

BENZENOID HYDROCARBONS AND MODERN FRONTIERS OF SCIENCE

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ABSTRACT

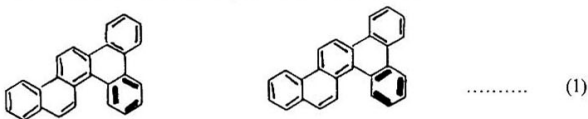
The concept of ordering/partial ordering is considered in the light of modern developments of graph theory of benzenoid hydrocarbons. Related topics include graph-generation, the conjugated circuits model (of Randić), fractals, quasicrystals and a general ordering scheme of objects of physico/chemical interest such as Young diagrams, caterpillar trees, rook boards, king polyomino graphs and Clar graphs. Furthermore, poset graphs derived from self-avoiding paths of lengths 2 and 3 are used to study Clar sextet theory of unbranched catacondensed benzenoid hydrocarbons.

During the past two decades several mathematical concepts assumed popularity and importance in the area of mathematical chemistry including especially *Chemical Graph Theory*¹. Some of these frontiers include ordering, partially ordered sets (posets)², fractals³, quasicrystals⁴, similarity⁵ and self-similarity⁶. In addition, it has been shown that the mathematical properties of unbranched catacondensed benzenoid hydrocarbons could be casted in connection with several objects of physico-chemical interest⁷ such as Young *diagrams*, rook *boards*, king *polyominoes*, caterpillar *trees*, and Clar *graphs*. This concept of modeling, as we shall see later (Section 2) may be used in conjunction with the ordering scheme of Gutman and Randić⁸ to order many objects of importance in physics and chemistry. In this work we shall briefly expose modern developments of these concepts along these lines.

1. Graph-Generation^{4,9}:

One equivalence relation, has been previously defined^{4,9} on a set of Kekulé structures of a benzenoid hydrocarbon, B, which may be called its Kekulé space, $K(B) = \{k_1, k_2, \dots, k_K\}$; $K=K(B)$ = the Kekulé count of B, k_i is the *ith* Kekulé structure where $i \in [1, K]$. Throughout this work B usually indicates a catacondensed (branched and/or unbranched) benzenoid system. It has been shown that $K(B)$ can be made to generate complete vertex-transitive clusters of size 2^n where $n = 0, 1, 2, \dots$ by the following steps:

- (a) Subdivide $K(B)$ into equivalence classes of Kekulé structure: $Cl_0, Cl_1, Cl_2, \dots, Cl_t$ such that each class contains all Kekulé structures which possess the same number of terminal conjugated circuits¹⁰ of type R_1 . Then, e.g., Cl_1 is a subset $\epsilon K(B)$, each of whose Kekulé structures has only one terminal R_1 and so on. The subscript t = the maximum possible number of terminal R_1 's in a Kekulé structure $\epsilon K(B)$.
- (b) Two Kekulé structures, k_i and $k_j \in K(B)$ are defined to be adjacent if one can be obtained from the other by a sextet rotation in only one R_1 through 60° . Naturally in Cl_0 no two k 's can be adjacent ! As an illustration, the following two k 's are adjacent in Cl_3 of the benzenoid hydrocarbon shown below:



The sextet to be "rotated" is drawn boldly. These two k 's belong to Cl_3 , because each one contains three terminal R_1 's.

- (c) Replace the individual k 's by vertices, i.e. $k_j \rightarrow v_i$ for all $i \in [1, K]$.
- (d) Two vertices v_i and v_j are connected (by an edge) only if k_i and k_j are adjacent.

The above steps partition $K(B)$ and therefore a suitable symbol for the above operation would be:

$$\epsilon \vdash K(B) \dots\dots\dots (2)$$

An illustration of eqn. (2) is given in **FIG 1** for the following benzenoid system for which $K=54$.

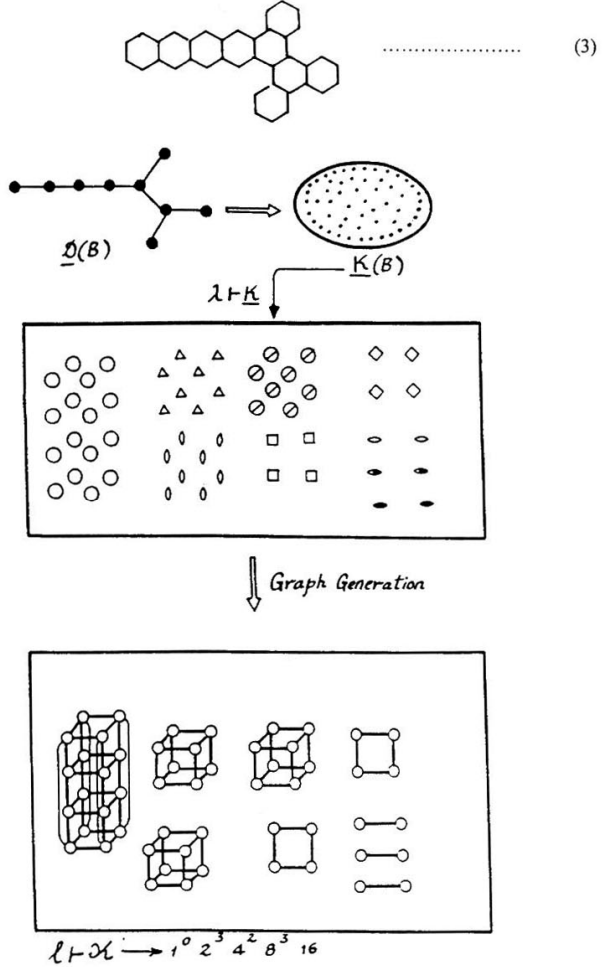


FIG Pictorial illustration of the graph-generation operation from the Kekulé space of a branched catacondensed benzenoid whose dualist, $\mathcal{D}(B)$ is shown, where $K = 54$. The operation results in one tesseract, 3-cubes, 2 squares and three edges. For more details see ref. 9.

