current in this ring*." Clar cites here the works of Katritzky and Reavill,[815] and Jones and Grant.[816] In continuation, he stated: "*There is also some degree of aromatic conjugation through this ring because an annellation effect can be recorded in the electronic spectra for the series **1/66**, **2/66** and **4/66** as shown by the shift of the β bands. This effect is bigger in the series **1/66**, **3/66** and **6/66**. In accordance with this latter hydrocarbons are more reactive then the linear ones*." (Numbers have been changed to correspond to the numbering in the current review.) Clar cites here the works of Cava and Napier,[817] and Cava and Stucker.[818] Clar then points out that "*This is in contrast to the acene series. These shifts are small by comparison with the acene and phene series*." [814] Thus, Clar already had idea of extending the model of aromatic sextet to non-benzeneoid. We hope here to briefly add arguments that support Clar's intentions. Observe that the above qualitative characterization of linear and bent biphenylene derivatives parallels the conclusions based on conjugated circuits, which also predict linear biphenylene derivatives to be less reactive ("in contrast to acene series").

Let us use the "criticism" on the conjugated circuits model by Kovaček et al. to point out how inadvertently, and most likely against the desire of the authors, this particular calculation on [3]phenylenes offers significant support for Clar's π-aromatic sextet and the model of conjugated circuits, particularly when applied to non-benzenoid derivatives of biphenylene. What in fact these authors have shown is that essentially the bent and the linear [3]phenylene have approximately the same relative stability. If we now wish to extend the Clar's notions on aromatic π-sextets to non-benzenoid derivatives of biphenylene, we have to ignore the Kekulé valence structures of low degrees of freedom. But, as we have discussed in section XXXII.B, Biphenylenes Revisited, in such situations all isomers of [*n*]phenylene have the *same* RE. Hence, both the linear and the bent [3]phenylene are predicted by Clar's model and the conjugated circuits model to have *approximately* the same stability. Since the changes due to re-hybridization and the strain due to bent bonds associated with four-member rings can be assumed to be approximately the same in linear and bent [*n*]phenylenes, we may interpret the results of Kovaček et al. as an independent quantum chemically based support that suggests that, indeed, the Clar formalism may be extended to non-benzenoids, biphenylene derivatives in particular. This is a welcome result that we hope will be confirmed by even more rigorous calculations in the future.

As we have seen from the above discussion of bent [*n*]phenylenes, the fact that a quantum chemical calculation suggests that such structures are stable is a welcome argument that favors extension of the Clar aromatic π-sextet beyond benzenoid hydrocarbons, for which it was designed, to non-benzenoid hydrocarbons. However, regardless of the sophistication of theoretical calculations, quantum chemical calculations are not a substitute for experimental evidence. The alternative models based on the count of conjugated circuits in all Kekulé valence structures and only those in valence structures of maximal degree of freedom suggest different outcomes regarding the stability of bent [*n*]phenylenes. The first alternative results in a progressive decrease of molecular RE for bent [*n*]phenylenes. In contrast, the stability of linear [*n*]phenylenes under the same assumptions remains rather constant, that is, independent of *n*, as can be seen from Table 25 and the calculations reported by Trinajstić et al.[819] The second alternative is to consider only Kekulé valence structures of the maximal degree of freedom, which is tantamount to extending the Clar aromatic π-sextet to non-benzenoid hydrocarbons. In this case we see that the molecular RE for bent [*n*]phenylenes remains fairly constant for both the bent [*n*]phenylenes and linear [*n*]phenylenes. Moreover, the two have the same molecular RE. On the other hand, Clar's comment that "*there is some degree of aromatic conjugation*" through the central four-membered ring may suggest that the dominant role in characterization of non-benzenoids is played by the Kekulé valence structures of the maximal degree of freedom, while the remaining Kekulé structures may still make some contribution to slightly reducing the molecular stability.

In view of this, the synthetic achievements of K. Peter C. Vollhardt of the University of California, Berkeley, and co-workers[820−822] are remarkable for two reasons: On one hand, from the experimental point of view, they show the resourcefulness of synthetic chemists in achieving the almost "impossible", and on the other hand, from the theoretical point of view, they offer a proof "beyond the reasonable doubt" that Clar's model of aromatic π-sextets extends to non-benzenoid hydrocarbon chemistry.

In chemistry, priority is to be given to experimental facts, not to calculations. Clar has offered experimental facts to support his model of the aromatic π-sextet, but as we know, theoretical chemists have for the most part ignored his works. Recall the opening remark by R. G. Parr in this section. That is what has happened to Clar's aromatic π-sextet. Now, with the synthesis of helical [*n*]phenylenes by Vollhardt and co-workers, we may expect additional quantum chemical computations from theoretical circles. These are welcome. However, to fully appreciate the conjugated circuits model and the work of Clar, and to accept his model of the aromatic π-sextet, apparently requires some imagination, or at least a

Table 52. Expressions for RE for [*n*]Phenylenes, RE (in eV), and REPE Using Only Kekulé Valence Structures of the Highest Degree of Freedom[a]

n	only Kekulé structures of maximal *df*	RE	RE/sextet
1	$2R_1/2$ (benzene)	0.841	0.841
2	$(8R_1 + Q_1 + 2Q_2 + Q_3)/4$	1.390	0.695
3	$(24R_1 + 4Q_1 + 8Q_2 + 4Q_3)/8$	1.938	0.646
4	$(64R_1 + 12Q_1 + 24Q_2 + 12Q_3)/16$	2.487	0.622
5	$(160R_1 + 32Q_1 + 64Q_2 + 32Q_3)/32$	3.035	0.607
6	$(384R_1 + 80Q_1 + 160Q_2 + 80Q_3)/64$	3.584	0.597
7	$(896R_1 + 192Q_1 + 384Q_2 + 192Q_3)/128$	4.132	0.590

[a] $R_1 = 0.841$ eV, $Q_1 = -0.650$ eV, $Q_2 = -0.260$ eV.

willingness to accept that "... *when you have a deep truth* (a quantum chemical model), *then the opposite of the deep truth may again be deep truth* (Clar's aromatic π-sextet)".

In Table 52 we have collected the expressions for RE for [*n*]phenylenes and show the RE as well as REPE, all based only on the Kekulé valence structures of the highest degree of freedom. Hence, these are the expressions for RE of Clar valence structures of [*n*]phenylenes. An attempt to extend the idea of aromatic π-sextets to non-benzenoid systems was suggested over 10 years ago[823] and illustrated on derivatives of biphenylene. At that time this was somewhat speculative, as there was no supporting evidence that would, beyond reasonable doubt, point to bent [*n*]phenylenes as relatively stable. Since that time, new developments have permitted a more rigorous approach to generalization of Clar's sextet model to non-benzenoids: Today we have (1) a rigorous mathematical definition of Clar structures as a subset of Kekulé valence structures of the maximal degree of freedom; (2) a more reliable quantum chemical calculation on linear and bent [*n*]-phenylenes; and (3) experimental evidence on the relative stability of bent [*n*]phenylenes. All three of these factors can be combined in support of extension of Clar structures to non-benzenoids, and [*n*]phenylenes in particular.

The expression for RE shown in Table 52 for bent [*n*]phenylenes, as discussed earlier, hold equally for linear [*n*]phenylenes. It follows then that the so-called anti-kekulene, which is cyclic [6]phenylene, may not be so elusive a structure to synthesize, as has been suggested previously in the literature. Trinajstić and collaborators[819] calculated RE for anti-kekulene and anticipated that its preparation will be difficult in view of its low RE. However, now we see that, according to the conjugated circuits model, which confines analysis of conjugated circuits solely to Kekulé valence structures of the highest degree of freedom, the expected RE is not going to be low, and the REPE of anti-kekulene is not going to be much different than the REPE for biphenylene. In view of the reported synthesis of [7]phenylene by Vollhardt and co-workers,[820−822] we may expect cyclic [6]phenylene to be synthesized in the near future. It will not be surprising if reports on its synthesis appear soon, even though such expectations have been around for the last 10 years! This fact, despite a prevailing optimism among scientists, probably well illustrates the difference between the real chemistry and the "pencil and paper" chemistry.

XXXVIII. Chemical Graph Theory — Prospects and Retrospect

We started this review with a list of important contributors and contributions toward the development of the notion of aromaticity (Table 1). We followed with a comprehensive review of applications of the graph theory to the chemistry of benzenoid hydrocarbons in particular. As has been demonstrated, graph theory offered a novel frame for formulation of chemical concepts of interest in data reduction and interpretation of data, and hence a better understanding of the chemistry of conjugated hydrocarbons. Chemical graph theory is, however, a broader field with application to other branches of chemistry, including biochemistry. We hope, however, that in addition to many readers finding numerous concepts of graph theory familiar, this article will induce interested readers to get more involved with chemical graph theory and not be fooled into believing that he/she has "mastered" the subject. In Table 53 we have collected numerous concepts that have originated in either quantum chemistry, structural chemistry, or chemical graph theory, all of which are essentially of graph theoretical content. On one hand, they are listed as a "warning" to those who tend to jump to the conclusion that they know "all about graph theory" and that there is nothing more to be learned. On the other hand, they illustrate the interlacing of many graph theoretical ideas with numerous early quantum chemical ideas, which at the time were not recognized as being graph theoretical by nature.

We also hope that this contribution will clarify much of the confusion around the notion of aromaticity. "Is Aromaticity Outmoded?" — this was the title of a paper Balaban published over 20 years ago.[31] Critics of the concept of aromaticity should take notice that Balaban is one of few theoretical chemists who is at the same time also an experimental chemist — thus he should be assumed to be familiar with both the theoretical and experimental aspects of aromaticity concept. In this article, Balaban convincingly argued that "*a reasonable balance of generality makes the concept of aromaticity extremely useful qualitatively; however, for quantitative determination, narrow, more precisely defined, area of aromaticity are to be specified*."[31] We believe that that is precisely what we did with the concept of conjugated circuits — which allow a well-defined quantitative notion of aromaticity for a narrow area of conjugated hydrocarbons and conjugated carbons (i.e., fullerenes). More recently, Krygowsky et al.[824] published a paper entitled, "Aromaticity: a Theoretical Concept of Immense Practical Importance". The title of this paper clearly supports what Balaban anticipated 20 years before. It is just difficult to see how a concept that survived so many attacks, and survived the transition from classical chemistry to quantum chemistry, from simple HMO calculations to ambitious ab initio computations, could suddenly become outdated.

There is no doubt that there has been much confusion about aromaticity, but confusion does not discredit the scientific concept; rather, it reflects the

Table 53. Concepts of Interest in Chemistry Developed within Chemical Graph Theory, As Well as Concepts Evolving from Early Quantum Chemistry and Which Are of Graph Theoretical Nature

concept	year	author(s)
Hamiltonian circuit	1856	Hamilton
Kekulé structure	1865	Kekulé
molecular graphs	1878	Sylvester
π-aromatic sextet	1925	Robinson and Armitt
Fries structure	1927	Fries
Hückel MO	1930	Hückel
$4n + 2$ rule	1930	Hückel
Rumer diagrams	1932	Rumer
resonance	1930s	Pauling
Pauling bond order	1935	Pauling, Brockway, and Beach
cycle index	1937	Polya
Coulson bond order	1939	Coulson
Meyer graphs	1940	Meyer
alternant hydrocarbons	1940	Coulson and Rushbrooke
path numbers	1947	Platt
topological index	1947	Wiener
alternant hydrocarbons	1947	Coulson and Longuet-Higgins
non-bonding MO	1950	Longuet-Higgins
subgraphs of secular determinant	1950	Coulson
parity of Kekulé structures	1952	Dewar and Longuet-Higgins
Gordon−Davison algorithm	1952	Gordon and Davison
Frost−Musulin diagram	1953	Frost and Musulin
isospectral graphs	1957	Collatz and Sinogowitz
Clar postulate	1958	Clar, Kemp, and Stewart
fully benzenoid hydrocarbons	1958	Clar and Zander
graphical enumeration	1961	Platt
graphical cluster expansion	1964	Smolenski
signed matrices	1963	Kasteleyn
degenerate rearrangement graphs	1966	Balaban
ring benzene character	1967	Polansky and Derflinger
dualist graphs	1968	Balaban and Harary
algebraic structure count	1968	Wilcox, Jr.
double coset labels	1970	Ruch and Hässelbarth
graph-like state of matter	1970	Gordon and Temple
Hosoya index	1971	Hosoya
Möbius diagram	1971	Zimmerman
computer enumeration of Kekulé structures	1972	Cvetković, Gutman, and Trinajstić
bay regions	1972	Jerina
leading eigenvalue	1973	Lovasz and Pelikan
resonance theory	1973	Herndon
vertex canonical labels	1974	Randić
isospectral points	1975	Živković, Trinajstić, and Randić
connectivity index	1975	Randić
factor graphs	1975	Joela
sextet polynomial	1975	Hosoya and Yamaguchi
conjugated circuits	1976	Randić
higher order connectivity indices	1976	Kier et al.
valence connectivity indices	1976	Kier and Hall
topological RE	1976	Aihara
topological RE	1977	Gutman, Milun, and Trinajstić
acyclic polynomial	1977	Gutman, Milun, and Trinajstić
information−theoretic indices	1977	Bonchev and Trinajstić
isoconjugate molecules	1977	Randić
parity of conjugated circuits	1977	Randić
periodic table of isomers	1978	Randić
disjoint conjugated circuits	1979	Gutman and Randić
Kekuléan long-range order	1979	Klein
anti-Hückel rule	1980	Sinković and Trinajstić
REPE	1980	Hess and Schaad
graphical enumeration of configurations	1980	Randić
complexity index	1981	Bertz
row distance sum; Balaban index	1982	Balaban
reduced graph model	1982	Jerman-Blažič and Trinajstić
N-tuple code	1983	Trinajstić et al.
ID numbers	1984	Randić
formula periodic table	1984	Dias
generalized Clar structures	1984	Herndon and Hosoya
leap-frog transformation	1986	Folwer
kappa shape indices	1986	Kier
unique vertex labels	1986	Randić
innate degree of freedom	1986	Randić and Klein
search for pharmacophore	1987	Randić et al.

