

On Enumeration of Kekulé Structures for Benzenoid Tori

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Abstract

Hypothetical benzenoid tori serve as models for estimating the properties of graphite because their electronic states are found rapidly to converge to that of graphite. We present an algorithm for enumeration of Kekulé structures of these benzenoid tori. The basis for our algorithm is consideration of those CC connecting lines which convert a 2-dimensional benzenoid into a torus. By successive selection of such "connecting" lines as CC single and CC double bonds we effectively transform a benzenoid torus into a collection of planar benzenoids, the Kekulé structures of which are thus enumerated. The number of benzenoids and rump benzenoids derived by excision of "connecting" bonds and adjacent bonds is governed by the binomial distribution. The approach is illustrated on benzene and coronene tori. The results for a few other simple benzenoid torus networks are presented including also the result for a torus based on circumcoronene with over 15,000 Kekulé valence structures.

Introduction

Theoretical calculations on very large systems are necessarily confined to very simplified approaches. One could almost say that an increase in the size of a system by an order of magnitude, i. e., by a factor of 10, requires one to consider an alternative theoretical approach. In Table I we summarized the present situation with theoretical calculations on benzenoid systems. The interest in large benzenoids is fueled by our interest in the electronic structure of graphite. It is believed that a model having some 10^5 carbon atoms ought to offer a fair insight into the electronic properties of graphite. However, the 10^5 number of π -electrons is too large to be considered by present computational schemes. In additions, one should be aware that the method as listed in Table I decreases in accuracy

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Table I. Theoretical methods appropriate for modeling molecular systems of various sizes.

| The number of carbon atoms | theoretical method |
|----------------------------|---|
| $\sim 10-10^2$ | Ab initio method |
| $\sim 10^2$ | Resonance theory Conjugated circuits |
| $\sim 10^3$ | Clar sextet model |
| $\sim 10^4$ | Hückel MO Free Electron model |
| $\sim 10^5$ | ? |

and hence reliability. For example, the Resonance Theory of Herndon¹ and the Conjugated Circuit model² can be parametrized to simulate SCF MO calculations such as carried by Dewar and de Llano on smaller benzenoids³. Hence, such calculations can give quite reliable estimates of the molecular stability (as measured by the molecular resonance energy). The model is essentially confined to π -electrons as contained in the Pariser-Parr-Pople approach^{4,5} and thus ignores the possible role of the σ -electron frame. However, while in smaller benzenoids σ -electron network can introduce contributions due to deformations of the regular hexagonal geometry by the presence of CC bonds of different lengths, this effect is to be negligible in the case of graphite. Herndon and Hosoya's method⁶ using Clar sextets is computationally simpler and appears to give satisfactory results for smaller benzenoids but its extension to much larger benzenoids has yet to be independently verified. Also, as has been recently reported⁷ already construction of Clar structures for large benzenoids is far from simple, and may present a restriction on unlimited model extension. The Hückel method⁸, which in fact represents a simple graph theoretical model based on the adjacency relationship of carbon atoms⁹, can be extended to large systems but this method fails to give adequate quantitative description even of small benzenoids, hence at best can offer some qualitative insight into the electronic structure of graphite.

One way to approximate graphite is to impose cyclic conditions on smaller benzenoids. Analysis of the π -electronic structure of infinitely large networks using cyclic polymers by consecutively joining selected carbon atoms in the repeating units has been reported. For example, Hosoya and coworkers reported the analytical expression for the densities of states of several cyclic polymers such as linear and zigzag polyacene and polynaphthalene¹⁰. Klein and coworkers¹¹ on the other hand applied a very powerful transfer-matrix method for subgraph enumeration and were able to speculate the relative resonance energies as a function of the length

of the strip of polypyrene. The transfer-matrix method allows finding the limit for the resonance stabilization as the length of the strips extends to infinity. When the size of the benzenoid network with different peripheral structure of a finite width is increased to infinity, the difference in the stability and density of states is found to remain¹². Thus the electronic states of these cyclic benzenoids do not converge to that of graphite. It was found that if such cyclic models are extended to more than a single direction to form a "torus", the peripheral dependency eventually disappears and they approach the limit of graphite¹³. Not only the HMO but also the PPP (Pariser-Parr-Pople method) calculations for those networks are found to converge amazingly rapidly to graphite. Several hypothetical torus networks only with several hundred carbon atoms are found to give the same convergence limit of graphite. On the other hand, from resonance theoretic standpoint, almost nothing has been discussed on the peripheral dependency and convergence speed of the electronic structure of the torus networks.

In contrast to 2-dimensional planar polycyclic carbon networks of benzenoids the number of Kekulé valence structures in torus networks dramatically increases. For example, in the case of coronene torus (to be examined later as an illustrative case) there are 120 Kekulé valence structures compared to 20 of coronene, while there are six for benzene torus compared to two for benzene.

As the first step of this new approach to the electronic structure of graphite, an elementary but novel technique for enumerating the number of Kekulé valence structures of torus benzenoids will be introduced and discussed in this paper.

Algorithm for Kekulé Count in Torus Benzenoids

We will assume that a parent benzenoid has been selected and the corresponding torus structure to be examined is constructed. Consider the binomial coefficients $\binom{n}{k}$, where n is the number of "long" bonds and k takes values $k=0, 1, 2, \dots, n$. The running index k indicates the number of paired vertices to be erased at each successive step.