Steps (a)-(d) above lead to the following partition:

$$\ell \vdash K(B) \rightarrow \{ 3G_2^1 \cup 2G_2^2 \cup 3G_2^3 \cup G_2^4 \} \quad \dots\dots\dots (4)$$

where in general G_{2i} is an i -cube. **TABLE 1** shows notation of these cube clusters.

TABLE 1

Notation of i -dimensional cubes generated by the equivalence relation ℓ on $K(B)$, viz., $\ell \vdash K(B)$.

Cube G_{2i}	size	notation	name
$i = 0$	1	1	vertex (0-cube)
1	2	2	edge (1-cube)
2	4	4	square (2-cube)
3	8	8	cube (3-cube)
4	16	16	4-cube (tesseract)
5	32	32	5-cube
i	2^i		i -cube

For the hydrocarbon shown in eqn. (3), the function ℓ partitions its $K(B)$ into four equivalence classes viz., Cl_1 includes 3 edges; Cl_2 contains two squares; Cl_3 comprising three cubes and Cl_4 which is simply a single tesseract. Then eqn. (4) may take several forms, viz.,

$$\ell \vdash K(B) \rightarrow \{ \mathbf{3.2} \cup \mathbf{2.4} \cup \mathbf{3.8} \cup \mathbf{16} \} \quad \dots\dots\dots (5)$$

Naturally one observes that $3 \times 2 + 2 \times 4 + 3 \times 8 + 16 = 54 = K(B) = K(B)$

Equivalently (5) may be expressed as:

$$\ell \vdash K(B) \rightarrow \{ \mathbf{3}^2 \cup \mathbf{4}^2 \cup \mathbf{8}^3 \cup \mathbf{16} \} \quad \dots\dots\dots (6)$$

Still a third notation would be:

$$\ell \vdash K(B) \rightarrow \{ \mathbf{1}^0 \mathbf{2}^3 \mathbf{4}^2 \mathbf{8}^3 \mathbf{16}^1 \} \quad \dots\dots\dots (7)$$

For a general case one may write:

$$\ell \vdash K(B) \rightarrow \{ \varphi_0 G_{2^0} \cup \varphi_1 G_{2^1} \cup \varphi_2 G_{2^2} \cup \dots \cup \varphi_t G_{2^t} \} \quad \dots\dots\dots (8)$$

where φ_i is the multiplicity of cluster G_{2i} ; $i = [0, t]$

In ref. 9 we illustrate how the equivalence relation ℓ partitions $K(B)$'s for several classes of benzenoid systems. The G_{2i} cubes are subgraphs of the "benzenoid resonance graph" previously discussed by Randić¹¹ and by Randić et al¹².

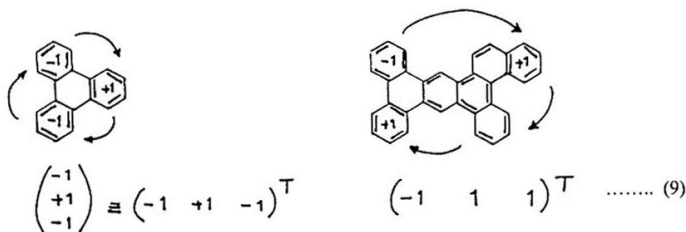
In the following sections we show how is this related to the concept of ordering/partial ordering problem.

1.1 The Hasse diagram is contained in G_{2i} ; $i \geq 3$

To demonstrate this fact we first define a vector notation of a Kekulé structure of a cata-condensed system in the following way:

- (i) Draw the molecular graph of the benzenoid system so that some of its edges are vertical
- (ii) If no terminal R_1 's exist in a particular k_i there is no vector notation for this k_i . (R_n is a conjugated circuit containing $4n + 2 \pi$ electrons).
- (iii) If the terminal R_1 shares a double bond with the adjacent ring, the hexagon which contains R_1 is given a label of +1.
- (iv) If the terminal R_1 does not have a double bond common to two rings, then this terminal hexagon is labeled as -1. When a terminal hexagon has no R_1 circuit it is not labeled.
- (v) The labels of the terminal R_1 's are then ordered starting from the upper left terminal hexagon of the benzenoid molecular graph and going in a clockwise mode to generate a $C \times 1$ vector, where $C = \#$ terminal R_1 's.

Some illustrations are shown below:



Now, it is trivial to show that a 3-cube is simply isomorphic to the Hasse diagram if we replace the sequence of +1's successively from left to right by the letters A, B, C, ... (in the natural ordering of the alphabets) after suppressing information on the -1 labels.

Examples:

$$\begin{aligned}
 (1, 1, 1)^T &\equiv (A, B, C), \\
 (1, 1, -1)^T &\equiv (A, B), \\
 (1, -1, 1)^T &\equiv (A, C); \\
 (-1, -1, 1)^T &\equiv (C) \\
 (-1, -1, -1) &\equiv \Phi \qquad \dots\dots\dots (10)
 \end{aligned}$$

and so on

FIG 2 illustrates this finding:

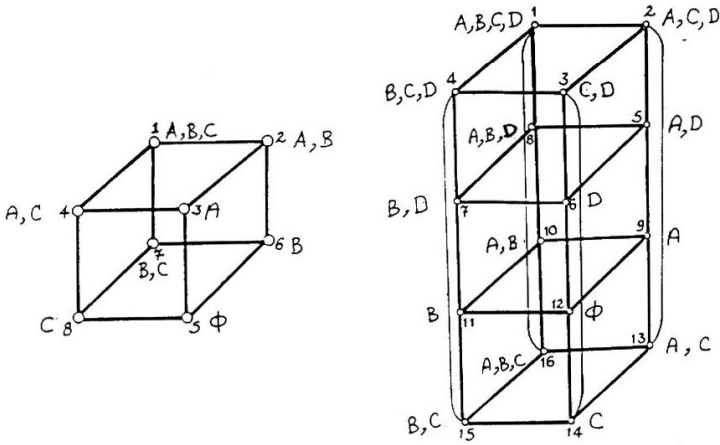


FIG 2 Hierarchical generation of the 4- and the 3-cube where eqn. (10) is used to illustrate that the Hasse diagram is contained in these cubes.