Table 53. (Continued)

concept	year	author(s)
topographic indices	1988	Randić
ring resonance energy	1988	Randić, Plavšić, and Trinajstić
conjugated paths	1988	Randić and Trinajstić
endospectral graphs	1989	Randić et al.
maximal valence structure	1990	Randić
hierarchy of π-network models	1991	Klein et al.
orthogonal molecular descriptors	1991	Randić
variable topological indices	1991	Randić
twin graphs	1992	Hosoya
resistance distance	1993	Randić and Klein
graphite cover by benzenoids	1993	Hosoya et al.
D/D matrices	1994	Randić, Kleiner, and DeAlba
posetic D/D measures		Klein
subspectral graphs	1994	Randić, Guo, and Kleiner
hyper-Wiener index	1994	Randić
reduced reaction graphs	1994	Gimarc and Brant
graphical DNA representation	1994	Nandy
graphical matrix	1997	Randić, Razinger, and Plavšić
graph theoretical chirality indices	1998	Randić
dominant Kekulé structures	1998	Flocke, Schmalz, and Klein
mean-field resonance theory	1998	Klein, Bytautas, and Ivanciuc
invariants for folded proteins	1999	Randić and Krilov
fullerene Clar-type structures	1999	Flocke, Schmalz, and Klein
DNA matrix invariants	2000	Randić
reaction poset (partially ordered set)	2000	Klein and Bytautas
map invariants (proteomics)	2001	Randić, Zupan, and Novič
Clar structure for non-benzenoids	2002	Randić
C_{60} fullerene Clar structure	2002	Randić
graphical count of π-aromatic sextets	2002	Klavžar, Žigert, and Gutman
2-D graphical DNA representation	2003	Randić, Vračko, Lerš, and Plavšić
compact 2-D DNA representation	2003	Randić, Vračko, Zupan, and Novič

limitations of the perpetrators, who apparently muddle the waters rather than letting the dust settle. For example, according to Castells, “*Fullerenes are not aromatic ... of course!*”[825] The argument is based on what aromaticity really means to him and (he thinks) to most organic chemists: “*Tendency to react with ‘reversion to type,’ that is, regeneration of the aromatic ring [by ‘expelling’ a hydrogen ion] appears to be the most, if not the only, distinctive attribute of the peculiar chemical behavior of benzene and benzene-like (i.e., aromatic) species.*”[826] If one assumes the above definition for aromaticity, it is difficult not to agree, but all depends on accepting Castells's definition in the first place — which we do not. I, of course, cannot speak for “most of organic chemists”, but at the beginning of this review I rejected the position that *properties* should be used to define aromaticity. Clearly, the property considered here is *one* of the properties of aromatic compounds, but one can object to the assumption that *this* particular property should be the basis for aromatic characteristic of *all* aromatic compounds. It would be less confusing and quite logical to coin a special label for this particular property, such as “reversibility”, and then claim that *most aromatic compounds possess reversibility*. With such a “minor” modification, the aromaticity of fullerenes would not be questioned!

Arguments similar to the one just exposed hold for other experimental aromaticity approaches, each of which should be given a specific label, because they do not always parallel each other to the same degree. Thus, we do not question the logic of classifying compounds as aromatic or not, but rather we question the premises on which conclusions are based. It appears that one can say for the present confusion on aromaticity that it arose not because one could not see the forest for the trees, but just the opposite — because of the forest (of aromatic properties) one could not see the tree — the tree blooming with Kekulé structures!

XXXIX. Tribute to Experimental Chemistry

We would like to end this article with a list of experimentalists who *made* those molecules that have intrigued us and induced us to give more thought to the concept of aromaticity (Table 54). These are the people who deserve our respect and to whom we owe much when our calculations, models, and theories come to be tested, accepted, modified, or rejected. Finally, we separately listed in Table 55 the benzenoid hydrocarbons that Eric Clar investigated during his more than 50 years of fruitful exploration of the properties of benzenoid hydrocarbons. Structural formulas for the compounds of Table 55 can be found in the *Handbook on Polycyclic Hydrocarbons*, by J. R. Dias.[331] As one browses through this handbook, in which are collected over 400 benzenoid structures, one cannot fail to observe that for just about half of these structures there is no publication reported. Hence, there are plenty of challenges awaiting those interested in synthetic work. As one can see, despite the outstanding efforts of Clar and several other chemists who were very much interested in the chemistry of benzenoid hydrocarbons, in particular W. Laarhoven, M. Zander, R. Martin, and A. T. Balaban (for references see the above-mentioned handbook by Dias), even the field

Table 54. Distinguished Contributions from Synthetic Chemists of Importance for Clarification of the Concept of Aromaticity

author	year	work on
Faraday	1825	benzene
Graebe	1874	phenanthrene
Gabriel and Michael	1887	tetracene
Thiele	1899	cyclopentadiene
Meyer	1912	fluorene, chrysene
Weitzenböck	1913	pyrene
Clar	1924	pentaphene
Clar	1929	1,2:5,6-dibenzoanthracene, pentacene
Cook	1931	3,4-benzphenanthrene
Scholl and Meyer	1932	coronene
Cook and Hewett	1933	benzo[*a*]pyrene, benzo[*e*]pyrene
Ružička	1934	picene
Pfau and Plattner	1937	azulene
Weinmayr	1939	perylene
Lothrop	1941	biphenylene
Prelog and Seitwerth	1941	adamantane
Bartlett et al.	1942	trypticene
Kealy and Pauson	1951	ferrocene
Doering and Knox	1954	tropylium ion
Thiec and Wiemann	1956	fulvene
Doering and Matzner	1958	fulvalene
Hafner and Schneider	1958	aceheptylene derivative
Sondheimer and Wolovsky	1959	[18]annulene
Doering	1959	heptafulvene
Katz	1960	cyclooctatetraene dianion
Prinzbach and Rosswog	1961	sesquifulvalene
Dauben and Bartelli	1961	heptalene
Cava	1963	derivative of naphthocyclobutadiene
Schroder	1964	bullvalene
Vogel	1964	bridged $4n + 2$ π-electron systems
Katz et al.	1965	aromatic anions
Barth and Lawton	1966	corannulene
Trost et al.	1971	pyracylene
Anderson et al.	1973	azupyrene
Martin	1974	large helicenes
Olah, Staral, and Paquette	1976	cyclooctatetraene dication
Staab and Diedrich	1978	kekulene
Paquette, Ternansky, and Balough	1982	dodecahedrane
Wilcox and Farley	1984	dicyclooocta[*def:jfk*]biphenylene
Vollhardt	1986	treefold [4]phenylene
Obenland and Schmidt	1987	tribenzo[*a,g,m*]coronene
Iijima	1991	buckytubes
Siegel	1995	trisbicyclo[2.1.1.]hexabenzene
Müllen et al.	1997	giant benzenoids
Scott	2002	C_{60} synthesis
Vollhardt	2002	helical [*n*]phenylenes
Nakamura et al.	2003	[10]cyclophenacene

of smaller benzenoids (those having at most $n = 13$ fused benzene rings) is at best less than half explored.

> *The legendary image of scientist as a humble searcher for truth is more and more replaced by the image of a scientist ... highly competent in a narrowly defined domain but arrogantly extending his competence into fields in which he knows nothing, and neglecting the fact that science is only a small subdivision of human knowledge.*
> Hans Primas[827]

Chemical graph theory is bound to remain terra incognita for some, who will, undoubtedly, continue to be hostile toward chemical graph theory, curse it, and find it faulty, rather than becoming acquainted with the basic concepts of the field in which they are, at best, novices. One should not underestimate the dangers of the situation in which chemical graph theory found itself, not by its fault. The situation is not novel. Confucius, about 500 years B.C. recognized such difficulties when saying, “*Those who do not know, and do not know that they do not know, are dangerous − avoid them*.” That is the reason that we limited our comments to just a single “critical” paper from authors who displayed unfamiliarity with elementary notions of chemical graph theory. It is fitting, therefore, to end this review with yet one additional quotation from Max Planck:[674]

> *It would certainly be a serious illusion on my part if I hoped that my remarks have carried general conviction, or even that they have been generally understood ... Surely much more will be thought and written concerning these questions, for theorist are numerous and paper is patient.*

Table 55. Benzenoid Hydrocarbons That Clar Synthesized and Investigated

benzenoid	year	benzenoid	year
pentaphene	1924	dinaphtho[8,1,2-*abc*:8′,1′,2′-*lmn*]peropyrene	1960
1,2:5,6-dibenzoanthracene	1929	dinaphtho[8,1,2-*abc*:8′,1′,2′-*mno*]peropyrene	1960
pentacene	1929	dibenzo[*de,op*]pentacene	1962
naphtho[3,2-*a*]pyrene	1936	dibenzo[*fg,st*]pentacene	1963
dibenzo[*c,m*]pentaphene	1939	dibenzo[*de,uv*]pentacene	1963
isoviolanthrene	1939	benzo[*a*]zethrene	1963
hexaphene	1940	dibenzo[*hi,uv*]hexacene	1963
dibenzo[*a,e*]pyrene	1943	dibenzo[*fg,wx*]hexacene	1963
dibenzo[*a,l*]pentacene	1943	dibenzo[*de,yz*]hexacene	1963
naphtho[2,3-*a*]pentaphene	1948	dibenzo[*e,p*]zethrene	1963
dibenzo[*a,c*]pentacene	1948	dibenzo[*f,q*]zethrene	1963
benzo[*b*]pentacene	1948	dibenzo[*hi,xy*]heptacene	1963
benzo[*c*]pentaphene	1948	dibenzo[*j,xyz*]heptacene	1963
dibenzo[*e,ghi*]perylene	1948	dibenzo[*jk,a′b′*]octacene	1963
ovalene	1948	naphtho[2,1-*a*]naphthacene	1964
benzo[*j*]heptaphene	1949	dibenzo[*g,p*]chrysene	1964
dinaphtho[2,3-*a*:2′,3′-*h*]pyrene	1949	benzo[*a*]phenanthro[9,10-*c*]tetracene	1964
dibenzo[*a,n*]perylene	1949	tetrabenzo[*de,hi,mn,qr*]tetracene	1964
dibenzo[*a,j*]perylene	1949	dibenzo[*fg,ij*]naphtha[1,2,3,4-*rst*]pentphene	1964
dibenzo[*a,o*]perylene	1949	dibenzo[*a,k*]naphtha[1,2,3,4-*ghi*]pentphene	1964
benzo[*xyz*]heptaphene	1949	dibenzo[*de,yz*]naphtha[8,2,1-*hij*]hexaphene	1964
tribenzo[*a,ghi,o*]perylene	1949	dibenzo[*ij,rst*]phenanthro[9,10,1,2-*defg*]pentaphene	1964
dibenzo[*a,s*]terrylene	1949	tribenzo[*a,d,g*]coronene	1964
dibenzo[*bc,ef*]coronene	1949	tetrabenzo[*b,g,k,p*]chrysene	1964
benzo[*a*]hexacene	1950	tribenzo[*f,ij,no*]tetraphene	1964
dibenzo[*b,n*]picene	1954	tribenzo[*a,c,j*]tetracene	1961
heptaphene	1954	benzo[*h*]pentaphene	1962
tetrabenzo[*de,h,kl,rst*]pentaphene	1954	hexabenzo[*a,d,g,j,m,p*]coronene	1965
tetrabenzo[*de,hi,op,st*]pentacene	1954	dibenzo[*de,st*]pentacene	1966
zethrene	1955	phenanthro[9,10,1-*hij*]tetracene	1966
dibenzo[*j,w*]terrylene	1955	dibenzo[*hi,wx*]heptacene	1966
benzo[*a*]perylene	1956	benzo[*st*]naphtha[2,1,8,7-*defg*]pentacene	1966
tetrabenzo[*a,c,l,n*]pentacene	1956	anthra[1,2,3,4-*ghi*]perylene	1966
dibenzo[*a,f*]perylene	1956	benzo[*uv*]naphtha[2,1,8,7-*defg*]pentacene	1966
naphtho[8,1,2-*bcd*]perylene	1956	benzo[*wx*]naphtho[2,1,8,7-*hijk*]heptacene	1966
tetrabenzo[*de,no,st,c′,d′*]heptacene	1956	naphtho[2,3-*h*]pentaphene	1968
dibenzo[*hi,qr*]anthanthrene	1956	naphtho[2,3-*j*]heptaphene	1968
dibenzo[*bc,mn*]peropyrene	1956	anthra[2,3-*j*]heptaphene	1968
dibenzo[*bc,qr*]peropyrene	1956	dibenzo[*a,c*]naphthacene	1970
dinaphtho[8,1,2-*abc*:2′,1′,8′-*jlk*]coronene	1956	dibenzo[*a,p*]chrysene	1970
dibenzo[*tuv,xyz*]naphtha[8,1,2-*bcd*]terrylene	1956	naphtho[2,3-*f*]picene	1970
benzo[*b*]picene	1957	benzo[*rst*]naphtho[3,4-*h*]pentaphene	1970
dibenzo[*a,f*]tetraphene	1957	anthra[1,2,3,4-*rst*]pentaphene	1970
benzo[*qr*]naphtha[2,1,98,7-*fghi*]pentacene	1957	benzo[*h*]naphtha[1,2,3,4-*rst*]pentaphene	1970
coronene	1957	tribenzo[*b,r,w*]terrylene	1971
dibenzo[*fg,ij*]pentaphene	1958	tribenzo[*fg,mn,xyz*]heptaphene	1971
tribenzo[*fg,ij,rst*]pentaphene	1958	tetrabenzo[*i,klm,opq,s*]terrylene	1971
terrylene	1958	pentabenzo[*b,ghi,qrs,r,w*]terrylene	1971
naphtho[2,3-*a*]coronene	1958	dinaphtho[3,2,1-*fg*:1′,2′,3′-*qr*]pentacene	1972
tetrabenzo[*a,c,j,l*]tetracene	1959	tetrabenzo[*a,d,j,m*]coronene	1972
naphtho[1,2,3,4-*ghi*]perylene	1959	dinaphtho[8,1,2-*bcd*:8′,1′,2′-*mno*]peropyrene	1972
tetrabenzo[*a,h,l,s*]peropyrene	1959	benzo[*b*]chrysene	1973
benzo[*a*]coronene	1959	benzo[*a*]tetracene	1973
dibenzo[*a,g*]coronene	1959	dibenzo[*a,j*]coronene	1977
tetrabenzo[*a,cd,fg,n*]anthanthrene	1959	tetrabenzo[*a,c,m,o*]naphtha[1,2,3,4-*rst*]pentaphene	1979
hexabenzo[*bc,ef,hi,kl,no,qr*]coronene	1959	naphtho[8,1,2-*cde*]heptacene	1979
dibenzo[*lm,a′b′*]heptacene	1960	dibenzo[*fg,op*]naphthacene	1979
tetrabenzo[*fg,lm,uv,a′b′*]heptacene	1960	dibenzo[*a,o*]naphtha[1,2,3,4-*rst*]pentaphene	1979
dibenzo[*bc,kl*]coronene	1960	tetranaphtho[3,2,1-*de*:1′,2′,3′-*jk*:3″,2″,2″-*op*:1‴,2‴,3‴-*uv*]pentacene	1979
dibenzo[*cd,pq*]bisanthene	1960	tetranaphtho[3,2,1-*de*:1′,2′,3′-*jk*:3″,2″,2″-*op*:1‴,2‴,3‴-*uv*]pentacene	1979
dibenzo[*ef,pq*]bisanthene	1960	dinaphtho[8,1,2-*abc*:2′,1′,8′-*klm*]coronene	1981

