# Clar Polynomials of Large Benzenoid Systems[†]

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We discuss the constructions of Clar-like valence structures and the associated Clar polynomials for large benzenoids. We have shown that Clar polynomial satisfy a theorem analogous to the Clarke's theorem for the characteristic polynomial of graphs, which allows one to reconstruct the polynomial of a system from the polynomials associated with qualified substructures. In the case of Clar's polynomial the substructures are obtained by deleting individual benzene rings from the considered benzenoid, one at a time. This property of Clar polynomial allows one to construct the polynomial of larger systems from known Clar's polynomials of smaller benzenoids.

## INTRODUCTION

Despite the breadth of chemical structures, the versatility of heterocycles, which tend to dominate the organic chemistry, the experimental and the theoretical interest in benzenoid hydrocarbons is far from waning.[1] It has been observed that a representative standard organic textbook[2] devotes less than 3% of its space to hydrocarbons.[3] This may reflect the ratio hydrocarbon structures to others, but nevertheless hydrocarbons, and aromatic hydrocarbons in particular, have kept the attention of theoreticians as well as experimentalists because of continuing diversity of their structural characteristics. Many hydrocarbons exhibit unusual structural features, some well understood, some of which still await resolution. To cope with the developments in this field an international and interdisciplinary journal devoted to all aspects of research related to polycyclic aromatic compounds was initiated in 1990.[4] Let us mention a few developments that may have been overlooked in some chemists' circles. A structural characterization of aromaticity displayed by planar benzenoids has been offered;[5] the concept of antiaromaticity was introduced by Breslow,[6] the "difficult" preparation of some polycyclic conjugated hydrocarbons, systems such as Hafner's hydrocarbon, was accomplished[7] and could be understood within the model of conjugated circuits; the rapid Cope rearrangements contemplated by Doering[8] was realized in a successful synthesis of bullvalene by Schröder;[9] and complexity of accompanying isomerization was theoretically successfully described by Živković.[10] The study of hydrocarbons and conjugated hydrocarbons, in particular, is of considerable interest and provides for a better understanding of the chemistry of fullerenes.

Polycyclic aromatics are of considerable interest in astrophysics and astrochemistry—an emerging discipline concerned with the occurrence of organic matter in the universe.[11] Probably the most important fact yet is that polycyclic aromatic hydrocarbons are ubiquitous in our environment as a product of incomplete combustion. Due to their thermodynamic and photochemical stability, they represent a health hazard. Benzanthracene, for example, one of quite common environmental impurity, is one of the most carcinogenic compounds that we are likely to meet. The synthetic and the industrial methods for efficient preparation of large benzenoid hydrocarbons are still being developed.[12] Finally, let us point to a very recent synthesis of giant benzenoids of unusually high stability, illustrated in Figure 1, the accomplishment of Professor Klaus Müllen and co-workers.[13] They have apparently opened a novel domain of chemistry of highly stable very large benzenoids. Previously Schmidt and co-workers[14] successfully synthesized some smaller benzenoids, like tribenzo(a,g,m)coronene (Figure 2) that also show exceptional stability.

In contrast to the spectacular experimental achievements in the chemistry of benzenoids, except for the interest of those developing chemical graph theory, large benzenoids have been overlooked by most theoretical chemists. Duke, O'Leary, and co-workers[15] did study some benzenoids of intermediate size by LCAO−SCF−MO approach, but clearly such computations have to remain confined to relatively smaller benzenoids. Molecules such as supernaphthalene of Müllen (Figure 1), tribenzo(a,g,m)coronene (Figure 2) of Obenland and Schmidt, and dicoronylene which has been known for more than 60 years (Figure 3), though whose structure was elucidated only 12 years ago,[16] are all beyond the rigorous quantum chemical calculations. Are we to wait indefinitely for ab initio calculations to expand and extend to large molecular systems? To phrase the same question differently: Is theoretical chemistry to ignore very large systems just because they are computationally inaccessible, i.e., could not be digested computationally?

Fortunately, chemical graph theory,[17] a branch of theoretical chemistry that is not constrained and/or obsessed with the computational idealization of the Schrödinger equation, is well and alive. Graph theoretical literature on benzenoids is considerable and rich in conceptual advancements.[18−21] In fact, in understanding large molecules one does not necessarily need to be in a position to calculate molecular wave function to a high accuracy. Polansky and Derflinger[22]
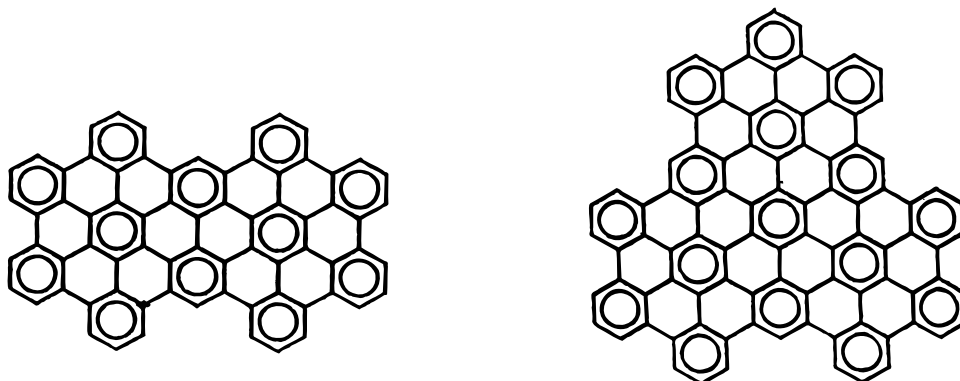
**Figure 1.** The smallest of the giant benzenoids recently synthesized by Müllen and co-workers.
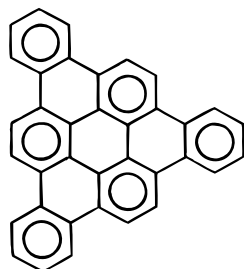


**Figure 2.** Tribenzo(a,g,m)coronene synthesized by Schmidt and co-workers.
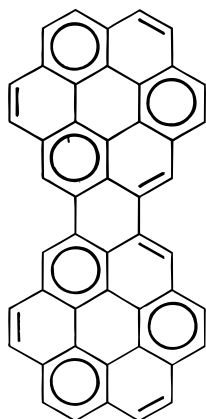


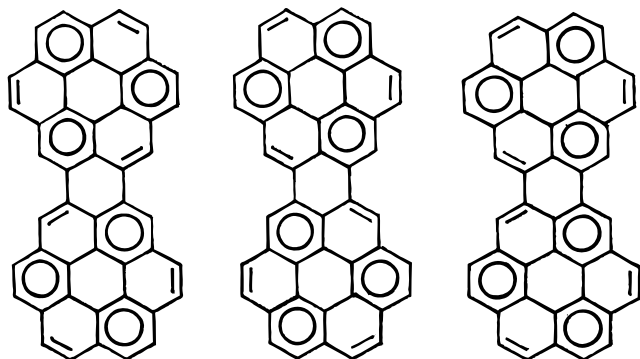**Figure 3.** Dicoronylene and one of its Clar's structure.