FIG 3 demonstrates that the Hasse diagram is actually contained in higher multidimensional cubes generated using equivalence classes of higher orders, i.e. using Kekulé structures which contain a higher number of terminal R_1 's.

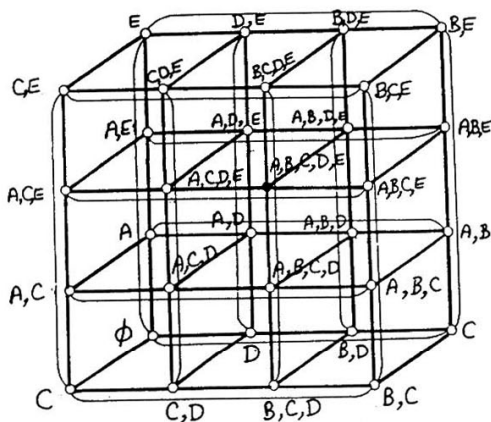


FIG 3 Hierarchical generation of the 5-cube where eqn. (10) is used to demonstrate that the Hasse diagram is contained in such higher multidimensional cubes.

1.2. Partially ordered conjugated circuits in a given $G_{2i}; i \geq 3$

We recall from the conjugated-circuit model of Randić¹⁰ that circuits are ordered according to their relative importance as $R_1 > R_2 > R_3 > R_4 > \dots$. Interestingly one can obtain a partial ordering of the conjugation content of the Kekulé structures forming a given equivalence class (= cluster, G_{2i}) following the rules of comparability of Muirhead as applied by Randić¹³. An illustration of this partial ordering is given in FIG 4 on the tesseract⁴, G_{24} (= 16).

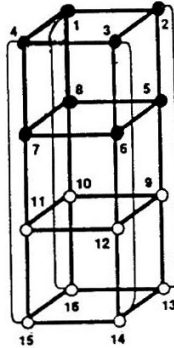


FIG 4 Four-dimensional cube generated from $B_2(3)$. The conjugated circuits which correspond to factor-graph positions⁴ are as follows: 1 = $(7R_1)$; 2 = $(6R_1 + R_2)$; 3 = $(6R_1 + R_3)$; 4 = $(6R_1 + R_2)$; 5 = $(5R_1 + 2R_2)$; 6 = $(5R_1 + R_2 + R_3)$; 7 = $(5R_1 + 2R_2)$; 8 = $(6R_1 + R_2)$; 9 = $(5R_1 + R_2 + R_3)$; 10 = $(6R_1 + R_3)$; 11 = $(5R_1 + R_2 + R_3)$; 12 = $(5R_1 + 2R_3)$; 13 = $(5R_1 + 2R_2)$; 14 = $(5R_1 + R_2 + R_3)$; 15 = $(5R_1 + 2R_2)$; 16 = $(6R_1 + R_2)$.

For example, if one starts at $7R_1$ and moves to the right following the vertices of the clusters labeled 1, 2, 13, 14, the conjugation content decreases as follows:

$$(7R_1) > (6R_1 + R_2) > (5R_1 + 2R_2) > (5R_1 + R_2 + R_3)$$

The partial sums of the above sequence follow Muirhead's comparability rules,¹³ They are:

$$(7,7,7) > (6,7,7) > (5,7,7) > (5,6,7) \dots\dots\dots (11)$$

If one traces the vertices labeled 1, 8, 10, 16, then one obtains:

$$(7R_1) > (6R_1 + R_2) > (6R_1 + R_3) < (6R_1 + R_2) \dots\dots\dots (12)$$

The corresponding partial sums are:

$$(7,7,7) > (6,7,7) > (6,6,7) < (6,7,7) \dots\dots\dots (13)$$

The last two points are inverted.

If one follows the points 1, 4, 7, 11, 15 one finds the following counts of circuits:

$$(7R_1) > (6R_1 + R_2) > (5R_1 + 2R_2) > (5R_1 + R_2 + R_3) < (5R_1 + 2R_2) \dots\dots\dots (14)$$

Again there is a discrepancy in the last two points. However there is a clear partial ordering trend. In addition these 4-dimensional cubes may be divided into “shells” such that, each shell represents one of the (sixteen) faces of the cluster. E.g., the upper shell (labeled 1, 2, 3, 4 [cf. **FIG 4**] contains (respectively): $(7R_1)$, $(6R_1 + R_2)$, $(6R_1 + R_3)$, $(6R_1 + R_2)$ while the third shell (the vertices of which are labeled 9, 10, 11, 12) has a conjugation content of significantly lower importance, viz., $(5R_1 + R_2 + R_3)$, $(6R_1 + R_3)$, $(5R_1 + R_2 + R_3)$, $(5R_1 + 2R_3)$.