XL. Apologies

> *Believe nothing, no matter where you read it, or who said it, no matter if I said it, unless it agrees with your own reason and your own common sense.*
>
> Buddha

We tried to give an overview on aromaticity from the graph theoretical point of view, and in doing this we tried also to give a broad underlying theoretical basis for chemical graph theory. To do less than this may only fuel confusion about the role of chemical graph theory because it may, in the eyes of some, maintain the impression that chemical graph theory is at best of “approximate and qualitative” nature — which of course is not the case. Thus, to some the presentation of alternative ways of enumerating Kekulé valence structure may appear redundant in view of the fact that one can get the results easily by computer — but does a computer result gives *insight* into how the results are obtained? Just as it is of considerable importance when examining experimental data to know how they are obtained, what instruments, what methods, what impurities, what uncertainties, what solvents, what temperatures, etc., it is equally important to know what algorithms, what approximations, what statistical procedures, etc. are used for obtaining theoretical data and for subsequent data reduction. So, we do not apologize to those who may think that there is too much tangential material embedded in this review. On the contrary, we apologize to those who find that not enough of such material has been included.

Much more is known and much more could have been said about many topics presented in this review. For example, when speaking of the characteristic polynomial of a graph, besides the graphical/combinatorial approaches initiated by Coulson[105] and completed by Sachs[106] for computation of the characteristic polynomial that we cited, we could mention the graphical approaches of Hosoya[828] as well as Jiang.[829] We also could have pointed to tables of computed characteristic polynomials for numerous graphs, such as those published by Heilbronner[830] almost 50 years ago, comprehensive tables compiled by Hosoya et al.[831−833] for large numbers of benzenoids, and tables presented by Cvetković et al.[259] for smaller graphs, as well as tables of matching polynomials for benzenoid hydrocarbons reported by Gutman and coworkers[834,835] Neither have we exhausted the list of computer programs and underlying algorithms for calculation of the characteristic polynomial and closely related matching polynomial. For example, calculation of the characteristic polynomials for trees can be accomplished efficiently by adopting the “pruning” procedure of Balasubramanian,[836−838] which shows how can one modify the adjacency matrix when all terminal vertices are erased. By repeating the procedure, large acyclic graphs can be reduced in few steps to matrices of relatively small size. Barakat[839] outlined a general procedure for construction of the characteristic polynomial which rests on the symmetric function theory, which itself can be traced to Newton’s identities.[840,841] He showed that the method of Frame,[842] later to be referred to as the Le Verrier−Fadeev−Frame method, which was employed by Balasubramanian[843] is equivalent to the symmetric function and Newton’s identities. Hosoya and collaborators[844] derived general expressions for the characteristic polynomials of various series of cyclic and linear polymers of polycyclic aromatic hydrocarbons. Hosoya and Ohkami[112] developed a simple and efficient method called the operator technique for obtaining the recurrence relation for periodic networks, which can be applied for construction of the characteristic polynomial and matching polynomial of polyacene graphs. Those interested in more details should examine the lengthy list of papers on evaluation of the characteristic polynomial given by Balasubramanian.[845] Similarly, a list of numerous problems in chemistry in which the characteristic polynomials are of interest has been given by Křivka and collaborators.[846] This article also includes a brief history on the evaluation of the characteristic polynomial of a matrix and sheds light on the origin of the Le Verrier−Fadeev−Frame name for this rather widely used approach: Le Verrier[847,848] developed this method in 1840 and used it to calculate the positions of planet, and some 100 years later Fadeev[849] modified the method, which apparently was rediscovered by Frame.

Another aspect of the computation of characteristic polynomials that has been mostly overlooked in the past is the format of the basis functions used to express the polynomials − which are routinely shown as linear combinations of powers x^n. However, there are some advantages when instead of x^n one uses characteristic polynomials of linear chains of length n, which are in fact Čebišev polynomials:[850−853]

$$L_0 = 1, \quad L_1 = x, \quad L_2 = x^2 - 1, \quad L_3 = x^3 - 2x$$

$$L_4 = x^4 - 3x^2 + 1, \quad L_5 = x^5 - 4x^3 + 3x, \quad \text{etc.}$$

Kirby[854,855] developed a computer program for evaluation of the characteristic polynomial expressed in terms of Čebišev polynomials (in BASIC) for conjugated systems that is suitable for small computers. Čebišev polynomials have an important property:

$$L_m L_n = L_{m+n} + L_{m-1} L_{n-1}$$

That is, their product can be expressed as a combination of polynomials of larger and smaller indices, which by repeated application eventually always yields a linear expression for any product of Čebišev polynomials in terms of Čebišev polynomials of order $(m + n)$ to $(m - n)$. This property allows one to find L_{m+n} from Čebišev polynomials of lower orders. Another useful application of Čebišev polynomials is to find factors of characteristic polynomials.[856−858] Factoring the polynomials help in finding common fragments and common eigenvalues in different structures. By knowing common fragments, one can rapidly calculate the characteristic polynomial of a larger system which has such fragments embedded in its skeleton.[859−862]

More could be said about the characteristic polynomials, their properties, and their use in chemistry. For example, self-returning random walks[264,265,283,863−877] and spectral moments[559,825,878−888] illustrate properties that have been recognized as being of interest in chemical applications and characterization of molecules. Instead of continuing to outline such applications, let us just point to one rather intriguing property of the characteristic polynomial that was recognized only 30 years ago, which is, in view of the long history of calculations of characteristic polynomials, a relatively recent time. It is known as Clarke’s theorem:[881]

Theorem: *The derivative of the characteristic polynomial of a graph G equals the sum of the characteristic polynomials of Ulam subgraphs of G.*

Ulam subgraphs[882] of a graph G are the collection of subgraphs obtained from G by erasing one vertex (and all pending edges) from it at a time. The “graph reconstruction conjecture” asserts that every finite simple undirected graph on three or more vertices is determined, up to isomorphism, by the collection of its vertex-deleted subgraphs.[882] A finite simple undirected graph is a graph having no directed bonds and no multiple bonds. A graph on two vertices has been excluded because its Ulam subgraphs consist of a single vertex, and for two such vertices one cannot assert whether they have been connected or not. If one restricts the conjecture to connected graphs, then graph on two vertices can be included.

Ulam's reconstruction conjecture is generally regarded as one of the foremost unsolved problems in graph theory.[883] According to mathematician O'Neal,[884] "*A clever amateur has equal chances to solve the problem as a professional*." Harary "*has even classified it as a 'graphical disease' because of its contagious nature*." [883] We have mentioned Ulam's subgraphs and Ulam's graph reconstruction conjecture not to spread the disease (which has many victims, including this author[886]) but rather to point to the intriguing relationship between the calculus (derivatives) which is associated with continuum and discrete mathematics (graph theory). On one side we have derivatives of polynomials and on the other side discrete objects, a graph and its subgraphs. We have seen similar relationships between the characteristic polynomial of a secular equation and the number of Kekulé valence structures of a benzenoid,[475] and the relationship between Coulson and Pauling bond orders as found by Ham, Ruedenberg, and Platt.[171]

Clarke's theorem, besides its curiosity, may have some practical use as it facilitates evaluation of the characteristic polynomial for large polycyclic systems like benzenoids that have no pending bonds. In the case of systems with pending bonds, one can apply recursions, but if there are no terminal bonds, then evaluation of characteristic polynomial is more tedious. Using Clarke's theorem, one can apply recursion to corresponding Ulam's subgraphs and then evaluate the integral for the resulting sum of characteristic polynomials of Ulam's subgraphs.[848] The constant of integration can be derived from K, the number of Kekulé valence structures, which can be obtained independently.

We could continue on this topic with additional material, such as construction of "characteristic equations" for a graph based on the count of walks,[869] which gives a much higher discrimination between molecules than does the characteristic polynomial; on the relationship between the characteristic polynomial and matching polynomial for some graphs;[887] on construction[117,118] and recursions[888,889] of characteristic and/or matching graphs for families of graphs; or on alternative routes to evaluation of the coefficients of the characteristic polynomial.[890,891] Finally, we could add the concept of partial ordering[892,893] and Marcus's concept of conformal sets,[864] which is based on self-returning walks in a molecule, which themselves are related to the coefficients of the characteristic polynomial, which in turn are related to higher powers of the adjacency matrix. Marcus has found that, to a reasonable approximation, the sum of the heats of combustion of a set of compounds equals the sum of that of another set that satisfy certain conditions. For example, benzene and benzanthracene as a set agree with naphthalene and phenanthrene, and anthracene and triphenylene as a set agree with phenanthrene and chrysene. Hence, in the findings of Marcus, we learn that the characteristic polynomials that played the central role in the Hückel MO model, and as such have been abandoned by many as the HMO theory has been abandoned, unexpectedly play a role in identifying additivities among the heats of combustion.

Similarly, we could have extended our exposition on the enumeration of Kekulé valence structures and discussion of their properties. For example, Cyvin[894] and Hosoya[895] examined the symmetry properties of Kekulé valence structures, Randić et al.[896] considered random generation of Kekulé valence structures, Guo and Randić[897,898] developed a recursive method for enumeration of linearly independent conjugated circuits of benzenoids, El-Basil[899] considered the ordering of Kekulé structures, Hall and Dias[900] developed a rapid topological test for discerning radical benzenoids, and Kirby[901] developed a simple algorithm for finding Kekulé valence structures which is based on a search for paths through the adjacency matrix, while Gutman[902] identified a triplet of CC double bonds having different relative orientation within any Kekulé valence structure as a molecular invariant.

We wish we could have given more space to these topics and others not even listed concerning benzenoid hydrocarbons, but that would require more space, more time, and more study. So, we offer sincere apologies to these and those others whose work should have been included but was not. We also should have given more space to some results of the HMO method, which in the hands of knowledgeable people, like Schaad and Hess,[618,903−905] Cioslowski,[906] or Hosoya[907−911] can offer valuable insights. Equally, we should have given some space to the present important results based on using ab initio calculations, but we hope that Paul von Ragué Schleyer, the guest editor of the special issue of *Chemical Reviews* on aromaticity, will do this not only more thoroughly but also much better, hopefully in the near future.