- (1) Assign labels (such as letters of the alphabets) to periphery of the parent graph in such a manner that vertices which are connected by a "long" bond have the same label.
- (2) Start with $k=0$ (one structure) which is the parent structure, i.e., the structure in which none of the vertices at the periphery was erased. Find the number of Kekulé structures (K) for the parent structure.

- (3) Increase the value of k to $k+1$.
- (4) Erase k pairs of the vertices at the periphery. Construct all $\binom{n}{k}$ such subgraphs consecutively in dictionary order.
- (4) Assign CC double and CC single bonds to all pending bonds and adjacent bonds as much as possible.
- (5) Find the number of Kekulé structures for the residual benzenoid fragment.
- (6) If $k=n$ add all the partial results to obtain K , if not repeat step (3). In step (3) grouping of symmetrically equivalent choices reduces considerable amount of enumeration.

Benzene torus

At the top of Figure 1 we have illustrated benzene torus which is equivalent to the Ladenburg's formula of benzene, or in graph theoretic terminology to Kuratowski graph $K_{3,3}$ ¹⁴. Our procedure for enumeration of the Kekulé valence structures of such systems is to convert a torus system to a set of planar benzenoids, or fragments thereof. This is obtained by successive assignment of CC single(s) and CC double(d) bonds to the set of the "long" bonds, which converted the parent benzenoid into a torus structure. A stepwise process is illustrated in Figure 1 on benzene torus with the family of its subgraphs. The thick "long" bond in each of the parent graph and subgraphs can be assigned as s or d to give two graphs in the next row. When bond e is assumed to be a CC single bond it is simply erased to give a subgraph G-e (shown as the left choice) and when assumed as a CC double bond it is erased together with the adjacent bonds to give $G \ominus e$ (shown as the right choice).

This procedure is implied already in Wheland's recursive expression for enumeration of Kekulé structures of various degrees of excitation¹⁵ and has been implemented for a systematic construction of Kekulé valence structures in arbitrary polycyclic systems¹⁶. What is novel and different in this algorithm is that we focus attention only to "long" or torus-closure bonds.

The final result of successive considerations of all three (thick) long bonds is shown by the eight ($=2^3$) structures in the last row of Figure 1, below each of which the number of d steps for generating it and the number of Kekulé structure (degeneracy) are given.

Among the eight structures we have a benzene ring (with 2 Kekulé structures), three "Dewar-type" valence structures (with central bond erased) and one final structure ϕ in which all bonds have been erased. Since a benzene ring generates two Kekulé structures, the number of Kekulé struc-

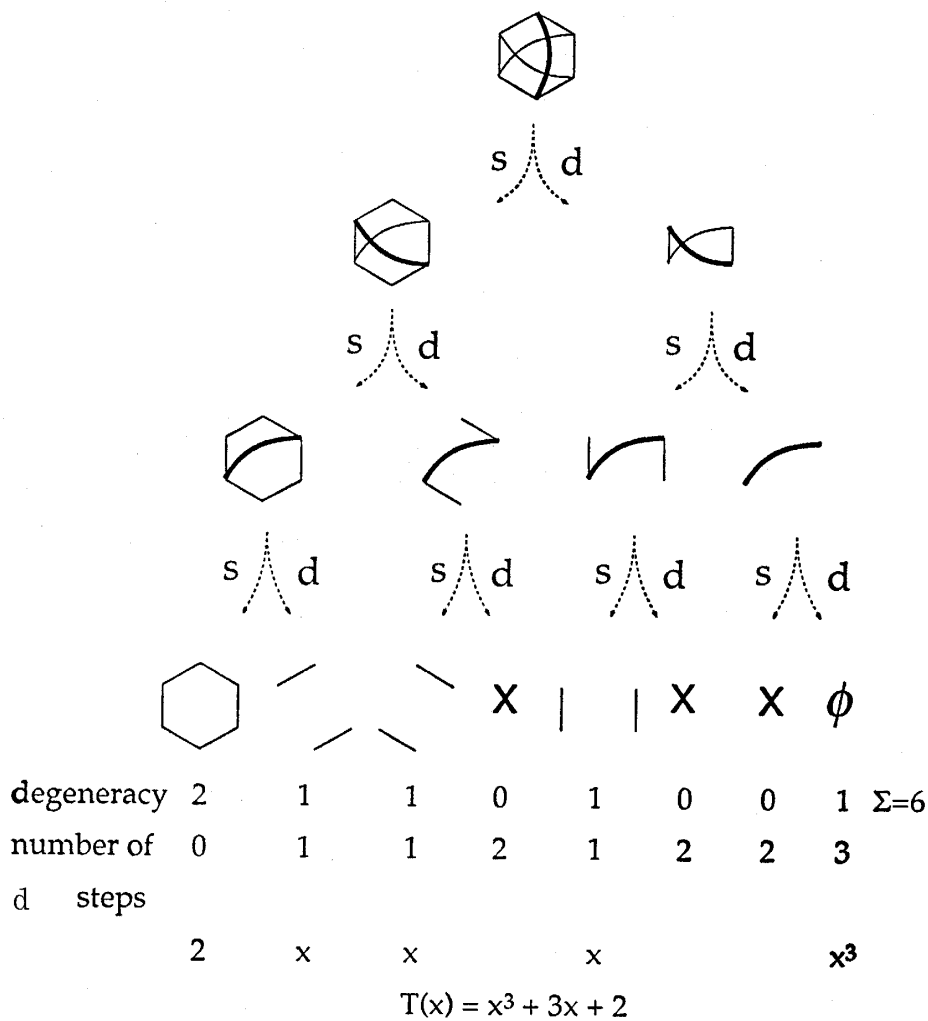


Figure 1. Successive elimination of long torus bonds in benzene.
 s: single and d: double
 x: no Kekulé structure
 ϕ : vacant graph ($K=1$)

tures for benzene torus is six.