**Figure 4.** The remaining three Clar's structures of dicoronylene.

used simple MO calculations and were able to develop the support for the notions of the $\pi$-electron sextet of Armit, Robinson, and Clar.[23,24] The paper of Polansky and Derflinger is the exception, rather than the rule, in which quantum chemical machinery was utilized to rationalize or justify purely empirical notions of Clar.

With the development of chemical graph theory VB formalism was found suitable for further elaboration of the novel concept of $\pi$-sextet. In particular, the Resonance Theory of Herndon,[25] which can be viewed as a mixture of quantum chemical and graph theoretical methodologies, combined with the Conjugated Circuit method,[26] a purely graph theoretical approach, opened possibilities for a quantitative, rather than a qualitative, description of selected properties of large benzenoid systems. Besides the capability of Resonance Theory and Conjugated Circuit method (which can be viewed computationally even though not conceptually equivalent) to produce molecular resonance energies of the accuracy typical of SCF-MO calculations these methods clarified long standing ambiguities about the meaning and characterization of aromaticity of benzenoid and nonbenzenoid polycyclic conjugated hydrocarbons. The concept of conjugated circuits allows in the case of polycyclic conjugated hydrocarbons quite simple and elegant characterization of aromatic and nonaromatic compounds. To find if a compound is aromatic or only partially aromatic one first has to examine the set of Kekulé valence structures of the molecule. If Kekulé valence structures contain only $4n+2$ conjugated circuits, then the compound is *fully* aromatic; if among Kekulé valence structures there are some that contain besides $4n+2$ conjugated circuits also $4n$ conjugated circuits, then the molecule is partially aromatic. If a hypothetical system has Kekulé structures that contain only $4n$ conjugated circuits, the molecule would be antiaromatic.

Polycyclic aromatic hydrocarbons built only from fused benzene rings are necessarily aromatic, those having five- and seven-membered rings can be aromatic (like azulene) or partially aromatic (like Hafner's hydrocarbon). Finally systems having four- and eight-membered rings can be either partially aromatic (e.g., biphenylene) or antiaromatic (e.g., cyclobutadiene). Despite this clarity, simplicity, and elegance the structural definition of aromaticity based on conjugated circuits continues in some circles to be overlooked or ignored. This is apparently a reflection of limited acquaintance of some circles with the chemical graph theory in general and the accomplishments of the chemical graph theory in chemistry of polycyclic aromatic hydrocarbons in particular. A recent review of aromaticity is an example.[27]

There is no doubt that most quantum chemists conspicuously overlook the developments in the chemistry of polycyclic aromatic hydrocarbons and, in particular, the Clar's notion of the $\pi$-sextets and, consequently, the valence
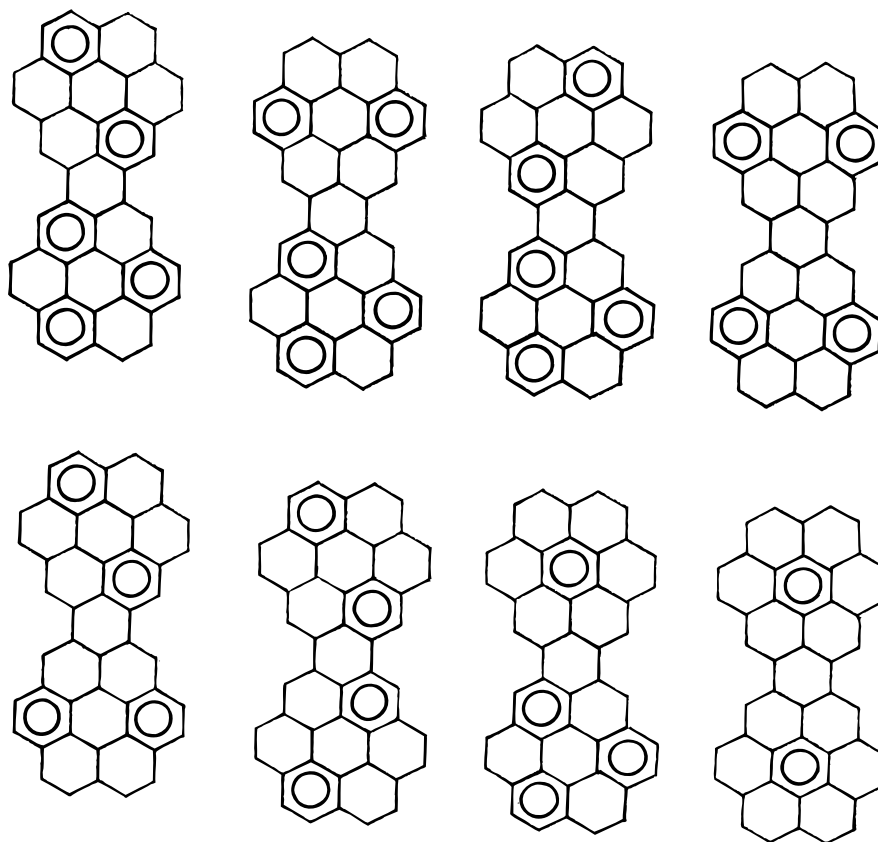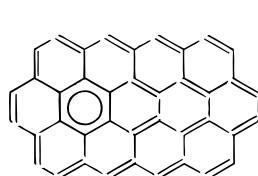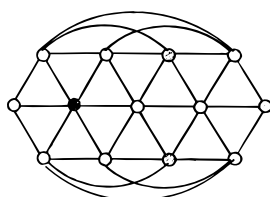
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**Figure 5.** Several extended Clar-type structures of dicoronylene.

**Figure 6.** One of the extended Clar's structure for circuman-thracene.

Clar structure

"Coloured" Clar graph which is *not* maximal vertex set

structures in which the $\pi$-sextets play the dominant role. Clar's arguments in favor of $\pi$-sextets were based on experimental evidence (the NMR splitting and the shifts in UV spectra among structurally related compounds). We believe that Clar's $\pi$-sextets deserve wide recognition among chemists, and in view of the recent synthetic successes in making larger and larger benzenoids, we are confident that a wider and wider circle of chemists (theoreticians included) will become intrigued and enlightened by Clar's courageous departure from the traditional view that all Kekulé valence structures in polycyclic aromatic compounds are equally important. They are, of course, in the case of benzene, but benzene may be the only molecular system in which all the Kekulé valence structures play an equal role. It was known already before the early development of the HMO method and the VB method that some Kekulé structures are more important than others. In 1927 Fries[28] formulated an empirical rule to that effect. According to Fries the dominant Kekulé valence structure is one which contains, formally looking, the largest number of Kekulé benzene rings, i.e., the valence structures having the maximum number of rings

with alternating CC single and CC double bonds. Clar went a step further and in essence stated that the dominant are those Kekulé valence structures which, when superimposed, give rise to the largest number of rings with isolated $\pi$-sextets.

## CLAR'S STRUCTURES

Eric Clar, the doyen of the benzenoid chemistry, left an impressive volume of experimental accomplishments, so much that one can say that he and his laboratory almost single-handed and single-minded revived the field of benzenoid chemistry.[29] He introduced a novel type of valence structures in which $\pi$-sextets are recognized. Clar's valence structures are defined as follows:

(a) inscribe inside benzene hexagons circles which represent $\pi$-sextets but so that no two adjacent rings have $\pi$-sextets;

(b) inscribed circles are permitted only if to the remaining carbon atoms of the benzenoid structure not involved in the rings with $\pi$-sextets can support full assignment of CC double and CC single bonds for the rest of the molecule;

(c) valence structure with inscribed $\pi$-sextets qualifies as Clar's structure only if it contains the *maximal* possible number of $\pi$-sextets.