One of the reasons for this ad hoc list of omissions is also to remind readers that there is *much more* about almost any of the subjects related to aromaticity of benzenoid hydrocarbons that this review has covered. Those who are ready to criticize graph theoretical methodology in general, and the graph theoretical approach to aromaticity in particular, have been warned that they ought to do their homework before offering their opinions. So far, one can summarize critics of chemical graph theory of the past by the well-known saying: "*Those with the least expertise have the most opinions*." It is fitting, therefore, to end the story of the graph theoretical approach to aromaticity with a saying of American Indians: "*Before you criticize your neighbor you should walk a mile in his moccasins*." The only comment that I could add to this is that most critics never even put moccasins on, and as readers may have seen, to catch the spirit of chemical graph theory, it could be a walk much longer than a mile. Chemical graph theory, which has a distinguished past, a rich present, and a promising future, itself has moved quite a distance from the simple notions of HMO theory, with which it was wrongly identified in the not so distant past.

Finally, I should apologize to readers for repeating some statements a few times which may insult their intelligence. Although this was done intentionally, the reason is that it is not expected that one will have time to read this review article without interruption. Hence, some important results have been repeated to facilitate continuation of examination of this review and avoid the need to search for some of the important results over and over the lengthy manuscript.

XLI. Acknowledgments

> *No person is an island; much is owed to many.*
> H. P. Schultz[910]

I would like to thank Professor Nenad Trinajstić (Rudjer Bošković Institute, Zagreb, Croatia) for valuable comments. Professor Alexandru T. Balaban (Texas A & M University, Galveston, TX) made lengthy comments on numerous parts of the manuscript and thus has significantly contributed to the improvement of the presentation of the article. I also thank Professor D. J. Klein (Texas A & M University, Galveston, TX) for his comments on several sections of this review. However, most of all I would like to extend my thanks to Professor Roger B. Mallion (Canterbury, England), who was not only willing to read the manuscript twice but had the patience and stamina to get involved in details and has been offering unusually useful critical remarks, even to points that the author may have though are of marginal importance. "*I have read it twice, the two readings being separated by a quite a considerable period ... I liked it much more the second time than I did the first*", he wrote. I wish to pass this message to other readers, hoping that they may find time to read this review once again. The manuscript has been visibly improved during the revision. However, I am the only one to blame for sections that may still be unsatisfactory. The last but not the least, I would also like to thank Professor J. Zupan, Dr. Marjana Novič, and Dr. Marjan Vračko of the National Institute of Chemistry, Ljubljana, Slovenia, for extending their warm hospitality during my enjoyable visits to Ljubljana, Slovenia, where most of this review was written.

I would like to thank Dr. Linus Pauling, Jr., for permission to reproduce the letter mentioning the conjugated circuits that his father Linus Pauling sent me over 25 years ago. I would also like to express sincere thanks to Paul v. R. Schleyer, the guest editor of the special issue of *Chemical Reviews* on aromaticity, for the invitation to write this article on aromaticity of conjugated hydrocarbons, and to John A. Gladyz, the Associate Editor of *Chemical Reviews*, for his great patience and willingness to extend the deadline for the invited contribution for a later date.

This work is dedicated to the memory of the outstanding scientists of my native Croatia and the neighboring Slovenia:

Herman Dalmata Slavus	(12th century) natural philosophy
Frano Petriš (Francisus Patricius)	(1529−1597) natural philosophy
Markantun Dominis	(1560−1624) natural philosophy
Janez Vajkard Valvasor, FRS	(1641−1693) natural philosophy
Rudjer Bošković, FRS	(1711−1787) natural philosophy
Jurij Vega	(1754−1802) mathematics: log tables
Jozef Štefan	(1835−1893) physics: Stefan law
Nikola Tesla	(1856−1943) multiphase currents, etc.
Andrija Mohorovičić	(1857−1936) Mohorovičić layer
Fritz Pregl	(1869−1930) Nobel Prize in Chemistry 1923, "*for his invention of micro-analysis of organic substances*"
Leopold Ružička	(1887−1967) Nobel Prize in Chemistry 1939, "*for his work on polymethylenes and higher terpenes*"
Stjepan Mohorovičić	(1890−1980) physics: positronium
Vladimir Prelog	(1906−1998) Nobel Prize in Chemistry 1975, "*for his research into the stereochemistry of organic molecules and reactions*"

XLII. Appendix 1. Biographical Notes

We give here brief accounts on a few of the outstanding players in the arena of "aromaticity", just to pay tribute to those mentioned, rather than doing them justice in reporting on the significance of their contributions. However, not all that could be mentioned has been included. In particular, we give no deserved space to two giants of theoretical chemistry, Linus Pauling and Erich Hückel, about whom readers can find information elsewhere without difficulty. A short biography of Linus Pauling was published in *Croatica Chemica Acta*[913] on the occasion of Pauling becoming an honorary member of the Croatian Chemical Society in 1988. A short biographical note on Ernest Hückel is to be found in the article (in German) "50 Years of the Chemical Bond", written by W. Haberditzl.[914]

We ordered the short list of persons according to the year of their death. We start with Arthur Cayley and James Joseph Silvester, both mathematicians, both undeservingly little known among chemists despite their early recognition of the importance of discrete mathematics for chemistry. For more details on them one should consult E. T. Bell's book *Men of Mathematics*[915] and an article by Rouvray[916] on the pioneering contributions of Cayley and Silvester to the mathematical description of chemical structure.

Arthur Cayley (1821–1895)

Arthur Cayley was born in 1821 in Richmond, Surrey, and died in 1895 in Cambridge. He was a leading mathematician of his time in England and is responsible for the introduction of the Leibniz notation for calculus in England, where because of a 100-year dispute between the followers of Newton and the followers of Leibniz about the priority of the "discovery" of calculus, the Leibniz notation (which was more sophisticated and more satisfactory) was not used, which was detrimental to the development of calculus in England. It appears that Newton may have discovered calculus before Leibniz, but he kept his discovery for his own use. The fact is that Leibniz was the first to publish his discovery of calculus, upon which Newton came with claim that he had also discovered it sometime before.

Disputes over priority in science are not so uncommon, though only when some major discoveries are concerned do we hear about them. The fact that several researchers come upon the same or similar ideas reflects the evolutionary aspect of science. The point is well illustrated with controversial claims for the invention of the cycloid, a mathematical curve that can be constructed by following a fixed point on a circle as the circle moves on a horizontal line. The following 17th century scientists were involved in the discovery of the cycloid:[917] Galilei, Toriccelli, Descartes, Fermat, Wren, Wallis, Huygens, Johann Bernoulli, Leibniz, and Newton. This is almost a "who's who" of 17th century science! "*Even as there were many discoveries at this period of time, there were also many arguments about who has discovered what first, accusations of plagiarism, and minimization of one another's work. As a result cycloid has been labeled the Apple of discord* ..." [917]

There are numerous contributions describing enumeration of isomers, an early topic of algebraic chemistry. Chapter 11 in the book by N. Trinajstić, *Chemical Graph Theory*, is devoted to enumeration of isomers, where the reader can find relevant references. Trinajstić, however, quotes Cayley's paper in *Berichte der Deutschen Chemischen Gesellschaft*,[29] published in 1875, as the "first to attempt to enumerate isomeric alkanes C_NH_{2N+2} and alkyl radicals C_NH_{2N+1}". This is not quite true, because it was Flawitskii who in 1871 was the first to enumerate isomeric alkanes C_NH_{2N+2}. Flawitskii published his work first in a Russian journal[26] and then in the *Berichte der Deutschen Chemischen Gesellschaft*.[27] It is true that Cayley was the first to consider the difficult task of enumeration of graphs,[28] which preceded his enumeration of molecular isomers by 18 years! It appears that it was Losanitch[918] who was the first to recognize that enumeration of isomers constitutes a novel area of chemistry that involves combinatorial algebra as a basic tool.

James Joseph Sylvester (1814–1897)

J. J. Sylvester was born in London (of orthodox Jewish parents). By the age of 24 he was already Professor of Natural Philosophy (that means science and physics in particular) at the University College, London, and at the age of 25 became a Fellow of the Royal Society. Three months after his first visit to the United States to be a professor of mathematics at the University of Virginia, he resigned over an incident when the university did not want to discipline a student who insulted him. Not able to find another position in the United States, he returned to England and spent 10 "difficult" years as an actuary for a life insurance company, difficult because he was so creative in mathematics that he could not fully pursue. He had a few private pupils, one of whom was Miss Florence Nightingale — later well known for improving military hospital services during the Crimean War. After a rather difficult life, at the age of 63 he was invited to be a professor of mathematics at the Johns Hopkins University (Baltimore, MD). He accepted the invitation and had seven "golden" years, literary and figuratively, at the Johns Hopkins University, which accepted his only condition: that his salary be paid in gold! This ought to break the stereotype that professors of mathematics are "absent minded". He was acquainted with German, French, and Italian and had an interest in suggesting technical terms (based on Greek and Latin), including the term "graph" as used in graph theory.

August Kekulé (1829–1896)

Fridrich August Kekulé von Stradonitz was a Czech chemists (born in Darmstadt, Germany) who spent most of his life studying and working in then leading countries in science: France (Paris), England (London), Germany (Heidelberg, Bonn), and Belgium (Ghent). Although he is famous for his formula of benzene, he made other important contributions to chemistry. He was influenced by Justus von Liebig and abandoned the study of architecture for chemistry. He got his Ph.D. degree in Giessen in 1852 and went to Paris and later to London. While in London in 1854, he found the first organic acid containing sulfur (thioacetic acid). In 1956 he went to Heidelberg, and in 1857 he deduced that a carbon atom always forms four bonds (counting double bonds and triple bonds as two and three bonds, respectively). The next year he went to Ghent, and in 1865 he went to Bonn, where he spent the rest of his life. His structural formula of benzene was proposed the same year. While in Bonn he received nobility, adding to his name "von Stradonitz", the name of a small Czech town where his family originated. In 1861−87 Kekulé published a monograph on chemistry, *Lehrbuch der Organische Chemie*, in four volumes.

On the 25th anniversary of the proposal of the formula of benzene, the German Chemical Society celebrated Kekulé in Berlin with a conference, at which Kekulé spoke. Maybe this fact and the fact that Kekulé was born in Germany and lived there most of his life contributed to the assumption that he was a German chemist — incorrect information which has been propagated among others by *Encyclopaedia Britannica*[919] and the *Grolier Encyclopedia of Knowledge*[920] (and I am sure many others). Pauling, in his famous *The Nature of the Chemical Bond*, stated that Kekulé was a German chemist, which was again repeated in his textbook on *General Chemistry*: "*The German chemist August Kekulé (1829−1896) in 1865 proposed that the six carbon atoms form regular hexagon in space...*". [921] This was believed then, but today we know better. Kekulé died when he was 67 years old, which at that time may have been a respectable life span, but today is in many parts of the world below the average life expectancy. If only he had lived five years longer, he would have reached the age of this author and been eligible for the first Nobel Prize in Chemistry that in 1901 went, very deservedly, to van't Hoff. Unfortunately, Kekulé and people of his time did not have the benefit of antibiotics and heart surgery, which have made it possible for many of us to still be around. Besides van't Hoff (Nobel Prize in 1901), Emil Fisher (Nobel Prize in 1902) and Adolf von Baeyer (Nobel Prize 1905) also spent a brief time working with Kekulé. In fact, in 1856, von Baeyer wanted to study chemistry but the University of Berlin had no chemistry laboratory at that time. He went to Heidelberg to the famous laboratory of chemistry of Bunsen, where he met Kekulé, whom he soon joined in Kekulé's private laboratory after a dispute with Bunsen. Baeyer joined Kekulé in Ghent, Belgium, after his Ph.D. thesis was apparently not appreciated by the establishment at the University of Berlin.

In passing, let us add that Baeyer got his Nobel Prize a few years *after* his student, Emil Fisher. It has been said that one should be kind to one's own students that are climbing up (at the beginning of their career) so that they can be kind to you when your are going down (near the end of your career)! But as we see from the case of Alfred von Baeyer and Emil Fisher, there may be an additional reason for being kind to your students — they may help you in getting a Nobel Prize! We may also add that in 1885, King Ludwig of Bavaria raised Baeyer to nobility for his achievements — a practice that is carried at the present time in the United Kingdom by Queen Elizabeth II, who recently promoted Harry Kroto to Sir Harry. Though there is a distinction, the promotion of von Baeyer has been hereditary, which is not the case with meritorious nobility of today's United Kingdom.