| #d | #K | degeneracy | Kekulé count | $T(x)$ |
|----|----|------------|--------------|--------|
| 0 | 2 | 1 | 2×1 | 2 |
| 1 | 1 | 3 | 1×3 | $3x$ |
| 2 | 0 | 3 | 0×3 | $0x^2$ |
| 3 | 1 | 1 | 1×1 | x^3 |
| 6 | | | | $T(x)$ |

The total count of the Kekulé structures for benzene torus, hence, gives as the answer $K=6$. The coefficients 1, 3, 3, 1 in the above table are nothing else but the binomial coefficients of the Pascal triangle.

Let us define the torus polynomial of benzenoids, or more correctly

the polynomial of torus benzenoids, $T(x) = \sum_{k=0}^n t_k x^k$, with the coefficient t_k , for the term x^k being the number of Kekulé structures with k long bonds. Here k runs from zero to n , the number of torus "long" bonds. Then for the benzene torus we have $T(x) = x^3 + 3x + 2$ (See above). In this polynomial the Kekulé number can be expressed as $K = T(1)$.

Benzene torus is too small to show all facets of the algorithm. So we will illustrate the approach once again on somewhat larger coronene torus.

Coronene Torus

In Figure 2 we illustrate coronene torus, a structure obtained by linking six pairs of carbon atoms at the opposite mirror sides of the molecular periphery. This graph has a high symmetry which is not apparent from its pictorial representation as D_{6h} . It consists only of hexagons, as was the case also with benzene torus. One can show that such systems have high symmetry using canonical labeling^{17,18}. It is precisely this "all-hexagon" character of the structure which is the reason for embedding benzenoid networks on torus, rather than on a sphere. In the case of embedding of graphs on a sphere twelve pentagons (just as in buckminsterfullerene) would necessarily have to be introduced. This makes the system less graphite-like. The carbon skeleton of the coronene torus represents an edge and vertex transitive graph, and also has been obtained using an approach based on graph generators, simple symmetric 3×3 permutation matrices¹⁹. Hence, not only all carbon atoms, and all carbon bonds but also all six membered rings in this torus structure are strictly equivalent. It is this high symmetry which we believe is behind fast convergence of such a model toward infinitely large graphite network which is also characterized by strictly equivalent carbon atoms, carbon CC bonds and all hexagonal rings. In any other finite model, except the torus, perturbation caused by boundaries will adversely affect the model, unless one extends computations to the limit of the infinitely large network.

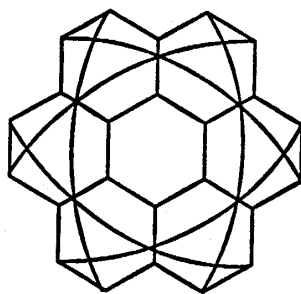


Figure 2. Coronene torus.

In Figure 3 we illustrate our approach on coronene torus. At the first of the figure we show labels used to distinguish different "long" bonds. We have abbreviated labels aa to A, bb to B, etc.

At the first step, case $k=0$ we have coronene, known to have $K=20$. Our next fragment, labeled as A (or aa) is illustrated in Figure 3 just beside the coronene structure. It is obtained by erasure of the vertices a, a together with incident (peripheral) edges from the coronene diagram to yield graph $G \ominus A$. Structure A has two pending bonds which are assigned as CC double bonds and which induce assignment of another CC double bond (at the left part of the diagram). By ignoring all the CC bonds with so assigned CC single and CC double bond types we obtain as a fragment pyrene with $K=6$. From symmetry consideration we got $6 \times 6 = 36$ structures for coronene torus from this kind of steps.

Next we consider pair of letters of the AB type, as shown in the second row of Figure 3. The first fragment comes with weight 6, there