1.3. A “re-visit” to the relative importance of Kekule’ structures in the light of cluster generation:

The relative importance of Kekule’ structures of a benzenoid hydrocarbon is an “old” concept usually associated with the so-called *Fries rule* which states that those structures which possess the largest number of “benzene Kekule’ structures” are those which have the greatest importance. This empirical rule was first published in 1927 and was re-visited some 40 years later by Graovac et al.¹⁴ Naturally the conjugated-circuit model of Randić¹⁰ is an elegant, graph-theoretical quantification of Fries rule. Indeed the equivalence relation, ℓ , is in harmony with all these studies. In fact one might say that this type of K-partitioning into equivalence classes C_0, C_1, \dots, C_t assigns a “dimension” to a given $k_j \in C_j$ ($j = 0, 1, \dots, t$). For example, $j = 3$ (i.e. each k_3 has 3 terminal R_1 ’s) leads to a 3-cube whose (topological) dimension is 3 and so on. It can be demonstrated that Kekule’ structures which contribute to a cube, e.g., are more important than those which contribute to a square (or lower j ($=2$)), and so on. A rather “popular” example (which was supported by experimental evidence) is provided by K(triphenylene), where $K = 9$ and we have:

$$\ell \vdash K(\text{triphenylene}) \rightarrow \{ \mathbf{1} \cup \mathbf{8} \} \dots\dots\dots (15)$$

Or, pictorially;

$$\ell \vdash K(\text{triphenylene}) \rightarrow \{ \mathbf{o} \cup \text{[cube diagram]} \} \dots\dots\dots (16)$$

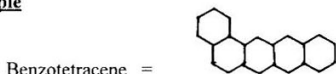
Naturally, **1** corresponds to the (lonely) Kekule’ structure whose dimension = 0 while each of the eight valence structures which form the cube has dimension of 3. This is not just


“meaningless” arithmetic: Indeed it is consistent with Clar’s findings¹⁵ on the NMR of triphenylene that this lonely structure has almost negligible contribution to the chemistry of the ground state of triphenylene. But one can push this concept a bit further as shown in the following section which, as we shall see, of remarkable relevance to the concept of ordering.

1.4. Cluster-generation and labeling of a Kekulé structures


An individual Kekulé structure $\epsilon \text{ Cl}_j$ may be labeled $k_{ij}^{(m)}$, where j is the number of terminal R_1 ’s and i is a serial number. The superscript m is also a serial number used to label several clusters of the same size*. If, however, *only one cluster a given type* is generated this superscript is omitted. (As we shall see, this is a rare case for small benzenoids).

Example



$$\ell \vdash \mathbf{K}(\text{benzotetracene}) = \{ \text{o U o-o o-o U } \text{  } \dots\dots\dots (17)$$

Then the equivalence classes Cl_0 and Cl_2 are both singly degenerate while Cl_1 is doubly degenerate and for this later class we need m ($= 1, 2$). The individual Kekulé structures are respectively labeled as follows (from left to right).

$$\{ \text{o U o-o o-o U } \text{  } \} = \{ (k_{10}); (k_{11}^{(1)}, k_{21}^{(1)}), (k_{11}^{(2)}, k_{21}^{(2)}); (k_{12}, k_{22}, k_{32}, k_{42}) \} \dots (18)$$

A semi-colon, (;), is used to separate classes of different importance. In equation (18) relative importance increases from left to right.

In addition to the notion of ordering associated with this type of graph-generation, the ℓ relation has a more interesting avatar, namely in the ordering of the stages of the *Cantor Set*³ (= Cantor dust), one of the most important fractals. This is discussed in the following section.

* I.e., several equivalence classes of the same cardinality which may be called degenerate classes.

1.5. Mapping Kekule structures on the Cantor set³

Sometimes it is possible to use the concept of labeling of Kekule^e structures to define bijective (i.e., one-to-one, onto) functions between equivalence classes of a given $K(B)$ and the various stages of the Cantor set. This however, requires that all equivalence classes of $K(B)$ must be distinct, i.e., no cluster of the same size is repeated.

For example:

$$\ell \vdash K(\text{benzanthracene}) \rightarrow \{1 \text{ U } 2 \text{ U } 4\} \dots\dots\dots (19)$$

In FIG 5 we show some of the early stages of the Cantor set

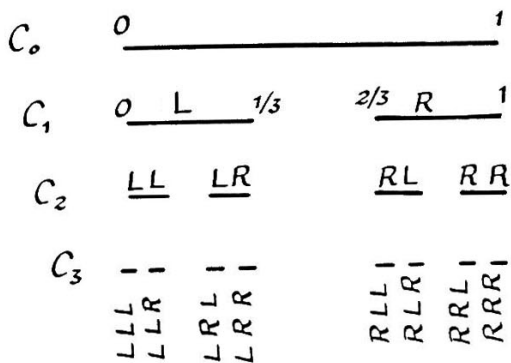


FIG 5 The first three stages of the Cantor set. The labels L (= left) and R (= right) are conventionally interpreted from left to right [See ref. 3].

One may define the following function on the first two stages of this fractal:

$$\{(k_{10}, C_0); (k_{11}, L); (k_{21}, R); (k_{12}, LL), k_{22}, LR), (k_{32}, RL); (k_{42}, RR)\} \dots\dots (20)$$

In eqn. (20), a comma (,) separates two intervals in a given stage while a semi-colon (;) separates two stages in the fractal.

Unfortunately such (lucky !) bijective maps require cases for which ℓ partitions K into *distinct equivalence classes only!* In a previous publication⁹ all catacondensed benzenoids which contain up to 9 hexagons have been investigated and it was found that only seven benzenoid hydrocarbons lead to distinct clusters ! These “unique” benzenoids (for which the ℓ function generates distinct powers of 2 and therefore correspond to their binary representations of Kekule` counts) are shown in FIG 6.

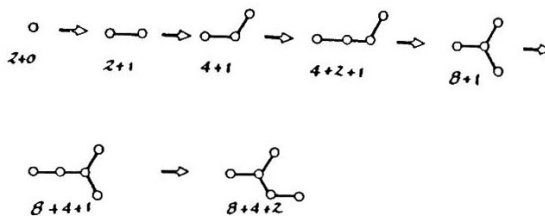
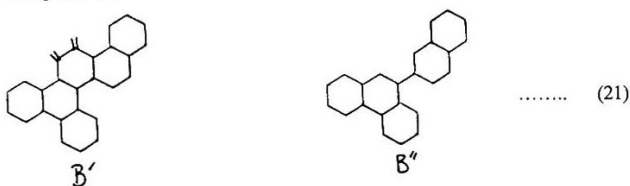


FIG 6. The only catacondensed benzenoids (containing up to nine hexagons) whose sextet rotation partitions lead to distinct (i.e. without repetition) powers of 2 and therefore correspond to their binary representations of Kekule` counts. These benzenoids are represented in terms of their “dualists”⁹.