Some molecules have all but a single Clar structure (like the giant benzenoids of Figure 1 and tribenzo(a,g,m)coronene of Figure 2); some may have several. Figures 3 and 4 depict the four Clar's structures of dicoronylene. In terminology of Clar dicoronylene possesses "migrating" sextets. According to Clar, molecules in which all $\pi$-sextets are "fixed" and there are no extraneous CC double bonds so that each benzene ring either has a $\pi$-sextet or is "empty" should be
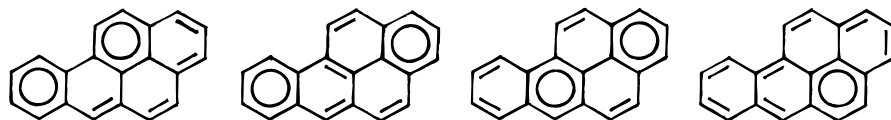
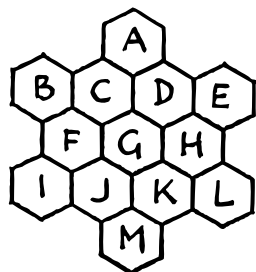**Figure 7.** All extended Clar's structures of benzo[*a*]pyrene.



**Figure 8.** Labeling of the 13 rings of hexabenzocoronene.

exceptionally stable. He referred to these systems as "fully benzenoid". Gutman and Cyvin called these molecules "all-benzenoid"[18] while Dias call them "total resonant sextet benzenoids".[30] The construction and the enumeration of fully benzenoid systems attracted considerable attention.[31−33]

Clearly Clar's structures can be viewed as a superposition of selected Kekulé valence structures. Each $\pi$-sextet is a result of a superposition of two Kekulé valence structures in which all CC single and all CC double bonds are at the same locations except for the CC single and CC double bonds within the benzene ring considered. Randić and Pisanski have shown that in many cases one can obtain Clar's structures from the Kekulé valence structures by first giving to each Kekulé structure a weight determined by the smallest Pauling bond order for any of CC double bonds present in the structure and then selecting only those Kekulé valence structures which have the highest weight.[34]

### EXTENDED CLAR'S STRUCTURES

In the present paper we consider more general Clar-like valence structures introduced by Herndon and Hosoya.[35] There are several ways in which one can generalize Clar's structures. To avoid possible confusion we will refer to the generalization due to Herndon and Hosoya as "extended Clar's structures", and when there is no possibility for confusion, simply as Clar's structures, even though they contain *additional* valence formulas than those considered by Clar. The term extended Clar's structures is appropriate and bears deliberately parallelism label used by Hoffmann[36] for a generalized HMO, to distinguish it from the traditional simple MO model of Hückel. Just as Hoffmann was successful in extending the simple HMO calculation to a

novel class of saturated hydrocarbons Herndon and Hosoya were able to extend their quantitative resonance theoretic studies to larger benzenoids with many Kekulé valence structures, which would be impractical to consider with the available computational techniques. The extended basis structures of Herndon and Hosoya supplement a single Clar's structure, or few Clar's structures in the case of migrating $\pi$-sextets, by a small set of "significant" Clar-type structures. In this way one avoids considering dozens, hundreds, and even thousands of Kekulé structures that larger benzenoids have. Extended Clar's structures are defined analogous to the definition of Clar's structures except that the last condition (c): "Clar structure contains the maximum number of $\pi$-sextets" is relaxed. Instead we have the following novel constraint:

(d) "Clar structure may contains less than the maximum number of $\pi$-sextets but no benzene ring should be assigned three CC double and three CC single bonds (i.e., no benzene ring should be assigned benzene Kekulé valence structures).

In Figure 5 we show several extended Clar's structures for dicoronylene.

Finding all Clar-like structures of Herndon and Hosoya for large benzenoids is far from easy. We want to outline a procedure for construction of all extended Clar's structures for a larger benzenoid. It has been incorrectly stated[33,35] that every extended Clar structure corresponds to the so-called maximal independent set of vertexes of Clar graph. If that would be the case the construction of Clar-like structures would follow the construction of an independent set of vertexes of the appropriate graph that depicts the resonance pattern of $\pi$-sextet in a large benzenoid. Gutman[37] described construction of such a graph, which he called Clar graph. In Figure 6 we show one of extended Clar's structure of circumanthracene and the associated Clar graph of circumanthracene. As one can see from Figure 6 the $\pi$-sextet that is shown as a black circle at the right diagram does not represent maximal independent vertex set.

For smaller benzenoids it is not difficult to generate extended Clar's structures. El-Basil and Randić[32,38] introduced the counting polynomial, referred to as Clar polynomial, that summarized the count of Clar-like structures having a different number of $\pi$-sextets. For example, for benzo[*a*]-pyrene, for which all the extended Clar's structures are shown in Figure 7, one obtains as Clar's polynomial $3x^2 + x$. Here powers of $x$ indicate the number of $\pi$-sextets in Clar's
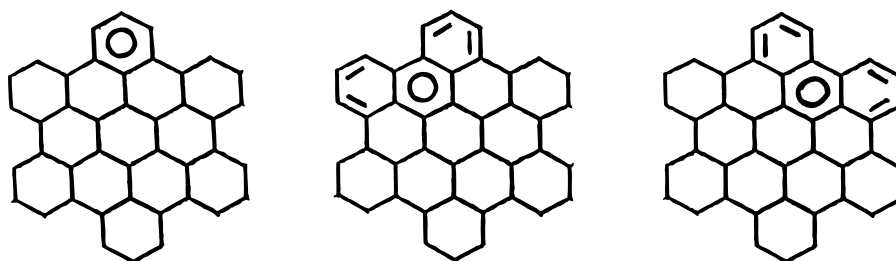