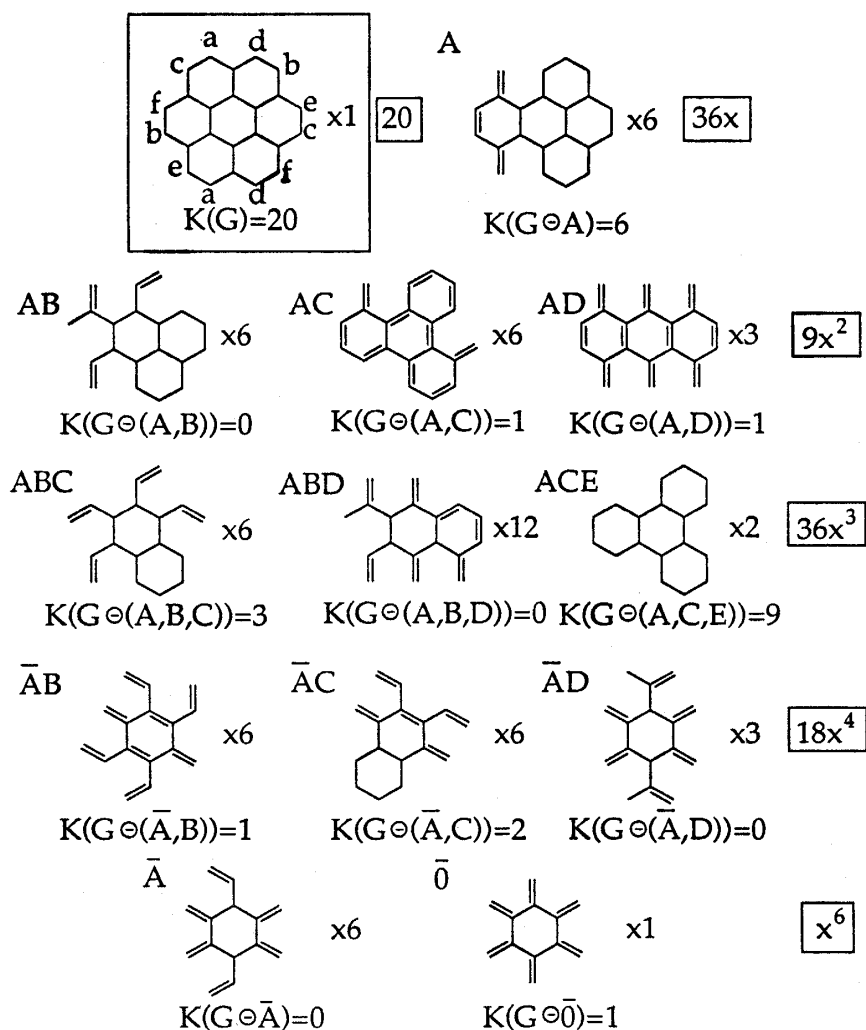


Figure 3. Successive elimination of long torus bonds in coronene.

being six symmetry equivalent such diagrams (combinations AB, BC, CD, DE, EF, FA obtained by cyclic substitutions). However, they can be ignored because of no Kekulé structure. The diagram AC, derived by erasure of vertices with labels a and c has a single Kekulé structure, and the same is true for the fragment AD. Thus AD has the symmetry equivalent counterparts: BD, CE, DF, EA, FB, in total of 6. The last structure has higher symmetry, in all there being three such structures: AD, BE and CF in which carbon atoms at the opposite sites define each structure.

The process continues as illustrated at the central part of Figure 3. Again there are only three symmetry nonequivalent combinatorial possibilities: ABC, ABD, and ACE. They come with symmetry numbers 6, 12 and 2 respectively. The first fragment, after the four pending bonds have been assigned as CC double bonds, results in a naphthalene fragment with $K=3$, and the last gives triphenylene with $K=9$. The middle fragment corresponds to a radical and has no Kekulé valence structure. Hence at this "level" of enumeration we have $6 \times 3 + 2 \times 9 = 36$ Kekulé valence structures, contributing the term $36x^3$ to $T(x)$.

By now we have reached half of the algorithm, there is no need to continue to keep the record of individual residual fragments any more, since the remaining fragments can be viewed as complements of those already listed. Thus ABCD correspond to \overline{EF} , which has been already listed, ABCE corresponds to \overline{DF} and so on. The derived structures are shown in the lower part of Figure 3. Again we have to complete the individual fragments and count the Kekulé structures. Notice that there is no symmetry in the count of structures such as AB and the complement \overline{AB} , that is CDEF (or symmetry equivalent ABCD). The former has no Kekulé structure, the latter has one Kekulé structure. The remaining

Table II. Contributions from Kekulé valence structure having different number of torus long bonds.

| | | | | | | | |
|---|-----------------------------------|------|-------------------|--------------------|-------------------|-----|-----------------|
| Binomial coefficients | 1 | 6 | 15 | 20 | 15 | 6 | 1 |
| | (Number of graphs to be examined) | | | | | | |
| Partial contributions | 1×20 | 6×6 | 6×0 6×1 3×1 | 6×3 12×0 2×9 | 6×1 6×2 3×0 | 6×0 | 1 |
| Total contributions | 20 | 36 | 9 | 36 | 18 | 0 | 1 |
| $T(x) =$ | 20 | +36x | +9x ² | +36x ³ | +18x ⁴ | | +x ⁶ |
| Number of Kekulé structures: $K = T(1) = 120$ | | | | | | | |

part of Figure 3 shows fragments obtained by erasure of five and six, i. e., all peripheral pairs of vertices. After completion of this procedure, one can check these numbers by taking into consideration of the symmetry of each Kekulé structure.

Table II summarizes the results. The torus polynomial for corenene torus is obtained as

$$T(x) = x^6 + 18x^4 + 36x^3 + 9x^2 + 36x + 20.$$

Ring Characterization

All hexagonal rings in many torus systems of interest are found to be equivalent. Hence, in such a case we need only count the number of Kekulé valence structures (K^*) for the subgraph $G \ominus R$ of the torus in which any ring R is selected to be deleted (Fig. 4). By applying the same algorithm we get eight different Kekulé structures with three long bonds, six Kekulé structures with a single long bond, and two Kekulé structures for 18-membered annulene (i. e., the valence structure without long bonds). The result of the count can be expressed by the following polynomial:

$$T^*(x) = 8x^3 + 6x + 2,$$

where the coefficient to the term x^k gives the number of Kekulé structures with k long bonds.