However none of the hydrocarbons shown in FIG 6 leads to an ordering of the stages of a fractal analogous to the case described by eqn. (20).

Nevertheless, one may draw systems which do not represent benzenoid hydrocarbons in the conventional meaning of the expression and for which no clusters of the same size exist, i.e. for which all generated i -cubes are distinct, $i = [0, t]$. The following two systems leads to an identical partitioning of K 's :

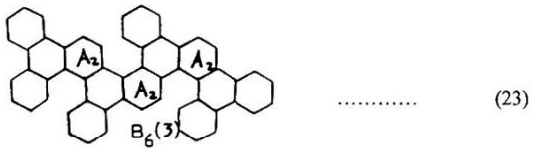


We can write:

$$\ell \vdash K(B') = \ell \vdash K(B'') = \{1 \cup 2 \cup 4 \cup 8\} \dots\dots\dots (22)$$

One may define a bijective map between the equivalence relation (22) and the third stage of the Cantor set, C_3 , c.f. **FIG 5**.

There is also another “solution” to the (more common) cases where the equivalence classes are usually multiply degenerate. Consider, e.g., $B_6(3)$ [$6 = \#$ terminal hexagons and $3 = \#$ hexagons which carry an A_2 label].



We have: $K(B_6(3)) = 869$; (24)

$$\ell \vdash K(B_6(3)) \rightarrow \{1 \cup 2^4 \cup 4^4 \cup 8^6 \cup 16^{10} \cup 32^4 \cup 64^8\} \dots\dots (25)$$

Then the following bijection orders the stages of the Cantor set up to C_6 [see **FIG 5**] provided *only one value of m is selected from each cube*. I.e., **ONLY CLASSES OF DISTINCT ORDINALITY ARE USED WITHOUT REPITITION!**

Then we can define the following function:

$$\begin{aligned}
 & \{ (k_{10}, C_0); (k_{11}^{(m)}, L), (k_{21}^{(m)}, R); \\
 & (k_{12}^{(m)}, LL), (k_{22}^{(m)}, LR); (k_{32}^{(m)}, RL), (k_{42}^{(m)}, RR); \\
 & (k_{13}^{(m)}, LLL), (k_{23}^{(m)}, LLR), \dots, (k_{73}^{(m)}, RRL), (k_{83}^{(m)}, RRR); \\
 & (k_{14}^{(m)}, LLLL), \dots, (k_{164}^{(m)}, RRRR); \\
 & (k_{15}^{(m)}, LLLLL), \dots, (k_{325}^{(m)}, RRRRR); \\
 & (k_{16}^{(m)}, LLLLLL), (k_{26}^{(m)}, LLLLLR), \dots, (k_{646}^{(m)}, RRRRRR) \} \dots\dots\dots (26)
 \end{aligned}$$

One observes:

- (a) The second subscript (to the right), $j = \#$ letters which label a given stage of the Cantor set. For example, the class of k 's which form the tesseract, $G_2^4 (= 16)$, as 16 Kekulé structures which are in one-to-one onto correspondence with the 16 intervals of C_4 where $C_4 = \{LLLL, LLRL, \dots, RRRR\}$, and so on.
- (b) In eqn. (26) m has **only one value** in each stage, i.e. between successive pairs of semi-colons. To elaborate this remark a little more, one observes that eqn. (25) states that $K(B_6(3))$ is partitioned into 8 six-cubes, 4 five-cubes, 10 four-cubes, 6 (three)-cubes, 4 squares, two edges and a lonely vertex. Eqn. (26) maps **one** cluster of **each** type into a particular stage of the Cantor set. Each cluster is composed of 2^j Kekulé structures, $j = [0,6]$ in this case.

Each Kekulé structure of a given dimension (i.e., in a given class) maps a given **interval** within a stage of the same subscript.

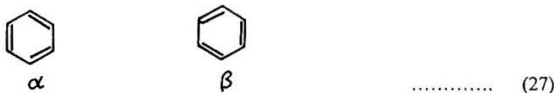
Indeed this correspondence results only because the number of intervals in stage $C_j = 2^j$ [e.g., C_0 has $2^0 = 1$ interval, C_1 has $2^1 = 2$ intervals, C_6 has $2^6 = 64$ intervals, and so on].

In addition, the sort of mapping given by eqn. (26) carries an element of *ordering*; Namely, a given $k_{ij}^{(m)}$ is *more important* than $k_{ij'}^{(m')}$, when $j > j'$ (the values of m and m' are not significant here. Similarly if C_j and $C_{j'}$ are two stages with $j > j'$, then C_j is *higher* than $C_{j'}$.

The sort of *“period-doubling”*; viz. $1 \rightarrow 2 \rightarrow 4 \rightarrow 8 \rightarrow 16 \rightarrow 32 \rightarrow \dots$ does not exist in other fractals, but it certainly does in the Cantor set, the most basic of all fractals !.

1.6. The “spin” character of the aromatic sextet

At this point one wonders if the above set of “observations” is just a *trivial* result of an *arbitrary* operation on a given $K(B)$. It turns out, however, that this may not be quite correct ! Indeed the equivalence relation ℓ is a direct consequence of an intrinsic property *fundamental* to the whole theory of aromatic benzenoids. Namely, the existence of *only* two states of the aromatic sextet:



Naturally, this notation is arbitrary ! , however is related to a comment made by Manfred Schroeder in his seminal book on fractals, chaos and power laws³ where he says “*There is a strong link between the physicist’s spin and the number 2*”. One, further quotes: “*And a spin glass is not spun glass, nor is there much spinning going on. Rather, a spin glass is a disordered arrangement of magnetic spins or by extension, the values of any other physical variable that has two preferred states*” .