**Figure 9.** The initial steps for the construction of Clar's valence structures of hexabenzocoronene.

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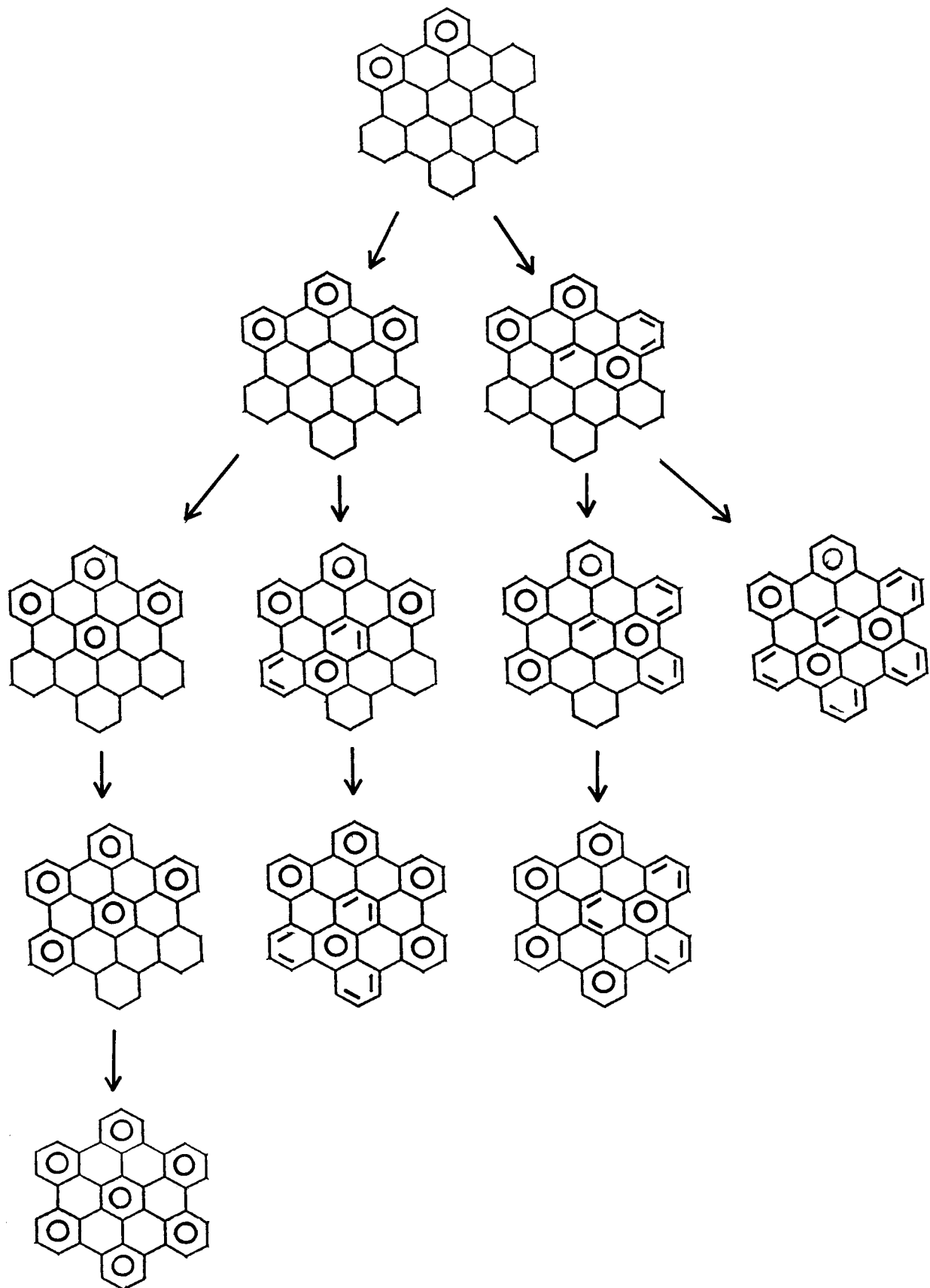


**Figure 10.** The continuation of construction of Clar's valence structures of hexabenzocoronene producing four extended Clar's structures.

extended structure, while the coefficient gives the number of valence structures having that number of $\pi$-sextets. Clar's sextet is analogous to the sextet polynomial of Hosoya and

Yamaguchi[39] which counts the number of generalized Clar's structures of a benzenoid for which the requirements (c) and (d) are dismissed.

### ALGORITHM FOR COUNTING EXTENDED CLAR'S STRUCTURES

We will describe an algorithm for enumeration of Clar's extended structures on hexabenzocoronene. To have a procedure that is valid for an arbitrary benzenoid we will ignore the apparent symmetry of this structure. The symmetry properties of the structures can be taken into account at various steps in the process or at the end of the procedure. First label all 13 rings in the structure with letters A−M (Figure 8), then:

(i) Inscribe the first Clar's sextet in the benzene ring A and all the rings adjacent to A;

(ii) Complete the assignment of the CC double bonds as much as possible;

(iii) Make additional copies of each structure that has not yet been completed;

(iv) Inscribe additional Clar's sextets in all the alphabetically subsequent rings (B, C, D, ...) if possible such that no ring of lesser alphabetic order could be assigned $\pi$-sextet.

(v) return to step (ii) or end if all rings have been consumed.

In the case of hexabenzocoronene the steps described above are illustrated in Figure 9. In the first step we inscribe Clar's $\pi$-sextet circle in rings A, C, and D, the latter two are the only rings adjacent to A. Because of the apparent symmetry we follow only further the steps on the first two cases, because the ring D will give the same outcome as the ring C. After the ring A has been assigned $\pi$-sextet no CC double bonds could be assigned, but in the case of the ring C one can complete the assignment of CC double bonds in the adjacent rings A and B as shown in Figure 9. In Figures 10 and 11 we follow the assignment of $\pi$-sextets to the remaining rings of hexabenzocoronene for the two cases separately. Under each structure we have indicated the partial assignment with letters corresponding to the rings having $\pi$-sextets. In step (iv) structure A gives rise only to the structure AB but not structures AE, AF, or AG. This is because in the cases of AE and AG one could inscribe a $\pi$-sextet circle in ring B, and in the case of AF one could inscribe a $\pi$-sextet circle in ring E, all of which alphabetically would have the priority. Because no further assignment of CC double bonds is possible we go to the next step. From AB we generate structures ABE and ABH, while structure ABG, which alphabetically precedes ABH, is not allowed because it would permit inscribing the $\pi$-sextet circle in ring E. This would be a violation of the requirements of the step (iv). The structure ABH allows one to assign five CC double bonds in rings adjacent to H (see Figure 10). In the next step the structure ABE give rise to ABEG and ABEJ, while the structure ABH leads to the structures ABHI and ABHJ. Except for the structure ABEG the remaining three structures permit assignment of one or more CC double bonds in the rest of the carbon skeleton. At this stage the structure ABHJ has been completely assigned, and thus it represents one of the sought extended Clar's structures of hexabenzocoronene. By following the procedure we obtain structures ABEGI, ABEJL (which is another completed Clar's extended structure), and ABHIM (also completed Clar's extended structure). Continuing the algorithm with the structure ABEGI we finally obtain the structure ABEGILM which has all rings consistent with the rules (a), (b), and (d) assigned $\pi$-sextets.

This particular structure, because it has the maximal number of $\pi$-sextets, is Clar's proper valence structure of hexabenzocoronene. As illustrated in Figure 11 in a similar manner from the structure C we generate four more Clar's structures resulting in the following seven extended Clar's structures:

ABEGILM, ABEJL, ABHIM, ABHJ, CEILM,
$$\text{CEJL, CHIM, CHJ}$$

Now we have to take into account the symmetry properties of hexabenzocoronene. The equivalence of the rings {A, B, E, I, L M}; {C, D, F, H, J, K}, and {G} is apparent. By cyclic substitution ABHIM becomes LEJAB, or alphabetically ABEJL, and similarly CEILM is equivalent to ABEJL, while CEJL is equivalent to ABHJ. Hence there are only four symmetry nonequivalent extended Clar's structures for hexabenzocoronene (illustrated in Figure 12):

### ABEGILM, ABEJL, CEJL, and CHJ

To construct Clar's polynomial we associate with the above four structures the powers $x^7$, $x^5$, $x^4$, and $x^3$ because they involve 7, 5, 4, and 3 disjoint $\pi$-sextets, respectively. The coefficients of the Clar's polynomial are given by the count of each kind of $\pi$-sextet structures, which are (due to symmetry, 1, 6, 6, and 2, respectively) given for the Clar's polynomial of hexabenzocoronene:

$$C(x, G) = x^7 + 6x^5 + 6x^4 + 2x^3$$

Clearly $C(1, G)$ gives the number of extended Clar's structures for graph $G$, which in the case of hexabenzocoronene is 15.