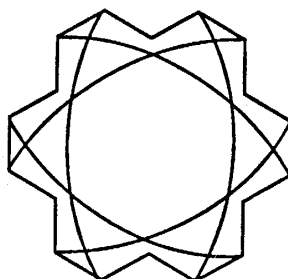


Figure 4. Coronene torus subgraph $G \ominus R$
(R represents a benzene ring).

Circumcoronene Torus

Next we will consider circumcoronene torus depicted in Figure 5, i. e., a torus derived from a coronene circumscribed with a layer of hexagons. We get the polynomial $T(x)$ and $T^*(x)$ as

$$T(x) = x^9 + 171x^7 + 978x^6 + 639x^5 + 3600x^4 + 5373x^3 + 1278x^2 + 2142x + 980$$

$$T(1) = 15,162$$

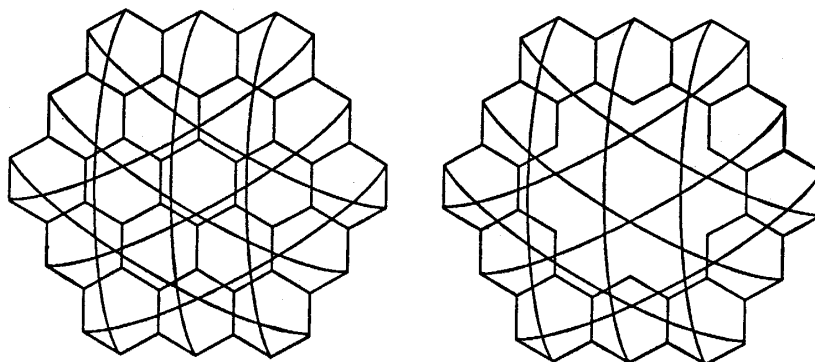


Figure 5. Circumcoronene torus and the subgraph obtained by deleting a benzene ring together with all the incident edges.

$$T^*(x) = 216x^6 + 504x^4 + 736x^3 + 240x^2 + 240x + 200$$

$$T^*(1) = 2,136.$$

By summing all the contributions we obtain for the number of Kekulé structures of circumcoronene torus an impressive number $K=15,162$. This number is even larger than the number of Kekulé structures of buckminsterfullerene though our structure has “only” 54 carbon atoms compared with 60 carbon atoms of buckminsterfullerene.

There seems to be some regularity for the derived polynomials in that the leading coefficient is 1 and the next power has coefficient zero just as is the case with the characteristic polynomial. The constant term is the number of Kekulé structures of the parent benzenoid. Whether these polynomials have some useful properties remains yet to be seen. However, as will be discussed in the later part of this paper, they have potentially interesting features related to the aromatic property of benzenoids and graphite.

On the Count of Kekulé Structures in Benzenoids

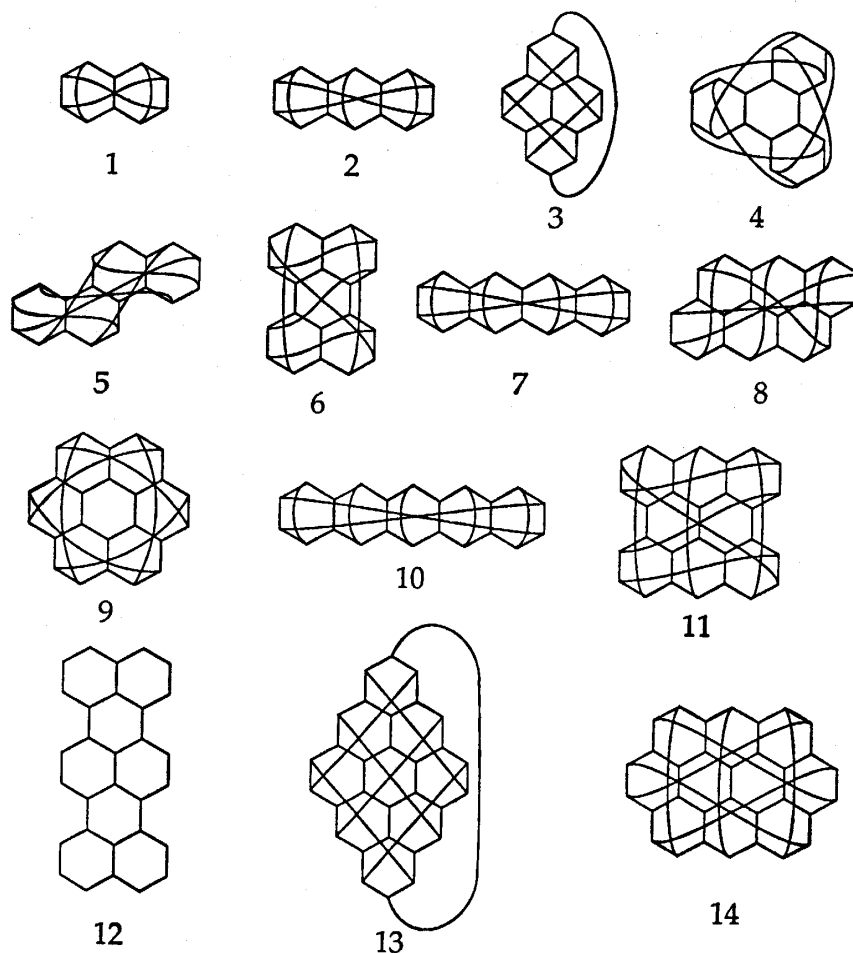
For all benzenoids having nine and less fused benzene rings Knop and coworkers have enumerated K structures²⁰. On the other hand Cyvin and Gutman have considered many types of large fused benzenoids and gave either the number of Kekulé structures or formulas which can be used to derive the count²¹. We found that to derive the Kekulé count for dozen or two dozen larger benzenoids can be time consuming unless one uses very efficient algorithms whenever possible. The following are the most efficient and most elegant algorithms that we have found very valuable:

| | |
|-----------------------------------|--|
| Benzenoid type | Algorithm |
| Catacondensed no branching | Gordon and Davison ²² : Insert numbers in hexagons following the addition rules for "kinks" |
| Catacondensed single branching | Randić ²³ : follow Gordon and Davison for individual branches, combine results for rings adjacent to center and rings of nearest kink |
| Lattices | Randić ²³ : Apply Gordon and Davison to peripheral rings, fill inside rings using Pascal triangle rule |
| Multilattices | John and Sachs ²⁴ Construct determinant using lattice rule to get elements of the determinant |

These approaches allow one to find the number of Kekulé structures for most cases of fragments derived by erase or vertices and already assigned bonds. Here we termed "multilattice" case which can be viewed as derived by fusion or overlap of lattices. Hence such benzenoids should have the same number of "master" and the same number of "slave" vertices. The approach of John and Sachs will cover most fragments not already covered by the algorithm of Gordon and Davison or not being a lattice. If one encounters a fragment which does not belong to any of the simply treated cases one can apply the standard recursion on selected edges and eventually reduce such cases to those already mentioned.

Results for Some Smaller Torus Benzenoids

In this section we will report on enumeration of Kekulé valence structures in smaller torus benzenoids in order to illustrate variations in the number of Kekulé valence structures and in the structure of the torus polynomials. In Figure 6 we illustrate smaller benzenoids considered which can be classified by the number of torus "long" connections. There are some restrictions on the form of benzenoids which can lead to a torus benzenoid. Tsukano reported the necessary conditions for a benzenoid to qualify as a "torus benzenoid"²⁵. The necessary condition is that the benzenoid fully "covers" the graphite grid. The "cover" is understood in the graph theoretical sense in that individual units have no common carbon atoms, analogous to the cover of a benzenoid with CC double bonds which produce Kekulé valence structures.



See Figures 9 and 10

Figure 6. Smaller benzenoid tori whose torus polynomials are listed in Table III.

In Figure 7 we illustrate such a cover for bisanthene, an eight ring pericondensed benzenoid. This is, however, not a sufficient condition. There is an additional restriction on the "mode" of covering. The pattern for covering must have translational symmetry to ensure that, after carbon atoms have been labeled, always the same labeled carbon atoms are adjacent to each other in all covering units. This is the case for carbon atoms on the periphery of bisanthene in Figure 7 but is not the case with the covering of the graphite plane by bisanthene as shown in Figure 8. In this case there is no translational symmetry. For example, the carbon atom 3 is at the right unit adjacent to the carbon atom 12, while at the carbon atom 3 from the left unit is connected to carbon atom 10. All the torus networks in Figure 6 are thus obtained.

A question arises: Does the translational benzenoid cover that produces the torus unique? In case of bisanthene it is unique (except for symmetry equivalent cases) and the same is true for many smaller benzenoids. How-

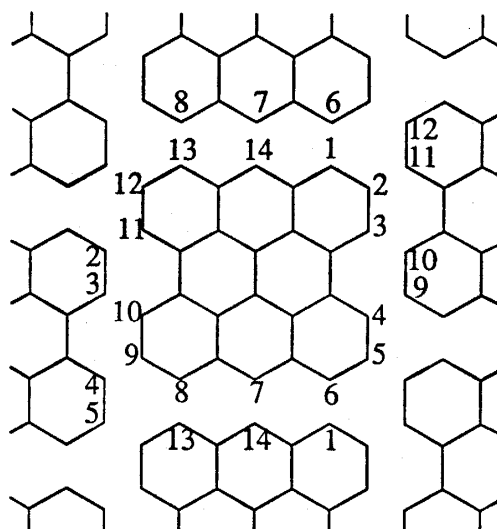


Figure 7. Bisanthene cover of graphite network, A cover is "legal" since adjacency relationship for carbon atoms is preserved (which implies translational symmetry).

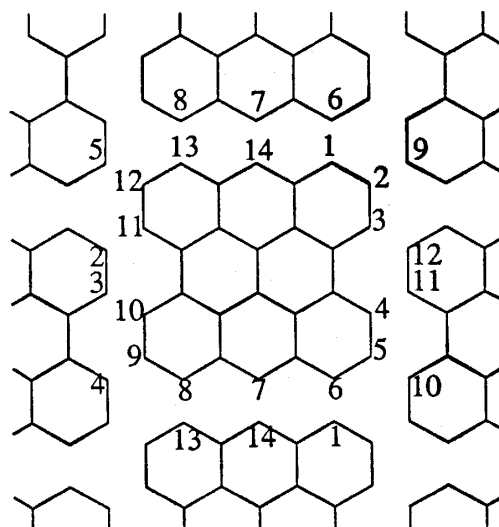


Figure 8. Bisanthene cover of graphite network. Illustration of "illegal" cover, since adjacency relationship for symmetry equivalent carbon atoms is not preserved.

ever, for some benzenoid molecules it is possible to have alternative covers of graphite network as will be later illustrated on terylene.