Hence one is tempted here to speak about the “*spin*” character of the aromatic sextet:

More specifically, the terminal R_1 ’s in a given $k_j^{(m)}$ possess such a “*spin*” character which *naturally* (but *not* arbitrarily) leads to the equivalence relation defined on a given K . Then two Kekule^c structures are adjacent if they possess a pair of terminal R_1 ’s which has opposite (= paired) spins while all other terminal R ’s in one of the Kekule^c structures have identical spins with the corresponding terminal R_1 ’s in the other valence structure.

On the algorithm of Randić^c for counting $K(B)$:

It is remarkable to observe that in his algorithm for the enumeration of a given $K(B)$, Randić^{c16} also makes use of the spin-character, so-to-speak, of a selected bond of B (either single or double). In fact our $\ell \vdash K(B)$ operation also leads to $K(B)$ (but in a partitioned form: more explicitly as sums of integral multiples of various powers of 2).

2. General Ordering of Graphs of Interest in Chemistry and Physics^{7,17}

2.1. Nonadjacency Relations

A successful method for analyzing the connectivity relations in molecular graphs (which may represent chemical compounds) involves the definition of nonadjacency relations between selected sets of graph invariants as shown in **TABLE 4**.

TABLE 4

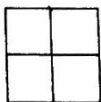
Nonadjacency relations of graphs of physico-chemical importance:

<u>Graph type, G</u>	<u>Graph invariant</u>	<u>Nonadjacency function* (G; k)**</u>
Trees*, T	edges	$p(T; k)$
Clar graphs*, Λ	vertices	$o(\Lambda; k)$
Benzenoid, B	hexagons	$r(B; k)$
King polyomino, P	cells	$X(P; k)$
Rook board, P_r	cells	$\Phi(P_r; k)$

* See text.

** $\Theta(G; 0) = 1$

In **TABLE 4**, $\Theta(G; k)$ is a general nonadjacency function defined for each graph-type as follows: **Trees**: $p(T, k)$ = the number of selections of k edges in T so that no two edges are adjacent (incident). This number is called the number of k -matchings. Trees of a special type are the caterpillar trees which are symbolized as $P_n(m_1, m_2, \dots, m_n)$. A caterpillar tree is constructed by the addition of m_1 *monovalent* vertices to the first vertex, v_1 of the **path graph**, P_n , m_2 *monovalent* vertices to v_2 and so on. For this particular (interesting) case the **line graph** of T is called the **Clar graph**, Λ , for which $o(\Lambda; k)$ is the number of selections of k nonadjacent vertices in Λ . For benzenoid graphs $r(B; k)$ is the number of selections of k **resonant** hexagons. For a king **polyomino**, $X(P; k)$ is the number of selections of k nonadjacent cells in P . In a king polyomino two cells are defined to be adjacent if they share at least one vertex. Hence, no more than *four* cells could be adjacent in a king polyomino viz.,



..... (28)

Finally for a rook **board**, P_r , the nonadjacency function $\Phi(P_r, k)$ is the number of selections of k nonadjacent cells in P_r . Two cells in P_r are **defined** to be adjacent if they share the same row or the same column in P_r . In general $\Theta(G; k) = 1$ for $k = 0$.

2.2. Caterpillar trees as generators of graphs of physico/chemical interest

Given a particular caterpillar tree with a given sequence $p(T; 0), p(T; 1), \dots, p(T; k_{\max})$ one can generate a set of what is called **equinumerical graphs** which possess identical (= the same) sequence of nonadjacency numbers. These graphs include Clar graphs, cell boards, and polyhex graphs. **FIG 7** shows examples of sets of equinumerical graphs. This topic has been dealt with in some detail sometime ago.^{17,7} Here we emphasize only how it is related to the concept of ordering. This requires one to define how a **Young diagram** is related to a (caterpillar) tree.

2.3. On the Ordering Scheme of Gutman and Randić⁸

Several years ago Gutman and Randić⁸ used conditions of comparability of Muirhead¹³ as criteria of ordering a set of trees (which includes caterpillars as well as noncaterpillar ones). Those authors employed a nonascending sequence composed of vertex degrees of a given tree. Namely, for two trees whose vertex degree-sequences are (d_1, d_2, \dots, d_n) and $(d'_1, d'_2, \dots, d'_n)$ and if the partial sums of one tree, T , are always greater than or equal to (but not smaller than) those of T' , one says that T **majorizes** T' , i.e., T **precedes** T' in the hierarchy, otherwise T and T' are said to be **noncomparable** and they lead to a **bifurcation** site in the ordering diagram.

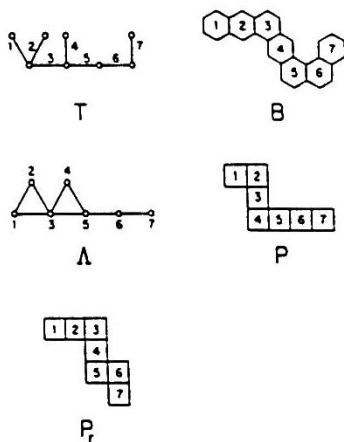


FIG 7 A set of equinumerical graphs: A caterpillar tree, T, a benzenoid system B, a Clar graph Λ , a king polyomino, P and a rook board P_r [See refs. 7, 17].

Gutman and Randić⁷, furthermore, made the significant observation that their ordering scheme can be made to overlap ordering schemes of Young diagrams of Ruch and Schönhofer⁸ by the following steps:

- (i) Suppress information of vertices of degree 1
- (ii) reduce the degree of each of the remaining vertices by one.

Then one may define a general ordering scheme of graphs as shown in **FIGS 8-10**.