### PROPERTIES OF CLAR'S POLYNOMIAL

For several families of benzenoids and for miscellaneous smaller benzenoids Clar's polynomial has been reported in the literature.[32,38] An inspection of the reported Clar's polynomials shows that different benzenoids can have the same Clar's polynomial. A collection of benzenoids having an identical Clar's polynomial are collected in Figure 13. In each case the pair of structures also has the same number of Clar's structures, but they may have the same or different number of Kekulé valence structures.

Extended Clar's structures are important in the Herndon−Hosoya extension of the Resonance Theory to larger benzenoids. Adjusting the empirical parameters in this resonance model to reproduce as much as possible the molecular resonance energies (RE) in smaller benzenoids that agree with those calculated by Dewar and de Llano[40] using Dewar's SCF TC-MO semiempirical method results in very reliable estimates for the RE for larger benzenoids.[41]

The construction of the extended Clar's structures in large benzenoid systems, and even the construction of the proper Clar's structures in large benzenoid systems,[42] is error prone. Clar's polynomial, if available for large benzenoid, offers the correct count of Clar like structures of different sextet degree and this facilitates checking the correctness of the construction of Clar's valence structures (given by the leading power of the polynomial) and Clar's extended valence structures (given by the sum of the coefficients in the polynomial).

For benzenoids which do not belong to any apparent benzenoid family checking the accuracy of the construction

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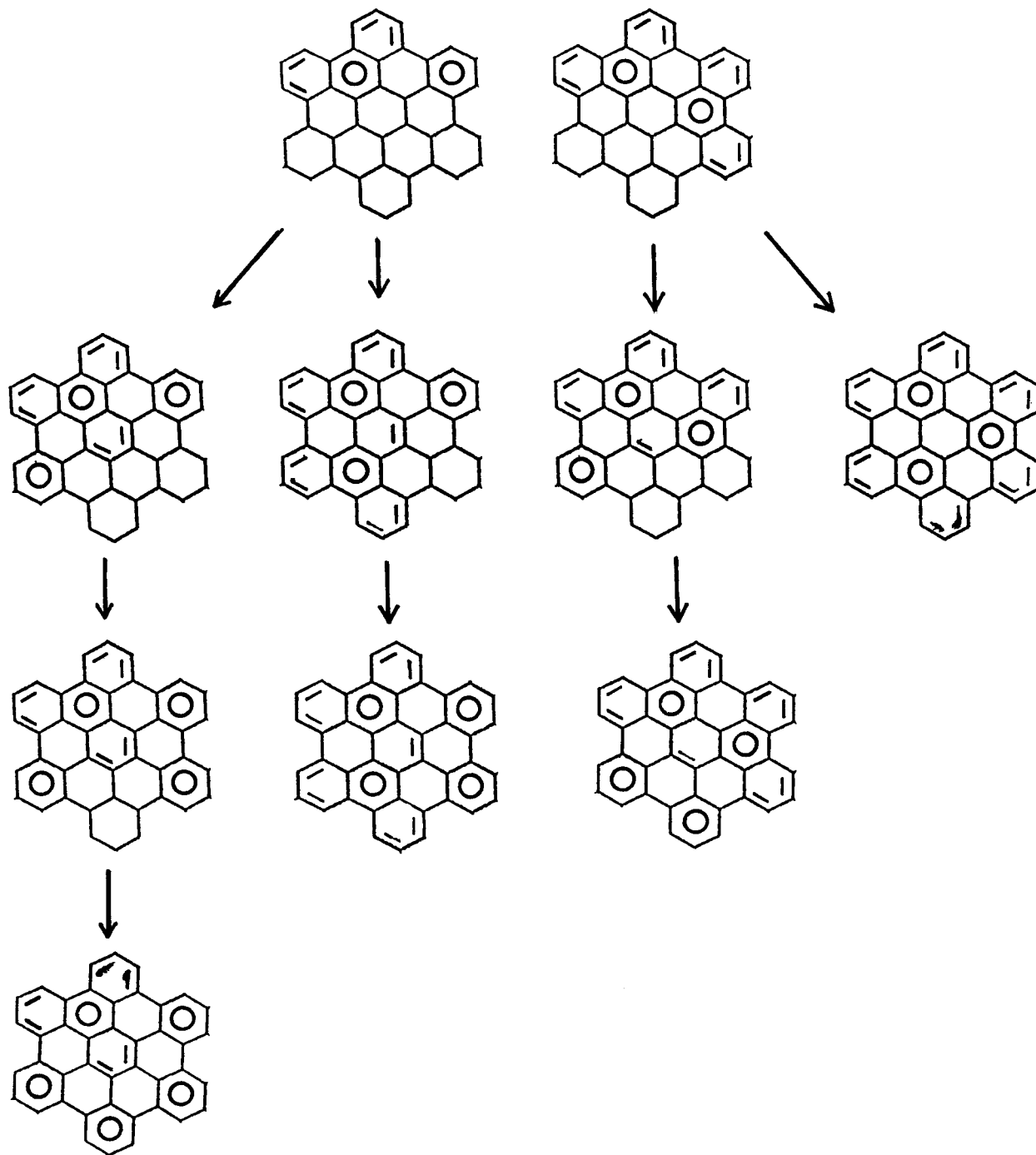*J. Chem. Inf. Comput. Sci., Vol. 38, No. 4, 1998* **569**



**Figure 11.** The final steps in the construction of Clar's valence structures of hexabenzocoronene producing additional four extended Clar's structures.
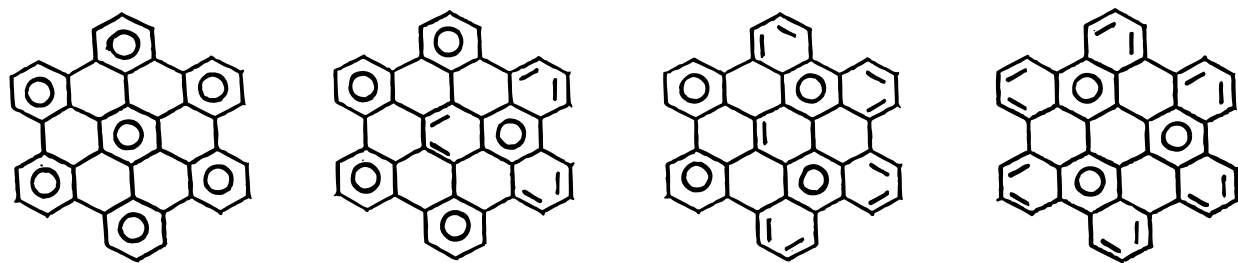