Besides common erroneous statements of Kekulé's German origin, in more recent times on more than one occasion statements have been made that cast doubt on his priority of suggesting a ring structure for benzene. The following quotation from a relatively recent book by P. Bell, *Designing the Molecular World*, summarizes such skepticism:[922]

> *The discovery that benzene (which is also found naturally in crude oil) is a carbon ring is usually attributed to the German chemists Friedrich August Kekulé, who reported it in 1865, but in fact another German, Johann Loschmidt, seems to have published the ring structure four years before. Legend has it that Kekulé insight came to him in a dream, in which he had visions of a snake with its tail in its mouth. But as this story seems to have arisen 25 years after Kekulé's "discovery", it is hard to give it much credence. Indeed, some suggest that Kekulé's supposed insight may have actually derived from a glance at Loschmidt's book!*

Neither is this the place nor am I the most qualified person to forward counter-argument to eradicate these attempts to misrepresent the role of Kekulé in proposing the structure of benzene. But this is the place to criticize speculations which were never supported by hard evidence. First, the dream of a snake biting its tail is not a "legend" but a part of Kekulé's autobiography (as presented by him at the celebration meeting in Berlin on the occasion of the 25th anniversary of his benzene ring structure). It is not unusual that this "legend" came 25 years after his "discovery", because this was the occasion of reminiscing about his work on benzene. If the German Chemical Society had overlooked Kekulé and not celebrated the 25th anniversary of his benzene ring structure, most likely we would never have heard the story of a snake biting its tail, just as if the German Chemical Society had celebrated the 10th anniversary of his benzene ring structure, most likely we would have heard the story of a snake biting its tail sooner than we did! To most of us, who are neither historians nor lawyers, it stand to reason to believe that if there were some reservations about the "discovery" of the ring structure of benzene by Kekulé, such concerns would have been raised in Berlin in 1890 by those who knew what was going on at that time and not a hundred years later by those who may be dreaming themselves about dreams of others! I mentioned lawyers deliberately as I would like to see proceedings in a court of justice in which a judge would allow an unsubstantiated statement "*that Kekulé's supposed insight may have actually derived from a glance at Loschmidt's book!*"

Charles A. Coulson (1910–1974)

Charles Coulson is one of the rare individuals who was willing to share his precious time with so many people, whether discussing scientific matters, humanitarian concerns, or devoting time to spiritual activities. He was a Ph.D. student of Lennard-Jones, which gave him the first views of theoretical chemistry — the subject that he pursued despite being formally a mathematician. During World War II he was in Dundee until the end of the war (as an objector) and moved later to London and eventually to Oxford as Rouse Ball Professor of Mathematics. Rouse Ball himself is well known for his book on *Mathematical Recreations*[923] — which is a quite serious book on various problems of discrete mathematics, more than the title may suggest. For many years he organized summer schools on theoretical chemistry which contributed significantly to the growth of theoretical chemistry in many countries of Europe. To this one should add his book *Valence*, published in the early 1950s, which was addressed to general chemists explaining the molecular orbital approach to molecules, and in a way can be viewed as complementary to Linus Pauling's *Nature of the Chemical Bond*, which was expanding valence bond descriptions of molecules. Coulson apparently recognized the merits of graph theory for chemistry, as he mentioned in a brief personal letter of 17 June 1973 to this author.

Erich Clar (1902–1987)

Erich Clar was born in Czech-Sudetenland. He received his Ph.D. degree in 1927 at the Technical University of Dresden for research on the synthesis of polycyclic aromatic hydrocarbons — the topic that he cherished all his life. His studies on polycyclic aromatic hydrocarbons concerned over 120 benzenoid compounds (see Table 55 for a list of the compounds synthesized, their physical properties, and spectroscopic properties studied by Clar). He published over 300 scientific papers and four books. Among his first papers was one on the synthesis of pentaphene, published in 1924; his last paper, about work on dinaphthocoronene, was published in 1981. His first book, *Aromatische Kohlenwasserstoffe Polycycklische Systeme*[924] (Aromatic Hydrocarbon Polycyclic Systems), was published during World War II by Springer Verlag in 1941 and was reprinted in 1944 in Ann Arbor, Michigan, "*Published and distributed in the Public Interest by Authority of the Alien Custodian.*" The second edition of this book, in which there was considerable expansion of the theoretical section, appeared in 1952.[925] In this second edition there is a section, "On the possibility of localization of π-electrons in individual rings of polycyclic systems", in which benzenoid hydrocarbons are discussed in terms of π-sextets.

For 10 years from 1936 to 1946, he worked at his private laboratory in his home in Herrnskretschem on the Elba River. In 1947 he moved to Glasgow, Scotland. From 1953 to 1972, he was a member of the Chemistry Department at Glasgow University. In 1965 he received the Kekulé medal of the Chemical Society of German Democratic Republic (East Germany). He died in 1987, shortly before he was to be awarded the first Polycyclic Aromatic Hydrocarbon Research Award at the 11th International Symposium on Polynuclear Aromatic Hydrocarbons (PAH) (Sept 24, 1987; his wife Louisa accepted the award on his behalf). Let us end with a brief quotation from the obituary of Professor Erich Clar, written by C. M. White and M. Zander:[926]

> *Professor Clar is considered by many scientists to be the father of modern polycyclic aromatic hydrocarbon chemistry. His most important contributions to polycyclic aromatic hydrocarbon chemistry were the discovery of the anellation principle (Aromatic ring condensation), his "pi sextet theory of PAH," the development of benzogenic diene synthesis known as the "Clar reaction," the synthesis of numerous new PAH systems, and classification of UV absorption bands of PAH corresponding to alpha, beta, and para bands.*
>
> *Professor Clar will be sorely missed.*

Before we start here with a quotation from the foreword that Robert Robinson wrote in June 1972 for Clar's booklet, *The Aromatic Sextet*, let us be reminded that the notion of the aromatic sextet was proposed in 1925, before the rise of quantum theory and quantum chemistry. Clar's *The Aromatic Sextet* appeared also five years *after* the paper by Polansky and Derflinger[582] in 1967, which has shown some compatibility of the model of aromatic sextets with simple MO calculations. Nevertheless, Robinson does not sound very enthusiastic; on the contrary, one can detect some doubts as to the validity of the aromatic π-sextet model. Here is part of the foreword written by Robert Robinson:[49]

> *... the sextet implies very little that can be stated with any degree of certainty about the actual distribution of the electrons in the resting phase of the molecule ... In all considerations of mechanism of reaction it is preferable to employ the Kekulé formulae and their analogues ... Like almost everything connected with the theory of benzenoid compounds, the aromatic sextet is controversial topic.*

Clar called the most stable benzenoid 6*n* π-electron hydrocarbons "fully benzenoid", suggesting these compounds to be very similar to benzene. In a number of publications, the same class of compounds has been called by Gutman, Cyvin, and Polansky "all-benzenoid hydrocarbons", while Dias in a number of his publications calls them "total resonant sextet benzenoids". The situation is somewhat unfortunate, because as far as I can see, there is nothing wrong with any of the three names, but Clar was the first to suggest his label, and I have not seen compelling arguments why these hydrocarbons should be called differently. The situation is somewhat different when considering fullerenes, to which, as Fowler and Pisanski[796] outlined, one can extended the notion of aromatic π-sextets. Fullerenes in which all disjoint hexagons are the site for π-sextets, so that all carbon atoms belong to one of the sextets, are analogous to "fully benzenoid" hydrocarbons. Fowler and Pisanski[796] refer to them as "perfect Clar structures".

Finally, we should mention that Clar was concerned with the difficulties that the early graph theory papers experienced, as was reflected in a brief personal letter of 20 May 1974 to this author.

Oskar E. Polansky (1919–1989)

Oskar Polansky was born in Vienna, where he studied preparative organic chemistry. He got his Ph.D. degree in 1957, as his studies were interrupted by World War II. Ten years later in 1967, he became the first professor of the newly founded Institute for Theoretical Chemistry in Vienna. Since 1973 he was at the Max-Planck Institute of Radiation Chemistry in Mülheim, Germany, as a member of Directorium. Besides his interests in thermal and photolytic processes in organic systems, Polansky was one of the early pioneers of chemical graph theory. In 1975 he organized a symposium on graph theory in chemistry which resulted in the initiation of *MATCH* (an acronym for *mat*hematical *ch*emistry, coined by A. Kerber[927]), a publication devoted to bridging the gap between mathematics and chemistry.

Michael J. S. Dewar (1918–1997)

> *Unlike many theoretical chemists, he was also a chemist; and his critical contribution to the subject has still to be appreciated.*
>
> John W. Cornforth[928]

Michael Dewar was the first among organic chemists to apply the MO method to larger organic compounds, which in his own words "*led to prediction of a whole series of new concepts which have now been generally accepted by organic chemists, for example,* *antiaromaticity, sigma conjugation, aromaticity and antiaromaticity in nonplanar cyclic systems, the idea that cyclic transition states may be aromatic or antiaromatic, and aromaticity in rings where one of the contributing atomic orbitals is a d atomic orbital instead of p atomic orbital.*" [929,930]

He also pioneered the use of quantum-mechanical calculations by developing very reliable *semi-empirical* procedures which for the first time produced molecular resonance energies for numerous benzenoid hydrocarbons. We have seen in this review the remarkably high degree of internal consistency of his RE calculations on a selection of benzenoids. Despite these successful applications of semi-empirical methods, his contributions apparently were not appreciated in some theoretical chemistry circles. At the same time, M. J. S. Dewar showed at best limited interest in the currently popular ab initio calculations and was disappointed, if not bitter, about difficulties he encountered in attempts to publish his work: "*... because I was not an official quantum chemist, I often had major problems getting my work published, even when it was really important, and I am sure that many others have found themselves in the same boat.*" [929,930]

Dewar, who described himself as a loner, may at least in one area, that of being very critical of the so-called "peer review" system, find himself in a bigger company of admirers. It is not that the concept of "peer review" is wrong but the practice apparently is, because it is not uncommon to come across hostile reviewers with hostile agendas — as Michael Dewar apparently experienced near the end of his scientific career.

In 1967 I invited Professor Dewar to be one of 10 speakers of a summer school on theoretical chemistry in Herceg Novi on the Adriatic coast, under the conditions that he give two lectures and deliver lecture notes at the end. (The conditions were set by then Yugoslav Atomic Energy, which financed the summer school). One afternoon I was observing Dewar making his notes with the help of a bottle of whiskey. As the level of whiskey in the bottle was going down, the pile of written pages of paper grew up, and when the bottle was empty, the contract was fulfilled!

XLIII. Appendix 2. Short Historical Comments on Graph Theory in Mathematics and Chemistry

Before outlining a few important steps in the development of graph theory in mathematics, we should draw the attention of readers to an outstanding book with historical information, *Graph Theory 1736−1936*, written by Biggs, Lloyd, and Wilson.[230] The years 1736 and 1936 were selected because in 1736 the first paper (by Euler[231]) appeared that could be taken as the beginning of graph theory, and 200 years later in 1936 the first book on graph theory (by König[232]) appeared.

A. Graph Theory in Mathematics

Graph theory as a mathematical discipline was initiated by a paper by Leonhard Euler in 1736, in which he considered the "problem of Köningsberg bridges".[231] In considering this problem, which has topological and combinatorial elements, Euler used algebraic methods to find the conditions under which the network has a circular path in which every edge is transversed only once. The next important contribution came from physics in 1847, when G. Kirchhoff[931] (1824−1887) solved the problem of current flow in a general electric network. About the same time, the English mathematician Cayley[28] considered the problem of enumeration of mathematical objects called trees, the special case of which are molecular skeletons of saturated hydrocarbons.

In the middle of the 19th century, the famous "four color problem", originating with Francis Guthrie[230] (1790−1868), appeared and has continued to challenge mathematicians for over 150 years. Another challenging problem in which a path is sought that visits every vertex of a graph was put forth by W. R. Hamilton.[230,932,933] This difficult problem, also known as the "problem of a traveling salesman", requires finding a cyclic route which will allow a salesperson to visit every city on his tour and return to the starting points without visiting the same place more than once.

The first book on graph theory appeared exactly on the occasion of 200 years of graph theory. It was written in German by the Hungarian mathematician König[232] (who committed a suicide in 1943 during World War II). Graph theory has seen great advancement in the second part of 20th century by contributions from Clude Berge, Oysten Ore, R. C. Read (who considered mathematical nomenclature for alkanes), William Tutte, H. S. M. Coxeter, Paul Erdös, and others. A standard introductory textbook is that by Frank Harary,[102] but there are numerous excellent books on graph theory, a short list of which can be found in the book on graph theory and applications by Bondy and Murty.[934] In one of appendices of this book, one can also find a collection of "unsolved problems" of graph theory of varying difficulty, which includes a number of conjectures not yet proven.