In Table III we give the torus polynomials $T(x)$ for the torus benzenoids of Figure 6. The values of the polynomials $T(1)$ and $T(0)$ give the count of the Kekulé valence structures in the torus and in the parent benzenoid unit respectively. The highest possible power of the polynomial is determined by the number of "long" connections. We see that in some instances the polynomial has lower degree than maximally possible (such is the case for dibenzoperopyrene). Also the leading coefficients of the

Table III. Torus polynomials for smaller benzenoids depicted in Figure 6. Kekulé count is given by evaluating $T(1)$, i. e., by adding all the coefficients.

| Cover unit | Torus Polynomial | Kekulé count |
|-----------------------|--|--------------|
| 1. Naphthalene | $x^4+2x^3+x^2+6x+3$ | 13 |
| 2. Anthracene | $x^5+4x^4+4x^3+6x^2+12x+4$ | 31 |
| 3. Pyrene | $4x^4+4x^3+6x^2+13x+6$ | 33 |
| 4. Triphenylene | $2x^6+3x^4+10x^3+12x^2+6x+9$ | 42 |
| 5. Chrysene | $x^6+2x^5+2x^4+13x^3+7x^2+12x+8$ | 45 |
| 6. Perylene | $x^6+4x^5+6x^4+10x^3+15x^2+20x+9$ | 65 |
| 7. Tetracene | $x^6+6x^5+11x^4+12x^3+21x^2+22x+5$ | 78 |
| 8. Anthanthrene | $3x^5+15x^4+13x^3+20x^2+30x+10$ | 91 |
| 9. Coronene | $x^6+18x^4+36x^3+9x^2+36x+20$ | 120 |
| 10. Pentacene | $x^7+8x^6+22x^5+30x^4+41x^3+56x^2+37x+6$ | 201 |
| 11. Bisanthene | $x^7+10x^6+12x^5+32x^4+35x^3+53x^2+70x+16$ | 229 |
| 12. Terrylene | $x^8+10x^7+8x^6+30x^5+46x^4+38x^3+90x^2+54x+27$ $x^8+8x^7+18x^6+35x^5+58x^4+72x^3+81x^2+79x+27$ | 304 379 |
| 13. Dibenzoperopyrene | $25x^5+48x^4+38x^3+100x^2+73x+20$ | 304 |
| 14. Ovalene | $x^7+6x^6+10x^5+96x^4+121x^3+50x^2+115x+50$ | 449 |

polynomial need not be equal to 1, as was the case with the family of benzene and coronene tori. The full significance of these differences has yet to be better understood, however, already we may say that torus polynomials offer a farther classification of the parent benzenoids, beside the already mentioned classification into those that permit a torus construction and those that do not.

Finally as we see from Table III in the case of terrylene, that more than

one benzenoid tori with translational symmetry are possible, and there are two different torus polynomials. In Figures 9 and 10 we illustrate the two different covers of the graphite by terrylene. The torus polynomial is, nevertheless an invariant of a given torus benzenoid network, but is not unique to the parent benzenoid structure. Since the ultimate use of

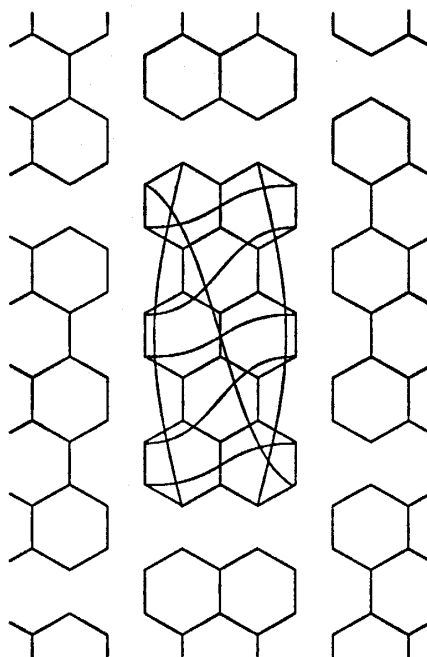


Figure 9. Terrylene cover of graphite network. A cover is "legal" since it possesses translational symmetry.

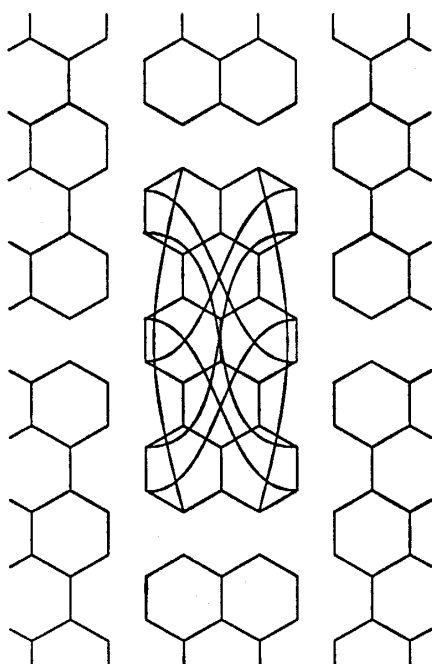


Figure 10. An alternative "legal" terrylene cover of graphite network with another translational symmetry.

torus benzenoids is to model infinitely large graphite-like structures, differentiation between alternative torus structures may be of lesser importance in the limiting cases. However when estimates of the properties of graphite are based on finite size models a benzenoid torus with fewer $4n$ rings is likely to give a better representation of graphite.