**Figure 12.** Symmetry nonequivalent extended Clar's structures.

of extended Clar's structure is facilitated by construction of the Clar's polynomial, which is a simpler task than the construction of the Clar-like extended basis. Clar's poly-

nomial, as we will shortly explain, can be obtained from selected fragments of the initial structure without the necessity to go through the construction steps outlined by
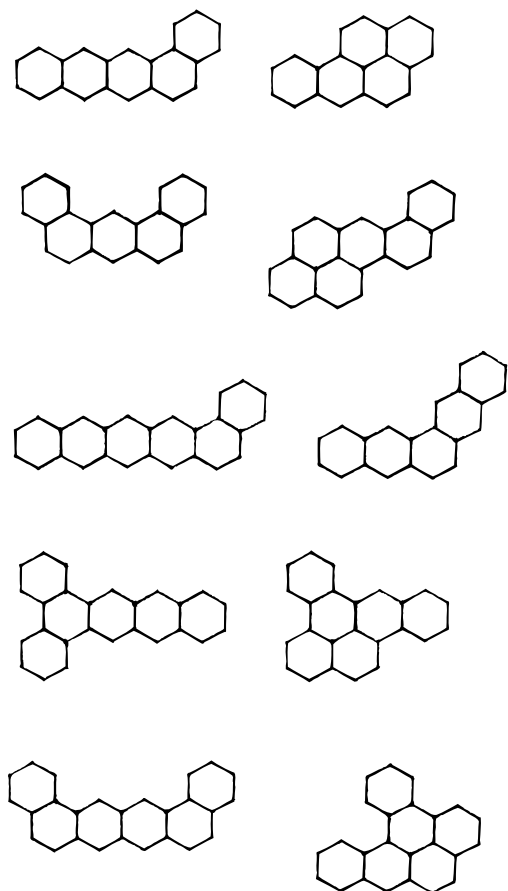
**Figure 13.** Five pairs of benzenoids having identical Clar's polynomial.

our algorithm in the previous section. Clar's polynomial, as we will prove, satisfies a theorem analogous to Clarke's theorem[43] valid for the characteristic polynomial. Using this theorem one can obtain Clar's polynomial of large benzenoids from smaller ones, and recursively the smaller ones from still smaller, till one comes to the fragments small enough for which one can easily write Clar's polynomial.

## GENERALIZED ULAM'S SUBGRAPHS

Ulam's graph reconstruction is one of the "famous problems" in graph theory.[44] The famous problems (like the four color conjecture and the Hamiltonian circuit problem) are those that anyone can understand but nobody can solve! In graph reconstruction problem one is given a set of Ulam's subgraphs of a graph *G*, which are defined as subgraphs in which one vertex at the time (and all incident edges) is deleted. The problem is to prove that the set of Ulam's subgraphs suffice for the reconstruction the graph *G*. In other

words the problem is to prove that the information content of the set of Ulam subgraphs has not been decreased. Ulam reconstruction problem has been proved for trees and a few special cases of cyclic graphs, but it is still unresolved.

Clarke considered another problem involving the reconstruction: Can the characteristic polynomial of a graph be reconstructed from the characteristic polynomials of the corresponding Ulam subgraphs? He was successful in solving this problem and proving a theorem that the sum of the characteristic polynomials of Ulam's subgraphs of a graph *G* is the derivative of the characteristic polynomial of *G*. Hence, by integrating the results, if one could determine the integration constant, the reconstruction would be possible. This finding of Clarke is very interesting and intriguing. It demonstrates an inherent connection between discrete objects (the Ulam's subgraphs) and continuous objects (the derivatives). Randić[45] outlined a possible practical use of the theorem of Clarke by illustrating how the characteristic polynomial of a larger molecule can be obtained from the characteristic polynomials of its selected subgraphs.

## GENERALIZED CLARKE'S THEOREM

The generalized Clarke-type theorem which we prove here considers erasure of the individual benzene rings of a benzenoid, rather than the individual vertices of benzenoid graph.

**Theorem 1.** The sum of Clar's polynomials of benzenoid subgraphs BH* obtained by erasing individual benzene rings (and incident CC bonds) in a benzenoid hydrocarbon BH is the derivative of the Clar's polynomial of BH.

**Theorem 2.** The characteristic polynomial of BH is the sum of the integrals of the Clar's polynomial of the collection of BH* with the integrating constant $c = 0$.

The above two theorems can be summarized in the equation

$$C(x, \text{BH}) = \sum \int C(x, \text{BH*}) \, dx$$

The asterisk indicates the rump benzenoid hydrocarbons with missing individual benzene rings corresponding to Ulam's subgraph in the Ulam reconstruction problem.

## ILLUSTRATIONS

**Hexabenzocoronene.** There are three symmetry nonequivalent rings in this structure (rings A, C, and G of Figure 8), hence there are three nonequivalent generalized Ulam subgraphs BH* in hexabenzocoronene. Figure 14 illustrates the corresponding subgraphs. We use an asterisk with a letter representing rings to indicate which ring of BH has been
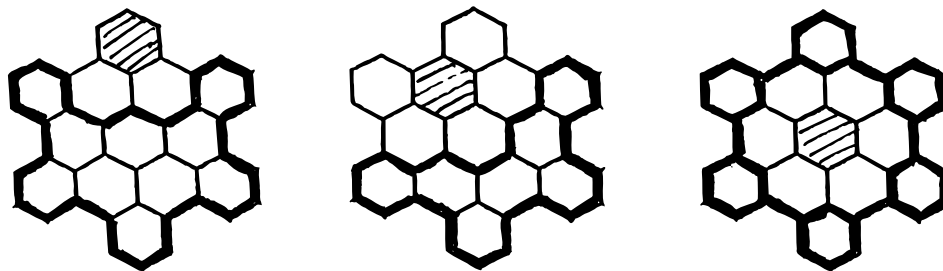


**Figure 14.** Symmetry nonequivalent generalized Ulam subgraphs of hexabenzocoronene.
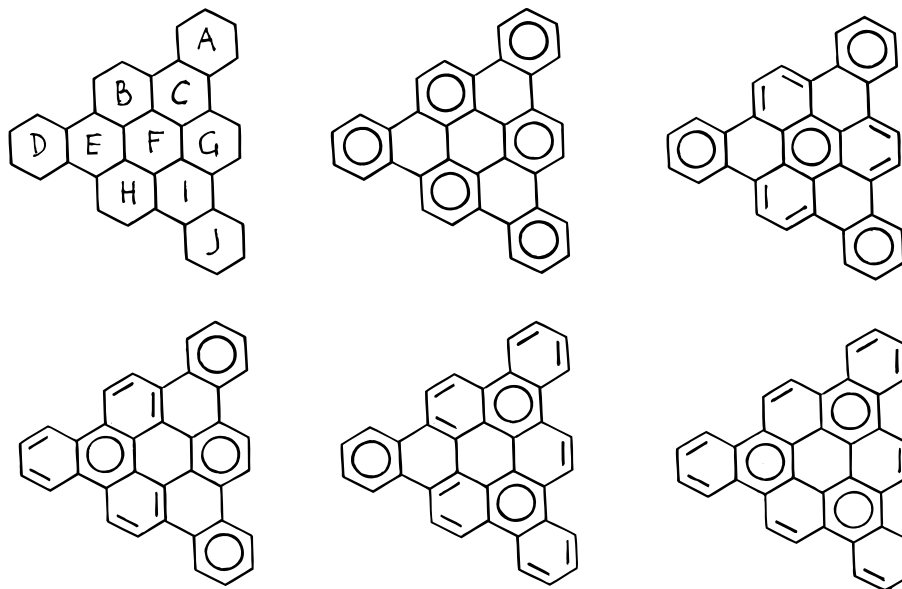
**Figure 15.** The five symmetry nonequivalent extended Clar's structures for tribenzo(a,g,m)coronene.