It is of interest to mention that the mathematician Fajtlowicz[935−943] developed a computer program, "Graffiti", which *makes* conjectures. After conjectures are made by the computer, the conjectures are announced and mathematicians are invited to prove or disprove them. Many have been proved, some disproved, and many still remain open. At first sight a reader may get an impression that we have drifted far from chemistry and in particular topics that are relevant for characterization of aromaticity. However, it may be of interest to chemists to learn that numerous conjectures that the "Graffiti" program proposed relate to concepts that originated within the literature on chemical graph theory. For example, several conjectures relate to various mathematical properties of the so-called topological indices. Conjectures were also proposed by "Graffiti" that concern fullerenes, which led to a paper by Fowler[944] on fullerene graphs with more negative than positive eigenvalues. According to Fowler, such fullerenes represent "*the exceptions that prove the rule of electron deficiency*". This work once again illustrates advantages to chemistry when it broadens its interests into interdisciplinary areas. In contrast to quantum chemistry, in which very few mathematicians were absorbed, chemical graph theory is more fortunate to have attracted a larger pool of mathematicians (T. Pisanski, B. Mohar, S. Klavžar, J. Žerovnik, V. Batagelj, and M. Petkovšek from Slovenia; D. Cvetković from Serbia; A. Kerber, R. Laue, P. Sachs, P. E. John, J. V. Knop, G. Brinkmann, and O. D. Friedrichs from Germany; A. Dobrynin and V. A. Skorobogatov from Russia; D. Veljan, D. Svrtan, and T. Došljić from Croatia; I. Tomescu and S. Marcus from Rumania; H. S. M. Coxeter, R. C. Read, T. Lee, P. Hansen, and G. Caporossi from Canada; K.-T. Fang, W. C. Shiu, and P. C. B. Lan (Hong Kong), X. Guo, Y. Liu, F. Zhang, H. Li, and W. He, P-a He and H. Zheng from China; O. Araujo and J. Rada from Venezuela; D. B. Redmond, from Ireland; A. J. Guttmann and C. D. Godsil from Australia; C. Hervas from Spain; H. Fripertinger from Austria; E. K. Lloyd from England; L. V. Quintas, J. Malkevitch, F. Harary, P. Slater, M. Lewinter, S. Fajtlowicz, R. Graham, D. M. Berman, and K. W. Holliday from the United States, to mention few).

B. Graph Theory in Chemistry

The first chemical problem considered by graph theory was enumeration of isomers by Flavitskii[26,27] in 1874, the same year that stereochemistry was born. Cayley and Silvester, both mathematicians, made important early contributions, Cayley by extending enumeration of chemically interesting graphs and Silvester by recognizing the role of graphs for molecular modeling. Enumeration of isomers was made simpler by a theorem of Polya's (another mathematician!) published in 1937.[372] For a while, there was no activity in application of graph theory to chemistry. Sporadically, publications would appear and consider some aspects of chemical graph theory. Thus, in 1940, Balandin[945] in the USSR considered the use of matrices for characterization of structure−property relationship.

The Hückel molecular orbital model, which was developed after the pioneering work of Hückel on the structure of benzene was expanding without being recognized by most people at the time, could equally be referred to as a graph theoretical model. Few theoreticians at the time, e.g., Ruedenberg,[171] Heilbronner,[830] Günthard and Primas,[475] Marcus,[864] and Schmidtke,[946] were well aware of graph theory and its role in chemistry. Similarly, the early development of the valence bond method was typical of the lack of appreciation of the role of graph theory in chemistry, despite the more apparent link between VB and graph theory.

A revival of interest in chemical graph theory was noticed in the mid-1960s, when several problems of interest of chemistry that reflect the methodology of graph theory appeared. One was a renewed interest in HMO theory,[947] especially as applied to larger systems, and another was the study of isomerizations,[505] but the most important was the "preparation" of chemical structures for computer manipulations. Balaban was the first to construct graphs representing degenerate rearrangements of "flexible" structures,[505] and continued to expand chemical graph theory in many directions. The *Journal of Mathematical Chemistry*, started by D. H. Rouvray in 1987, was an early messenger of theoretical results in chemical graph theory, while the *Journal of Chemical Information and Computer Science*, under the editorship of W. A. Milne for the past 10 years, became the major reporter on applications of chemical graph theory, particularly on chemical documentation, canonical labeling of molecules, computer searches of large data files, computer manipulation of molecular structures, mathematical modeling of structure−property−activity studies, mathematical modeling of proteins, and recently mathematical modeling of DNA and mathematical modeling of proteomics maps. The first and the only single-author book on *Chemical Graph Theory*, by Trinajstić,[70] appeared almost 20 years ago (in 1983 and revised edition in 1992).

Chemical graph theory has also an abundance of unsolved problems that challenge researchers. Not all the problems may be equally important for chemistry, but all require some imagination, some ingenuity, and some novelty, and all present considerable a challenge to novices as well as to old-timers. For a brief review on unsolved problems of chemical graph theory, consult articles by Randić et al.[948] and Balaban.[949]

C. Further Readings

Although we covered a large territory and reported on various aspects of aromaticity, citing numerous papers, including some of peripheral relevance, it has to be recognized that we could not give due attention to every worthy contribution in this area of theoretical chemistry. Thus, we have collected a brief list of additional references that could be consulted for more information on the topics covered in this review. In order to assist interested readers, papers have been grouped according to topic:

Characteristic polynomial and related, refs 950−957; graph spectra and related, refs 958−960; automorphism, refs 961−966; enumerations of Kekulé structures, refs 967, 968; enumeration of walks and related, ref 969; more on Kekulé structures, refs 970−977; Pauling bond orders, refs 978−980; more on Clar structures, refs 981−990; aromaticity, refs 991−994; and fullerenes, refs 995, 996.

D. Personal Note

I would like to end this brief overview of graph theory and its use in chemistry with a personal comment on my own work. A stimulus for this came after having a look at a list of the 125 most cited papers published in the *Journal of the American Chemical Society*, displayed on the Internet by the American Chemical Society (http://pubs.acs.org/JACS) on the occasion of the 125th anniversary of this journal (2003). Among a sizable list of Nobel Laureates and numerous equally illustrious chemists, I was pleased to find a paper of mine listed in position 94. The paper, entitled "On Characterization of Molecular Branching” (ref 61), considers construction of a structural invariant, “the branching index”, designed to parallel numerous physico-chemical properties of alkanes. The index was later generalized to “higher order” connectivity indices and valence connectivity indices that found application in numerous structure−property−activity studies. In my view a different paper of mine, entitled “Aromaticity and Conjugation”, from which this whole review article grew, published in the *Journal of the American Chemical Society* just a year later, should have got meritorious distinction but it did not; it fell short of qualifying by some 700 citations.

When Linus Pauling was asked which of his contributions he considers the most important (and as we all know he had very many very important contributions from which to choose), he selected his work on hybridization as the most important. I take this opportunity to proclaim my paper on conjugated circuits as my most important contribution to chemistry. The first paper was published in *Chemical Physics Lett*ers in 1976 (ref 51), to be followed the next year with two full-size papers in *Journal of the American Chemical Society* and *Tetrahedron* (refs 52 and 53, respectively). Despite being available in some of the best chemistry journals, these contributions have received apparently limited attention, except perhaps within the chemical graph theory community. Nevertheless, the conjugated circuits method continued to gradually evolve during the past 25 years, to culminate in the recent synthesis of the notions of aromatic π-sextet of Clar structures with the idea of innate degree of freedom of Kekulé valence structures. Besides making it possible to arrive at *quantitative* characterization of Clar structures, for the first time it became possible to extend Clar’s notion of aromatic π-sextets to the chemistry of nonbenzenoid hydrocarbons and fullerenes.

Conjugated circuits not only have led to an analytic expression for molecular RE but also can be viewed as the *definition* of molecular RE for conjugated systems. For the first time, one need not define RE as the *difference* between the energy of conjugated polycyclic hydrocarbon and an acyclic standard. In this sense the concept of conjugated circuits may be viewed as “primitive”, where I use the attribute as a complement, in the sense of being of “prime importance”, fundamental. Thus, “conjugated circuits” could become a recent addition to the exclusive list of the most primitive concept of structural chemistry initiated by the idea of van’t Hoff about tetrahedral carbon atoms, the idea of the cyclic structure of benzene of Kekulé, and the idea of sp^n hybrids of Pauling.

XLIV. Appendix 3. Errors−Omissions

Errare humanum est.
Saint Jerome (c. 347−c. 420)

Here we will list errors, misprints, omissions, etc. that we detected in the literature. Either earlier or during the preparation of this review, some of these errors may have been detected by others, and hence some corrections may have been reported. Nevertheless, for those readers who will consult the original literature cited in this review, it might be convenient to group all such observations in a single place. The reference number in the text dictates the order in which corrections and comments proceed.

(30) Randić, M.; Trinajstić, N. *Croat. Chem. Acta* 1994, *67*, 1−35.

On p 12 near the end of the section is shown a 4 × 4 matrix $\mathbf{A}^{-1}$, but it was labeled as $\mathbf{A}^2$. On p 16, where additivity of the HMO π-energies of benzenoid hydrocarbons, discussed by R. A. Marcus (*J. Chem. Phys.* **1965**, *43*, 2643), is discussed, the second row of set I was shown as anthracene and benzene instead of tetracene and benzene.

(45) Dewar, M. J. S.; de Llano, C. *J. Am. Chem. Soc.* 1969, *91*, 789.

The reported RE for pyrene is in error. Instead of being 2, the corrected value is 2.098 eV, as reported by M. J. S. Dewar to W. C. Herndon (see footnote to Table 2 in ref 162.

(48) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

August Kekulé was quoted as a German chemist, which many thought to be the case at that time.

(49) Clar, E., *The Aromatic Sextet*; J. Wiley & Sons: London, 1972.

Hydrocarbon XXXII on p 118 has a missing C=C bond between the two benzene rings below the empty ring (indicated by E).

(51) Randić, M. *Chem. Phys. Lett.* 1976, *38*, 68.

The reported numerical value for contributing conjugated circuit R_4, taken to be 0.041 eV, does not follow as the solution of the equations considered, which according to Gutman should be 0.140 eV. As Gutman points out, the error may have been in transcription. However, since the relative magnitudes ought to satisfy the inequality $R_n > R_{n+1}$, the “exact” value for R_4 is not acceptable. Most likely, inconsistencies are cause by minor inaccuracies of SCF MO computations, which may not be reliable to the precision needed to extract R_4 from such computations.

We should add here that Herndon’s approach and the conjugated circuits model, when restricting attention solely to R_1 and R_2 contributions, can be made mathematically equivalent if the same parameters for R_1 and R_2 and molecular integrals γ_1 and γ_2 are assumed.

(53) Randić, M. *Tetrahedron* 1977, *33*, 1905:

In Table 2, the last listed expression for RE of ovalene should be $(200R_1 + 160R_2 + 110R_3 + 26R_4 + 4R_5)/50$ (and not “/500”).

(178) Heilbronner, E. *Helv. Chim. Acta* 1962, *45*, 1722.

Matrix element (1,8) of the figure on p 1724 is omitted in the original paper of Heilbronner [because we use different carbon atom labels, it corresponds in his notation to element (1,6)].

(219) El-Basil, S.; Randić, M. *J. Math. Chem.* 1987, *1*, 281.

Erroneous df was reported for the Kekulé valence structure shown in Figure 2 of this paper for pyreno-[*4,5-e*]pyrene (two fused pyrene units), which was reported to have $df = 3$, but in fact it has $df = 2$ (because the structure has only two disjoint conjugated circles).

(433) Randić, M. In *Valence Bond Theory and Chemical Structure*; Klein, D. J., Trinajstić, N., Eds.; Elsevier: Amsterdam, 1990; p 469.

Of the five benzenoids shown to have $K = 21$, only four have $K = 21$. For the second cata-condensed benzenoid in fact $K = 31$.

(457) Randić, M.; Henderson, L. L.; Stout, R.; Trinajstić, N. *Int. J. Quantum Chem.: Quantum Chem. Symp.* 1988, *22*, 127.

In Figure 1, in Table 3, and in Table 4, the code (2,4,2,4) should be replaced by the code (2,5,2,5).

(530) Došljić, T. *Croat. Chem. Acta* 2002, *75*, 881.

On p 882 are listed the first few Catalan numbers. The C_8 was misprinted as 1030 instead of the correct value, 1430.

(539) Herndon, W. C.; Hosoya, H. *Tetrahedron* 1984, *40*, 3987.

In Figure 2 in the last Clar-type structure, the CC double bonds in one of the benzene rings are in the wrong locations.

In addition, these author claimed that every Clar structure which forms the basis for VB calculations corresponds to a maximum independent set of a Clar graph, which however is not the case, as outlined in ref 793. As a consequence, enumerations of Clar structures by El-Basil et al.[219,986,997−999] are in error. For correct values see ref 793.

(569) Randić, M.; Trinajstić, N. *J. Am. Chem. Soc.* 1984, *106*, 4428.

In Figure 2, conjugated circuit R_4 is drawn incorrectly (as a circuit involving 15 carbons). Correct R_4 circuits should involve four benzene rings on the molecular periphery.

(752) Clar, E.; McAndrew, B. A. *Tetrahedron* 1972, *28*, 1137.

The formula of 2,3:4,5:8,9:10,11-tetrabenzoperylene in the chart on p 1138 and in Figure 1 on p 1139 are missing two CC double bonds which are exocyclic to the central ring of perylene.

XLV. Appendix 4. Errors—Prevention

> *This paper, whose intent is stated in its title, gives wrong solution to trivial problems. The basic error, however, is not new.*
>
> C. Truesdell[1000]

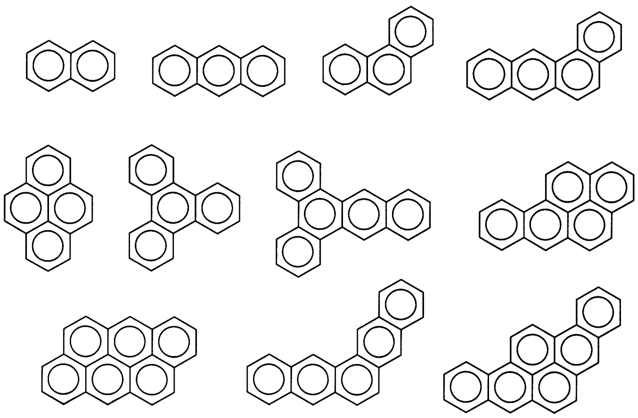


Figure 131. Misuse of the "circle" notation illustrated on several smaller benzenoids (top) and a suggested remedy: use of the Greek letter π for rings involving π-electrons instead of the circle.