The Family of Benzenoid Tori

Among the small benzenoids considered in Table III there are several which could be viewed as a family of benzenoid linear polyacene tori, which are nothing else but the cyclic fence graphs defined by Hosoya and Harary²⁶. These graphs have such a novel character that all the component hexagonal rings are equivalent, which of course is also the case with infinitely large graphite lattice. Then the resonance stability of these networks, or the total index of aromaticity²⁷, can be expressed by the ratio of $2K$ and K^* , the numbers of the Kekulé valence structures in a benzenoid torus and those in the same torus when one benzene ring is excised. In Table IV we show these numbers. The K^* 's are immediately recognized

Table IV. K and K^* for linearly fused acenes.

| n | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|-----------------------------------|---|---|----|----|----|-----|-----|------|
| K | 3 | 6 | 13 | 31 | 78 | 201 | 523 | 1366 |
| Alternating Lucas Diff | | 3 | 7 | 18 | 47 | 123 | 322 | 843 |
| Alternating Lucas | 1 | 4 | 11 | 29 | 76 | 199 | 521 | 1364 |
| Alternating Fibonacci K^* | 1 | 1 | 2 | 5 | 13 | 34 | 89 | 233 |

as the Fibonacci numbers, while the K numbers are closely related to alternating Lucas numbers. Lucas numbers are defined by the recursion $L_N = L_{N-1} + L_{N-2}$, with $L_1 = 1$ and $L_2 = 3$ ²⁸. By recognizing the sequences we can write the respective general terms:

$$K_n = L_{2n+1} + 2 = \left\{ \frac{(1 + \sqrt{5})}{2} \right\}^{2n+1} + \left\{ \frac{(1 - \sqrt{5})}{2} \right\}^{2n+1} + 2$$

$$K_n^* = F_{2n-2} = \left[\frac{\left\{ \frac{(1 + \sqrt{5})}{2} \right\}^{2n-1} - \left\{ \frac{(1 - \sqrt{5})}{2} \right\}^{2n-1}}{\sqrt{5}} \right]$$

where L_n and F_n are Lucas and Fibonacci numbers respectively. Now we can evaluate the limit for the ratio $2K^*/K$ as n tends to infinity, which represents the resonance stability for graphite in the model of

acene tori:

$$\lim_{n \rightarrow \infty} 2L_{2n+1}/F_{2n-2} = 2\{2/(1 + \sqrt{5})\}^2/\sqrt{5} = (3\sqrt{5} - 5)/5 = 0.3416408 \dots$$

Note that for the seventh member of this family this ratio almost converges to this limit, agreeing with the above by three digits.

We suspect that the limit represents the upper bound to the true value for the resonance stability of graphite and as the width of the benzenoid tori is increased the limit (if it could be calculated analytically as was the case illustrated on linearly fused benzene) will make even tighter upper bound.

By focusing attention of such family of structurally related systems one may hope to be able to find a regularity also in the coefficients of the torus polynomials for such tori. In Table V we collected the coefficients of the torus polynomial for benzene—naphthalene family. Regularity for some of the coefficients is apparent, others are somewhat more involved. In the lower part of the Table we show the differences between successive terms in various diagonals (from top left to bottom right). The bottom part of Table V gives the second differences. The regularities can be observed for the first and the second differences, which allow us to predict all but one of the coefficients for the next row (for $N=7$). As

Table V. The torus coefficients for benzenoid linearly fused acene family and the first and second differences for coefficients for the same power.

| N | Coefficients | | | | | | | | | |
|-----|--------------|----|----|----------------------|----|----|-----|-----|----|---|
| 1 | | | | 1 | 0 | 3 | 2 | | | |
| 2 | | | 1 | 2 | 1 | 6 | 3 | | | |
| 3 | | 1 | 4 | 4 | 6 | 12 | 4 | | | |
| 4 | | 1 | 6 | 11 | 12 | 21 | 22 | 5 | | |
| 5 | | 1 | 8 | 22 | 30 | 41 | 56 | 37 | 6 | |
| 6 | | 1 | 10 | 37 | 58 | 90 | 126 | 126 | 58 | 7 |
| | | | | Diagonal Differences | | | | | | |
| | | | | 1 | 1 | 3 | 1 | | | |
| | | | 3 | 2 | 5 | 6 | 1 | | | |
| | | 5 | 7 | 8 | 15 | 10 | 1 | | | |
| | 7 | 12 | 19 | 29 | 35 | 15 | 1 | | | |
| 9 | 29 | 36 | 60 | 85 | 70 | 21 | 1 | | | |
| | | | | Second Differences | | | | | | |
| | | | | 1 | 4 | 3 | | | | |
| | | 4 | 6 | 10 | 4 | | | | | |
| | 7 | 12 | 21 | 20 | 5 | | | | | |
| 22 | 24 | 51 | 56 | 35 | 6 | | | | | |

one sees from Table V the differences are either the binomial coefficients or they occur in the top part of the table among the diagonals for smaller N .

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