deleted. The Clar's polynomial of the first subgraph $A^*$ can be found following the algorithm described. The second subgraph $C^*$ gives immediately for its contribution $(x^2 + x)^2$ because the residual $C^*$ can be viewed as two independent phenanthrene units, each contributing the factor $(x^2 + x)$, which is Clar's polynomial of phenanthrene. The last structure $G^*$ leads to another term $x^6$, there being six $\pi$-sextets in $G^*$, all independent of one another. Hence for the derivative of the Clar's polynomial of hexabenzocoronene we obtain from $A^*$ (and its symmetry equivalent rings) $6x^6 + 24x^4 + 12x^3$, from $C^*$ and its symmetry equivalent rings $6x^4 + 12x^3 + 6x^2$, and finally from $G^*$ we obtain $x^6$. All this adds to $7x^6 + 30x^4 + 24x^3 + 6x^2$ which when integrated gives the expected $x^7 + 6x^5 + 6x^4 + 2x^3$.

**Tribenzo(a,g,m)coronene.** In Figure 15 we depicted the five symmetry nonequivalent extended Clar's structures of tribenzo(a,g,m)coronene which, when symmetry weights are taken into account, yield for Clar's polynomial $x^6 + 4x^4 + 4x^3$. The four nonequivalent rings (A, B, C, and F in Figure 16) give rise to the following Clar's polynomials

$$A^* \quad x^5 + 3x^3 + x^2$$

$$B^* \quad x^2(x^3 + x)$$

$$C^* \quad x^3 + 3x^2$$

$$F^* \quad x^3$$

The factor $(x^3 + x)$ is Clar's polynomial of triphenylene, while the last structure of Figure 16 makes no contribution, because while it represents a valid Kekulé valence structure of the residual $F^*$ it has no isolated $\pi$-sextets that would contribute to a Clar's structure. When the symmetry weights of various rings are taken into account we obtain for the derivative of the Clar's polynomial of tribenzo(a,g,m) coronene

$$3A^* + 3B^* + 3C^* + F^* = 6x^5 + 16x^3 + 12x^2$$

Indeed the above is the derivative of the Clar's polynomial of tribenzo(a,g,m)coronene demonstrating the correctness of the theorems 1 and 2.

**Dicoronylene.** Figure 17 illustrates a construction of Clar's polynomials for structures obtained by erasure of symmetry nonequivalent rings of dicoronylene. Because the CC bonds of the central ring that connect the two coronene fragments are essentially single CC bonds the contributions of the two coronene units can be considered separately, each giving a factor of the Clar polynomial for the composite structure. Clar's polynomial for coronene is $2x^3 + 3x^2 + 2x$ which is one of the constant factors in all the contributions. The upper fragment of dicoronylene, considered in isolation (because of the presence of the essential CC single bonds), then gives the second factor resulting in (Figure 17)

$$A^* \quad (x^2 + x)(2x^3 + 3x^2 + 2x)$$

$$D^* \quad 2(2x^3 + 3x^2 + 2x)$$

$$H^* \quad 0$$

The factor two in $D^*$ comes because one can write two Kekulé valence structures for the "super-ring" which doubles the number of Clar's structures for the lower coronene fragment. By taking into account the symmetry of dicoronylene we finally obtain for the derivative

$$6A^* + 2D^* = 12(x^2 + x)(2x^3 + 3x^2 + 2x) +$$
$$4(2x^3 + 3x^2 + 2x) = 24x^5 + 60x^4 + 68x^3 + 36x^2 + 8x$$

Upon integration this gives for the Clar's polynomial of dicoronylene

$$4x^6 + 12x^5 + 17x^4 + 12x^3 + 4x^2$$

Several symmetry nonequivalent extended Clar's structures are illustrated in Figure 5.

DISCUSSION

Clar-like structures considered here represent a generalization of the initial structures as proposed by Clar. These
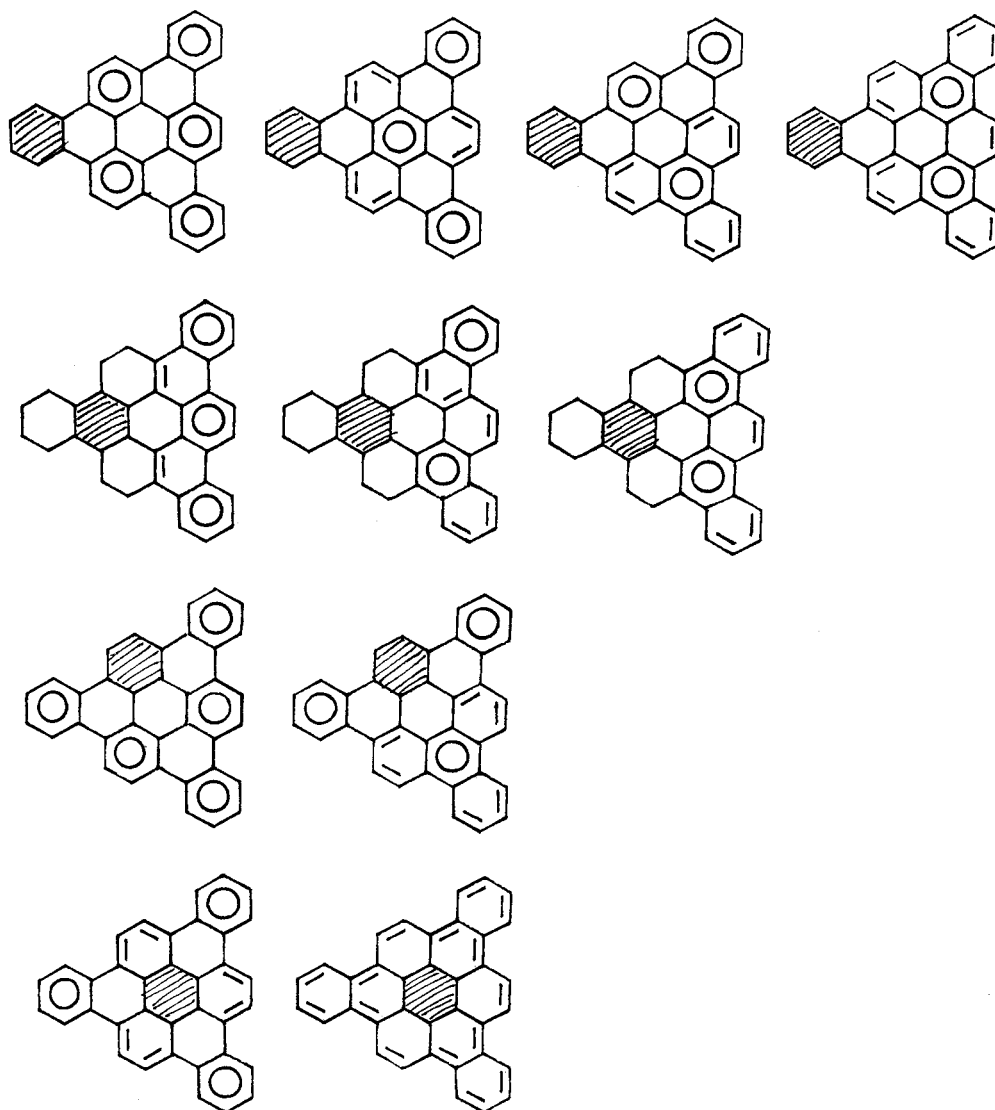
**Figure 16.** Symmetry nonequivalent extended Clar's structures for generalized Ulam's subgraphs of hexabeznocoronene.