Errors in scientific papers are not uncommon even though co-authors, colleagues, and reviewers screen many papers. It is not uncommon to spot minor errors by authors upon the first look at a paper as it appears in press. Referees tend to focus attention to major aspects of scientific papers, often from very personal points of view, which often results in nonconstructive comments that have little value to authors, particularly in preventing future mistakes. A good illustration of such a lofty report is that of a well-known German chemist, Hermann Kolbe (1918−1984), on a paper by equally distinguished French chemist, Marcellin Bertholet (1827−1907):

> *Paper has new and true things, but what is new is not true, and what is true is not new.*

It is not so important whether this particular report itself is true or not, but it shows the limitations of the system of anonymous referees who often end up promoting their own agenda rather than assisting authors and editors to improve the quality of scientific papers. For years I thought that the above is the worst possible evaluation of one's work; however, I came across a quotation from *The Mathematics Reviews* (by Clifford Truesdell listed above) which appears even worse, because, according to the reviewer, the author considered trivial problems, gave a wrong solution, and even the errors were not original!

Be that as it may, we can still try to do something to reduce the errors that tend to be repetitious. The occurrence of such errors continues because the propagators are not aware that they are in error. This is the case with the continuing misuse of the "circle" notation of aromatic π-sextet in representing benzenoid hydrocarbons, mentioned at the beginning of this review article. One of the reasons that this malpractice continues may be the awkward format of the correct notation. However, a widespread misuse of the notation by so many organic chemists will not make the wrong notation right. Something ought to be done to change the situation.

In Figure 131 we have illustrated the misrepresentation of smaller benzenoid hydrocarbons by drawing circles in all fused benzene rings. The

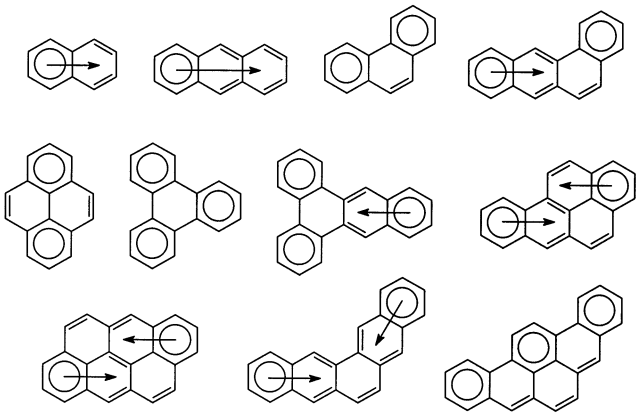


Figure 132. Correct notation for the benzenoids shown in Figure 131, as dictated by Clar's model of aromatic π-sextets.

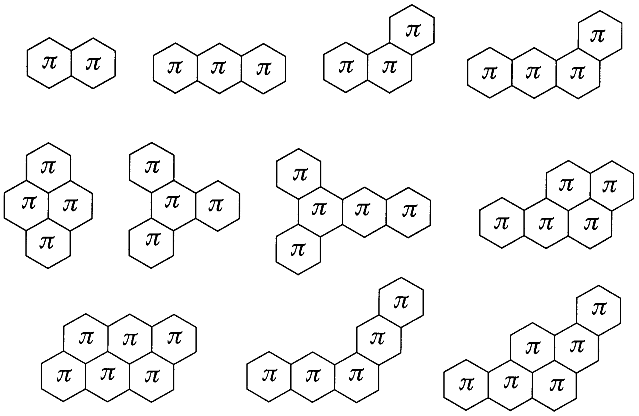


Figure 133. Proposed alternative simple notation for benzenoids not contradicting Clar's model.

widespread use of this erroneous notation cannot be attributed solely to mischievous behavior of so many chemists, but rather points to a lack of a suitable replacement notation. The correct drawing of the benzenoids shown in Figure 131 is shown in Figure 132. Because the correct representation of such molecules may require some acquaintance with Clar's ideas on the aromatic π-sextet, which go beyond the issue of notation, many find an easy solution by maintaining the incorrect "circle" notation, because there is no suitable alternative. In Figure 133 we illustrate the "missing" suitable alternative, which is as simple as is the incorrect "circle" notation, yet does not contradict any existing molecular models. Here, each fused ring, rather than being represented by an inscribed circle, is simply indicated by an inscribed Greek letter π, as shown in Figure 133.

Numerical Kekulé Valence Structures. Kekulé valence structures, like Clar's valence structures, may be viewed as "geometrical" formulas because they are drawn. Similarly, the novel notation for benzenoid hydrocarbons using an inscribed Greek π represents a *pictorial*, *qualitative*, *non-numerical* representation of such molecules. However, well-designed or selected notation may have advantages that initially one did not anticipate. This has been the case with the Leibniz notation for derivatives in mathematics, and with graphical codes of configuration of *n*-alkanes in structural chemistry.[1001] We will show now that the just introduced *qualitative* π-notation of fused benzene rings can be generalized into *quantitative* characterization of Kekulé valence structures as well as benzenoid hydrocarbons in general. We may refer to the novel quantitative representations as "numerical Kekulé valence structures" and "numerical molecular formulas of benzenoids", respectively, in contrast to more familiar geometrical Kekulé valence structures and geometrical molecular formulas of benzenoids.[1002]

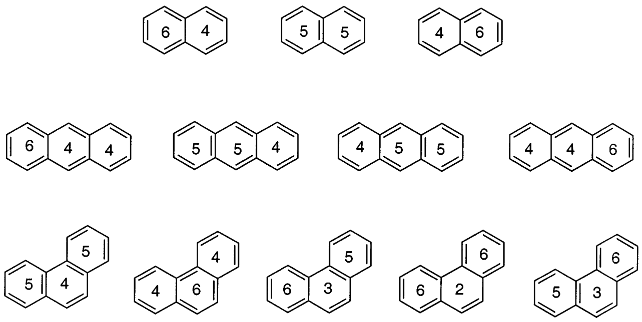


Figure 134. Kekulé structures of naphthalene, anthracene, and phenanthrene, showing the count of π-electrons involved in each ring.

We start with the smallest benzenoids, naphthalene, anthracene, and phenanthrene, illustrated in Figure 134, where we inscribed some numerals within individual rings of each Kekulé valence formula. The numbers inscribed have a simple structural meaning: they count π-electrons belonging to a ring. To arrive at the count of π-electrons for each ring, we divide electrons belonging to a CC double bond common to two rings equally, one electron to each ring. Thus, the first Kekulé formula of naphthalene, which contains three CC double bonds, has six π-electrons, and the adjacent ring, with two CC double bonds, has four π-electrons. The two rings together have 10 π-electrons, which is the number of π-electrons of naphthalene. However, in the case of the central Kekulé structure of naphthalene, each ring is associated with five π-electrons, because the two rings share a common central CC bond. Again, the total number of π-electrons is 10, as it should be. To obtain the numerical molecular structure of naphthalene, we take the average count of π-electrons for each ring over all Kekulé valence structures.

As we can see from Figure 135, where we have listed the nine numerical Kekulé valence structures of benzo[*a*]pyrene, the numbers in each structure represent a *partitioning* of all π-electrons to individual rings for each Kekulé valence structure. In Figure 136 for a collection of smaller benzenoids we show the corresponding numerical molecular formulas obtained by averaging ring contributions of all Kekulé valence structures. The numerical formulas shown in Figure 136 can viewed as alternative local aromaticity ring indices. A comparison with Figure 96, in which we had simple graph theoretical ring indices, shows considerable parallelism between the two approaches. There are also significant (though minor) differences between the two approaches. As can be seen already in the case of anthracene, the central and the peripheral rings now have slightly different ring indices. Apparently, terminal rings have the largest ring value, paralleling in this way

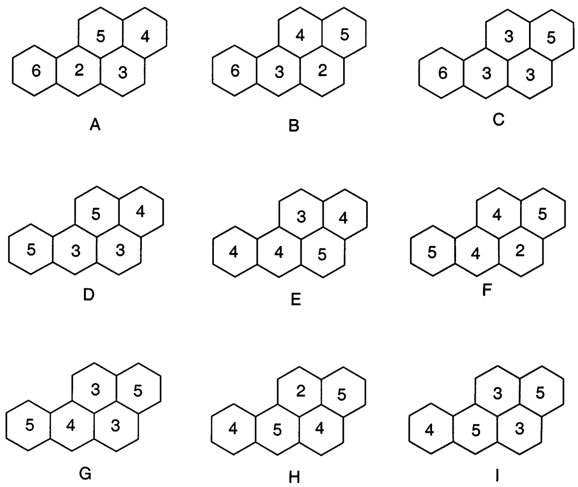


Figure 135. Numerical Kekulé valence structures of benzo[*a*]pyrene.

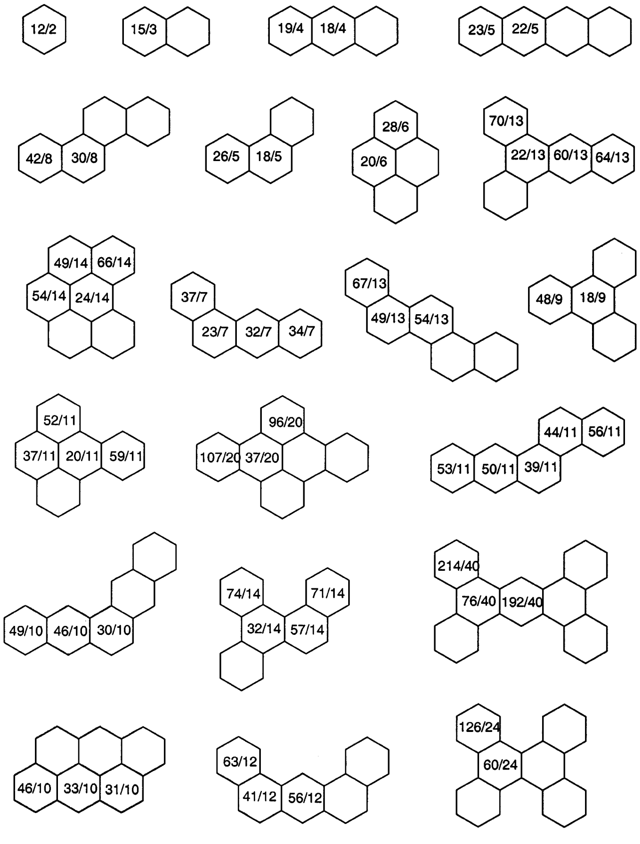


Figure 136. Partitioning of π-electrons to individual rings for smaller benzenoid hydrocarbons based on *all* Kekulé valence structures.

characterization of rings on the basis of ring RE. If we add all ring indices for benzenoids in Figure 136 and divide the sum by K, we obtain the number of π-electrons in a benzenoid. If we add all ring indices in Figure 96 and divide it by K, we obtain the number of fused rings.

One can confine the count of π-electrons by considering only Kekulé valence structures of the maximal degree of freedom. In this case there is a redistribution of π-electrons between various rings, because unfavorable Kekulé valence structures were not considered. In Figure 137 we show the π-electron counts for individual rings for the same collection of benzenoids shown in Figure 136. As expected, terminal rings and rings which are the sites of π-aromatic sextets have slightly increased their benzene character, at the expense of the "empty" rings of Clar structures.

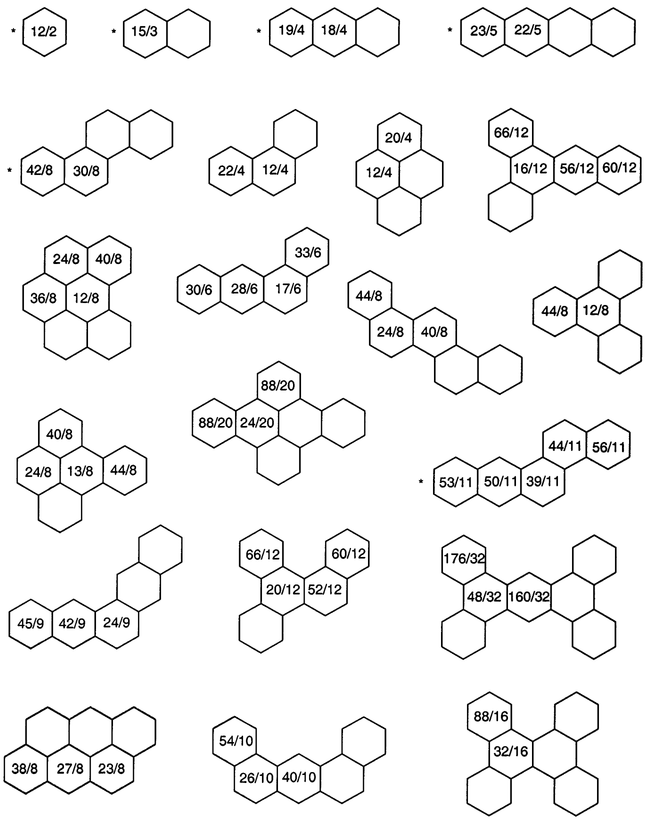


Figure 137. Partitioning of π-electrons to individual rings in smaller benzenoid hydrocarbons based on Kekulé valence structures of maximal *df*.