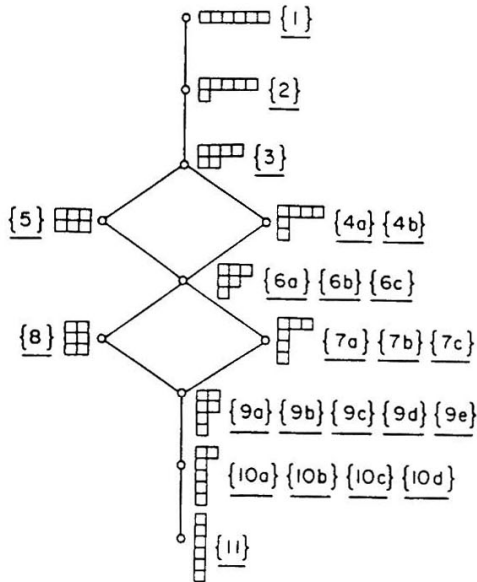


FIG 8 Ruch ordering of all Young diagrams containing six boxes. Sites of bifurcations indicate noncomparable diagrams.^{7,17}

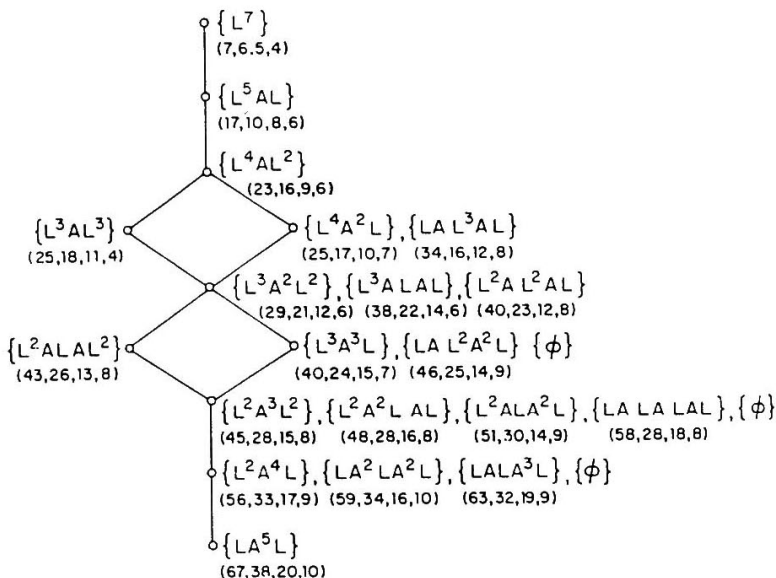


FIG 9. Ordering of nonbranched benzenoid hydrocarbons which are in one-to-one correspondence with the Young diagrams. The polyhex graphs are denoted by their L-A sequences.¹⁸ Numbers in parentheses are $(\gamma_1^\#, \gamma_2^\#, \gamma_3^\#, \gamma_4^\#)$, respectively, where $\gamma_i^\#$ is the number of Herndon permutation integral¹⁹ involving permutation of $(4i + 2) \pi$ -electrons. Twice these numbers lead to $(R_1^\#, R_2^\#, R_3^\#, R_4^\#)$, the numbers of the corresponding conjugated circuits of Randić¹⁰ $(R_n^\# = \text{number of conjugated circuits containing } 4n + 2 \pi\text{-electrons})$.

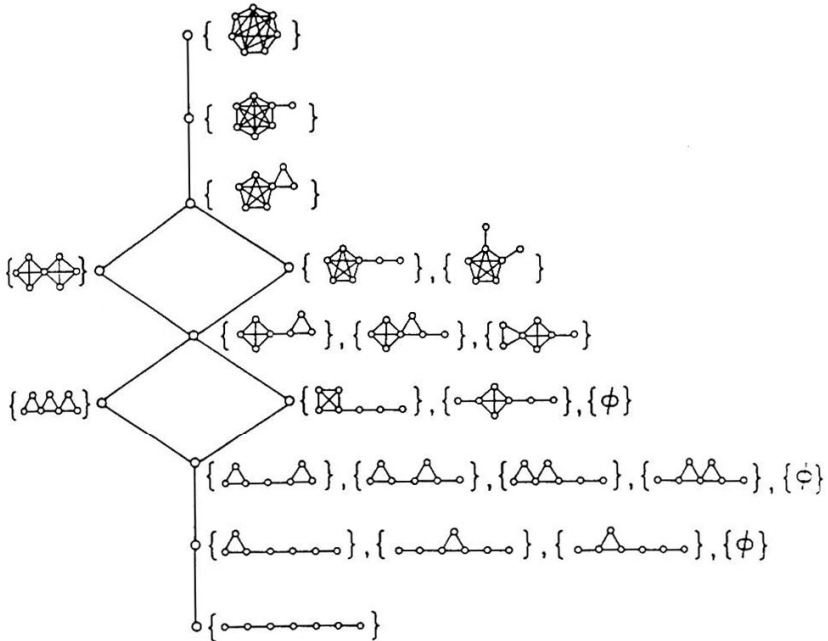


FIG 10 Ordering of all Clar graphs containing 7 vertices according to Ruch's ordering relation defined for a set of Young diagrams containing six squares. The ordering makes use of the equivalence relation defined between a Young diagram, a caterpillar (Gutman) tree and Clar graphs. The $\{\phi\}$'s correspond to places on the diagram which correspond to non-caterpillar trees and thus do not have an equivalent Clar graph.

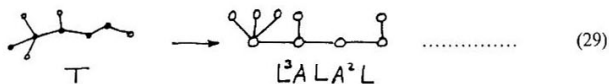
2.4. On the posets of Randić et al.^{5,20,21}

In a series of papers, Randić⁵ and others used self-avoiding paths of lengths 2 and 3; p_2 and p_3 of sets of isomeric alkanes to generate grid-like graphs, the vertices of which define relative positions of alkane isomers. These graphs, which represent types of posets, lead to a partial ordering of a number of physical properties of alkanes.