structures have been sometimes referred to as generalized Clar's structures, but the same term has been used by Gutman for a different generalization of Clar structures.[37] The label "extended Clar's structures" can be shortened to simply Clar's structures when no confusion is likely to occur, rather than referring to them as generalized Clar's structures which may cause confusion with Gutman's Clar-like generalized structures. We have used here elongated label "extended Clar's structures" systematically primarily to avoid confusion with more general Clar-like structures of Gutman, but Clar's structures may be more convenient label for the future use. When a distinction need be made between the structures as proposed by Clar and the structures considered here (proposed by Herndon and Hosoya) one can refer to the former as the "proper Clar structures" and the later as the "Clar structures".

There is an interesting consequence of using the extended Clar's structures instead of the "proper Clar structures" even in qualitative descriptions of benzenoids. Clar's approach recognized not only the presence of the rings that have $\pi$-sextets but also the presence of the rings that are devoid of $\pi$-sextet content, the so-called "empty" rings. In contrast to Clar's original approach when generalized Clar's structures of Herndon and Hosoya are used some of the "empty" rings

of a benzenoid need not any longer be empty. Thus the central ring of triphenylene according to Clar is an "empty" ring but that rings contribute to the overall conjugation when the systems is described with the generalized Clar structure
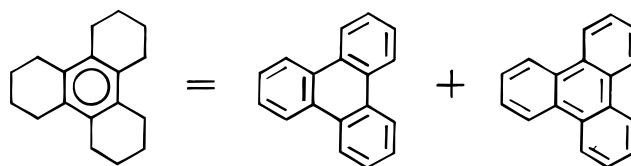


which as we see can be viewed as a superposition of two Kekulé structures. Because the other Clar's structure of triphenylene
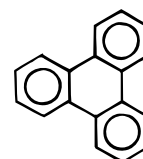


require eight (out of the nine) Kekulé structures of triphenylene the extended Clar's structures use all nine Kekulé valence structures, with the first of the two Kekulé structures

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shown above being used twice, i.e., with the weight 2. It is interesting to observe that the Kekulé structure having the largest weight is precisely the structure that the empirical Fries rule indicates as dominant. Thus the Clar's approach amounts to neglect of some Kekulé valence structures, while the Herndon−Hosoya approach amounts to giving greater weight to some Kekulé valence structures.

In contrast to the central ring of triphenylene the central ring of perylene (and the same is true of the central ring of dicoronylene) remains "empty" not only in Clar's original approach but also in the approach of Herndon and Hosoya. If one analyzes the conjugated circuits[26] involved in the underlying Kekulé valence structures, then one sees that the rings with essentially single CC bonds cannot contribute to the molecular RE. Hence, one can differentiate between the "apparently" empty rings of Clar (as predicted by proper Clar's structures) and the "genuinely" empty rings, such as the central ring of perylene. We may say that the former have, in the first approximation, the zero content of $\pi$-sextet (Clar's theory), to which the refined models, such as the Herndon-Hosoya approach,[35] the Herndon's Resonance Theory,[25] and the Conjugated Circuit Method,[26] would attribute small nonzero value. For example, the "empty" rings of supernaphthalene (shown as "empty" in Figure 1) vary in their resonance content between 0.25 and 0.32 eV which is two to three times less than the contribution of the $\pi$-sextet rings in this molecule.[46] The same again is the case with the "empty" rings of superphenalene.[47] It seems therefore useful to maintain the distinction between the two kinds of "empty" rings. We suggest that the former rings, e.g., the central ring of triphenylene, should be referred to as "empty" (with the quotation marks), while the letter, e.g., the central ring of perylene, is referred to as empty (without the quotation marks). If one is to assign a mathematical symbol, the former would be indicated by zero (0) and the latter with the sign for empty set (ø).

### PROOF OF THE THEOREMS

Let $\{h_1, h_2, ..., h_n\}$ be a subset of hexagons belonging to B(H) such that each $h_i$, $1 \leq i \leq n$, can have a Clar circle simultaneously and thence contribute $x^n$ to $x$ [B(H); $x$]; i.e., the above subset of hexagons is resonant. There are n routes (paths) to $x^n$, viz.

$h_1$ resonant with $h_2$, $h_3$, ..., $h_n$;

$h_2$ resonant with $h_1$, $h_3$, ..., $h_n$;

⋮

$h_i$ resonant with $h_1$, $h_2$, ..., $h_{i-1}$, $h_{i+1}$, ..., $h_n$;

⋮

$h_n$ resonant with $h_1$, $h_2$, ..., $h_{n-1}$

Then, the term $x^n$ will be generated $n$ times in the algorithm and therefore must be divided by $n$ to yield the correct term in $x$ [B(H); $x$]. The operation is carried out in the following way:

(a) Divide the sum of $x^n$ terms in $x$ [B(H); $x$] by $x$ and

(b) Multiplication by $n$ leads to the polynomial $z$ [B(n); $x$] which can be obtained by a stepwise deletion of the $h_i$'s; $i = [1,H]$ (where $H$ = total number of hexagons in B) and summation of the resulting Clar polynomials of BQ$h_i$ (i.e.,
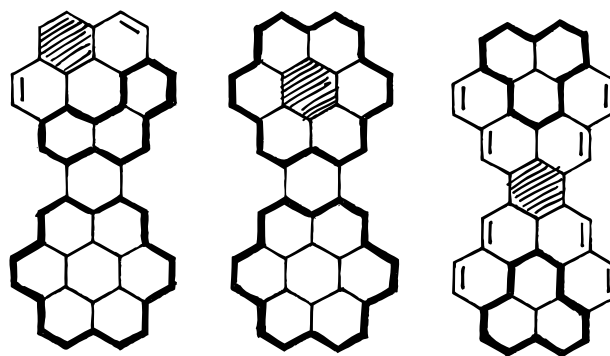


**Figure 17.** Fragments contributing to extended Clar's structures for generalized Ulam's subgraphs of dicoronylene.

B after $h_i$ and all edges incident to it are deleted). However, steps (a) and (b) are equivalent to finding the derivative of $x$ [B(H); $x$], i.e.:

$$\mathrm{d}/\mathrm{d}x \, [x \, (x)] \int [x \, (x)]' = z \, (x) \qquad (6)$$

Then, if each term in $z$ $(x)$ is

(a′) multiplied by $x$ (to account for contribution of $h_i$ to be removed from B)

and

(b′) divided by $n$ (to account for the fact that each $x^n$ is generated in times in the algorithm), the Clar polynomial is obtained

$$\int z \, (x) \, \mathrm{d}x = x \, (x) \qquad (7)$$

because steps (a′) and (b′) are equivalent to integrating $z$ $(x)$.

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