In Figure 138 we have summarized the results of the short critical review on *misuse* of "circle" notation and *use* of the count of π-electrons on benzo[*e*]pyrene. In the top part of Figure 138 we show the *incorrect qualitative* structural formula depicting misuse of π-aromatic sextet notation, and the novel *correct qualitative* structural formula with inscribed π-electrons in all rings. In the lower part of Figure 138 we give the average count of ring π-electrons based on *all* Kekulé valence structures, and based on the *subset* of Kekulé valence structures involved in the Clar valence structure (i.e., Kekulé valence structures of the maximal *df*).

Apparently, novel *quantitative* Kekulé structures better describe local properties of benzenoid hydrocarbons than the simple local graph theoretical indices. In the first case one incorporates contributions from CC bonds in all conjugated circuits, but the in latter one considers only CC bonds within a single benzene ring. Briefly, the novel quantitative notation for fused benzene rings has introduced novel ring indices for benzenoid hydrocarbons. Hence, by coming to the *end* of this review, we may be at the *beginning* of a novel alternative characterization of benzenoid and non-benzenoid hydrocarbons. With the new quantitative Kekulé valence structures, the focus has shifted to the *distributions* of π-electrons among

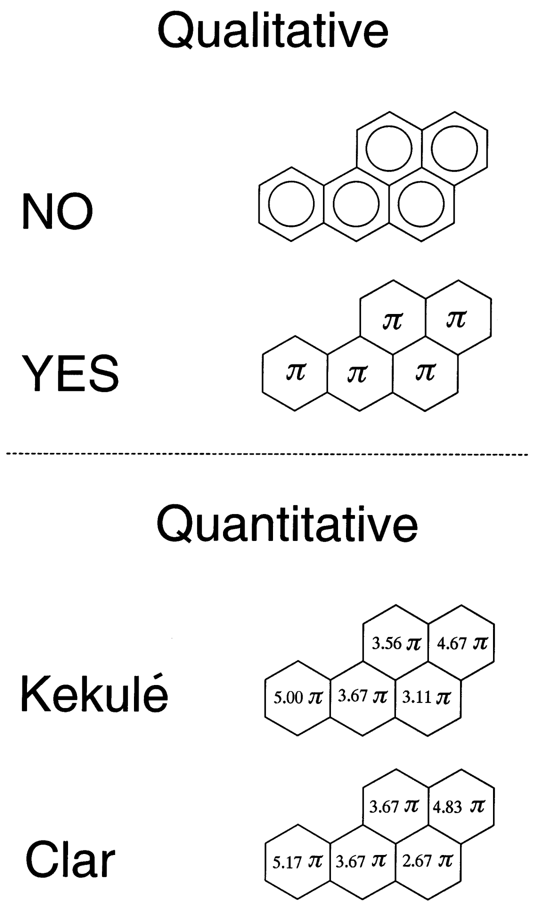


Figure 138. *Incorrect qualitative* structure of benzo[*e*]pyrene, *correct qualitative* structure of benzo[*e*]pyrene compared to *correct quantitative structures* of benzo[*e*]pyrene based on *all* Kekulé valence structures, and *correct quantitative structures* based on valence structure of the maximal degree of freedom.

different rings rather than among different conjugated circuits.

We may add that the partition of π-electrons to individual rings can be obtained by summing the Pauling bond orders for all CC bonds of a ring but taking only half of the value in the case of CC bonds common to two rings. The final sum has to be multiplied by 2, because each C═C has two π-electrons.[1003]

XLVI. Note Added in Proof

A. Clar Structures of C_{60}

In the discussion the Clar structures of fullerene C_{60}, I neglected to mention two papers in which these structures[1004,1005] have been discussed. S. El-Basil[1004] was the first to report on the five Clar structures of buckminsterfullerene, while mathematicians W. C. Shiu and P. C. B. Lam (from Hong Kong) and H. Zhang (from P. R. China) elaborated on the corresponding sextet polynomials of buckminsterfullerene.[1005] I am grateful to Professor W. C. Herndon (El Paso, TX), who drew my attention to these recent papers on Clar structures of fullerenes.

B. Benzenoid [10]Cyclophenacene Belt

Recently, Nakamura and co-workers[1006] reported the first example of a cylindrical benzenoid fragment embedded in a suitably substituted buckminsterfullerene molecule. They added five methyl groups to five carbon atoms adjacent to one of pentagonal faces of C_{60}, and five phenyl groups to five carbon atoms adjacent to the antipodal pentagonal face, while both pentagonal faces have one carbon hydrogenated. As a result, the conjugation of C_{60} was effectively reduced to a belt of 10 zigzag fused benzene rings. Thus, one obtains an equatorial band of 40 π-electrons, with the π-electron system embedded but not conjugated to the remaining parts of the molecule. Cylindrical benzenoid systems are present in nanotubes and as portions of fullerene toroidal structures, but this is the smallest such constellation of benzene rings, and thus is of considerable theoretical interest. First to consider macrocyclic conjugation of cylindrically fused benzene rings, referred to as circumpoliacenes, were Ege and Vogler almost 30 years ago.[1007] Their hypothetical structures, however, were linearly fused cyclic structures, the fragments of which were naphthalene, anthracene, tetracene, etc. In contrast, the benzenoid belt of Nakamura involves zigzag fused benzene rings, the fragments of which are phenanthrene, chrysene, picene, fulminene, etc. Balaban, in fact, considered zigzag fused cycloacenes (and their Möbius counterparts) in a paper on open problems in the area of condensed polycyclic benzenoids.[1008]

The numbers of Kekulé valence structures for phenanthrene, chrysene, picene, and fulminene, 5, 8, 13, and 21, respectively, are members of the well-known Fibonacci sequence, in which each member is given as the sum of the proceeding two members in the sequence. Hence, the zigzag system having 10 fused benzene rings would have 144 Kekulé valence structures. In contrast, [10]cyclophenacene is expected to have fewer Kekulé balance structures because the bond types of the CC bond that is common to the first and the last ring when 10 rings are connected into a cylindrical shape ought to be compatible. Recently, Lukovits et al.[1009] reported on the number of Kekulé valence structures for benzenoid belts of different lengths and widths. It is not difficult to establish that, for [10]cyclophenacene, $K = 125$, which interestingly is exactly 100 times less than K for buckminsterfullerene.[155] With 125 Kekulé structures, [10]cyclophenacene is considered a relatively small benzenoid system. To obtain the count of conjugated circuits instead of examining the individual Kekulé valence structures, one considers contributions from a single benzene ring, all rings being symmetry equivalent. One then obtains[1010] the expression for molecular RE for [10]cyclophenacene:

$$\mathrm{RE} = (680R_1 + 420R_2 + 130R_3)/125$$

if we ignore contributions from $4n$ conjugated circuits, the smallest of which has 20 and the largest 40 π-electrons. Assuming $R_1 = 0.869$ eV, $R_2 = 0.247$ eV, and $R_3 = 0.100$ eV, we obtain for a numerical value of 5.661 eV for RE of [10]cyclophenacene and RE per electron, REPE = 0.1415 eV. This value is typical of REPE values of smaller benzenoid compounds; hence, [10]cyclophenacene shows considerable similarity with planar benzenoid compounds of similar size. The values of the graph theoretical parameters R_1-R_3 will change somewhat with a better estimate for the partial loss of RE due to the spherical curvature of buckminsterfullerene. However, such improvements will not dramatically change the overall picture, because, as Herndon pointed out,[1011] many of the smaller benzenoids on which the estimates of the parameters R_1-R_3 were based themselves are not strictly planar. We may add that [10]cyclophenacene has two symmetry-equivalent Clar structures, each having five aromatic π-sextets and five benzene rings with one CC double bond.

C. Historical Remark on Clar π-Sextets

There is an earlier paper on aromatic sextets that appeared before the paper of Armit and Robinson, written by E. C. Crocker.[1012] Crocker's paper was not fully overlooked, as it was mentioned in the brief history of aromaticity published in the *Journal of Chemical Education*.[1013] Although there is no doubt that Crocker recognized the significance of the π-aromatic sextet, he was mainly concerned with aromatic rings having six π-electrons, while Armit and Robinson were considering polycyclic aromatic systems, where the number of p-electrons can vary considerably. I would like to thank to Professor Schleyer for drawing my attention to the above papers that were important for the development of the notion of aromatic π-sextets.

D. More Support for Clar's π-Aromatic Sextets

We started this review by pointing out three independent supports for Clar's aromatic π-sextet model of benzenoid hydrocarbons: (1) calculation of the ring RE of benzenoids based on SCF MO calculations; (2) calculation of molecular RE using the "preferred" Kekulé valence structures; and (3) experimental evidence of stable bent [*n*]phenalenes. By the time we ended this review, additional strong and independent theoretical evidence that supports Clar's notion of aromatic π-sextets emerged. This time, rather than relying of 30-year-old semi-empirical quantum chemical calculations, the results were based on ab initio Gaussian computations. Schleyer and collaborators[1014] calculated nucleus-independent chemical shifts (NICS) for individual aromatic rings of a dozen benzenoid hydrocarbons, including several larger systems. In Figure 139 we show a selection of the benzenoids for which Schleyer and collaborators reported NICS values, and in Table 56 are listed their reported NICS values for various benzene rings. In the adjacent column we show the graph theoretical ring indices for the same rings. A qualitative parallelism between the NICS values and the graph theoretical ring indices can be observed. The NICS values represent additional strong theoretical support for Clar's picture of aromatic π-sextets. The computed ring values of NICS correspond to Clar's picture of benzenoid compounds and thus offer an independent (and up-to-date) support for the π-sextet model of Clar. It is interesting that only the four fully polybenzenoid hydrocarbons (having only π-sextets and empty rings), $C_{42}H_{18}$ (hexabenzocoronene), $C_{114}H_{30}$, $C_{186}H_{42}$, and $C_{222}H_{42}$, show the extreme NICS values, while compounds having migrating π-sextets show for several rings intermediate NICS values. In the case of the fully benzenoid hydrocarbons having only aromatic π-sextet rings and "empty" rings, we see that the largest NICS values belong to the central rings, while the largest graph theoretical indices are found in peripheral rings. The relationship between the NICS values and GT ring indices clearly need to be further investigated.[1015] I am indebted to Professor Schleyer for sending me his results prior to their publication.

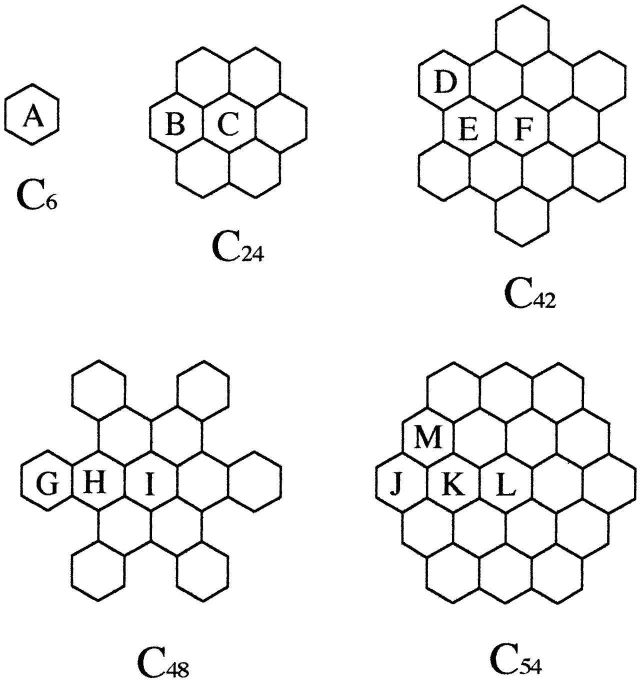


Figure 139. Highly symmetrical benzenoid hydrocarbons studied by Schleyer and collaborators.

Table 56. Parallelism between ab Initio Calculated NICS Ring Currents and the Graph Theoretical Ring Indices for a Selection of Highly Symmetrical Benzenoid Hydrocarbons (Shown in Figure 139)

benzenoid	ring	NICS	ring index
C_6	A	−11.2	1.000
C_{24}	B	−12.9	0.500
	C	−5.3	0.200
C_{42}	D	−11.5	0.800
	E	−3.2	0.200
	F	−15.1	0.512
C_{48}	G	−11.4	0.778
	H	−7.5	0.407
	I	+0.8	0.074
C_{54}	J	−9.2	0.316
	K	−8.8	0.224
	L	−16.2	0.408
	M	−17.5	0.478

XLVII. References

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we adopted Čebišev, which is the transcription used by *Mathematical Reviews* (of the American Mathematical Society), which adopted the Croatian Latinic alphabet for transcription of Russian cyrilic script (both languages being Slavic). Alternative spellings include Chebishev, Tchebicheff, Chebisev, Tschebyshev. See: Davis, P. J. *The Thread*; Birkhauser: Cambridge, MA, 1983.
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