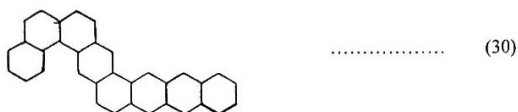
Here we demonstrate that these posets can also order a set of nonbranched benzenoids according to the following steps:

- (a) Transform a given alkane molecule into its H-suppressed molecular graph, T.
- (b) If T is a caterpillar tree^{7,17}, find the corresponding LA sequence¹⁸, LA(T),
- (c) Draw the corresponding nonbranched benzenoid hydrocarbon as described elsewhere.^{7,17}

For example, 1,1,1-trimethyl, 2-methyl pentane is one of the nonane set of isomers, the molecular graph of which is a tree graph:



The above sequence is consistent with the following benzenoid hydrocarbon



Of course there are other benzenoids which also share this LA sequence but they all have the same Kekulé counts.²²

Sometimes, however, the molecular graph of the alkane is not a caterpillar tree in which case there is no equinumerical benzenoid,^{7,17} as, e.g. the case of 3,3-diethyl pentane. Nevertheless in a typical set of alkane isomers the majority of graphs are caterpillar trees.

It is convenient to take Clar polynomials²³ as a measure of aromatic stability of a set of benzenoids. According to the original hypothesis of Clar,¹⁵ the larger the number of circles

one can draw in the hexagons of a given benzenoid the more stable it will be. In **FIG 11** we show the original poset of the octane isomers and the poset of the corresponding benzenoids, where Clar polynomials are computed in relevant positions of the grid. In **FIG 12** the same thing is done for the nonane isomers. We observe that the original alkane grid partially orders the benzenoid hydrocarbons according to their aromatic stabilities. On horizontal coordinates stability (power of x) goes down from left to right while vertically it increases as one moves upwards. Indeed the least branched alkane corresponds to the most stable benzenoid hydrocarbon and vice-versa.

Acknowledgment: Professor Klein's comments are greatly appreciated.

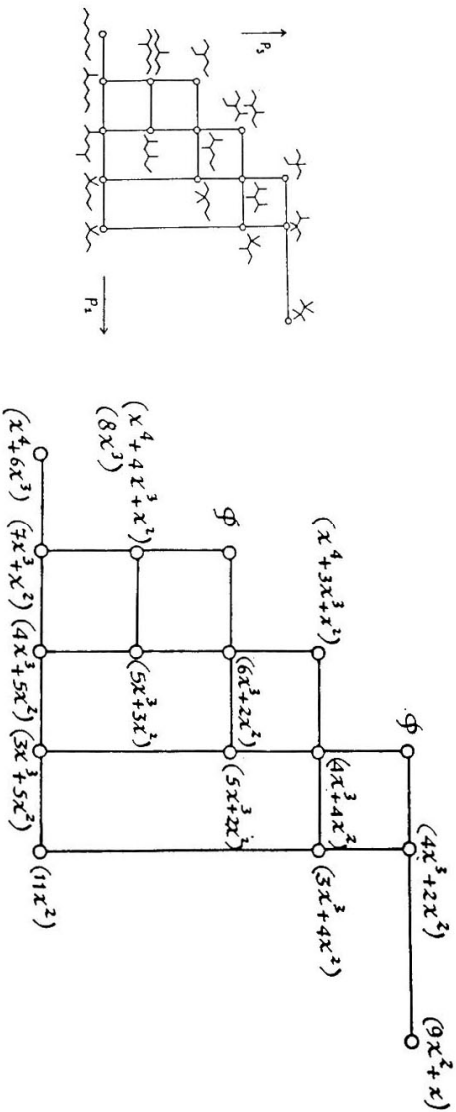


FIG. 11. The octane-poset to the left, the coordinates of each vertex of which are p_1 and p_3 the number of paths of lengths 2 and 3 respectively. The grid to the right is the poset of the corresponding benzenoids where Clar Polynomials²³ are indicated. Vertices which are labeled ϕ indicate an octane whose molecular graph is a non-caterpillar tree. Stability increases horizontally from right to left and vertically from bottom to top.

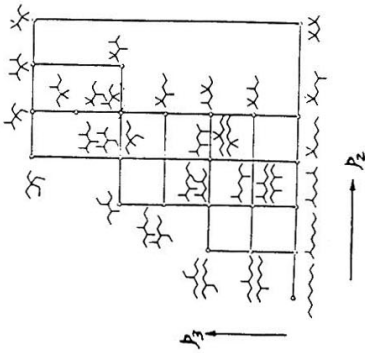
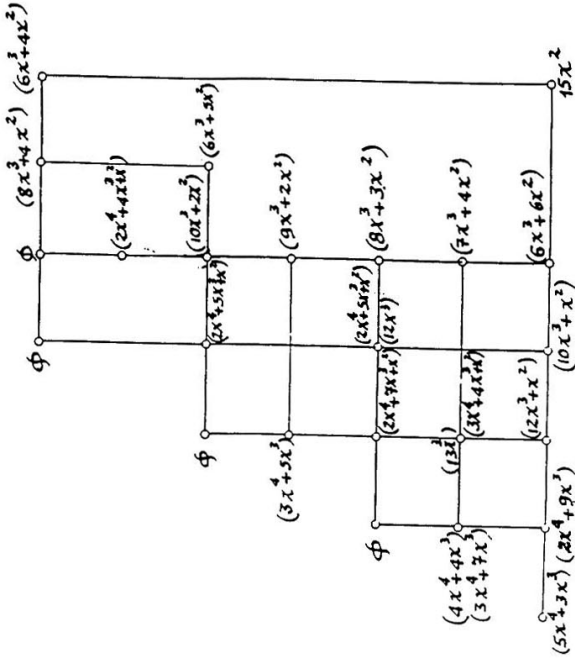
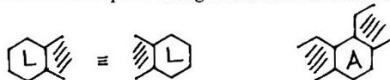


FIG 12. The nonane-poset (to the left) and the Clar polynomials of the corresponding benzenoids (right poset) cf. FIG 11.

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