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ON A NOVEL GRAPH-THEORETICAL BASIS OF ORDERING KEKULÉ STRUCTURES

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ABSTRACT

Sextet rotations in individual Kekulé structures of benzenoid hydrocarbons are used to construct a hierachical diagram comprising all nonequivalent members of the Kekulé patterns. Certain VB characters were found to be simple functions of just the locations of their representative points in the hierarchy. A relation to Clar's sextet theorem is illustrated.

1) INTRODUCTION

Ordering of structures occupies a central part of graph theory. In chemical literature the most important developments are comparison tests of Muirhead[1] which were later generalized by Karamata[2]. Such tests depend on the construction of sequences of numbers whose values depend on certain molecular parameters associated with graphs to be ordered. Partial sums are then constructed out of their sequences. If, then, for every entry in two such partial sums, members of one structure are larger or equal (but not smaller) than the corresponding entries of the other sequence of partial sums, the structures can be ordered with the first preceding the second. Gutman and Randić[3] applied Muirhead's theory to order alkanes using sequences of numbers representing vertices of various degrees in

the corresponding hydrogen-suppressed graphs. Randić[4] employed Karamata's theorem to arrive at a partial order of individual Kekulé valence-bond structures of benzenoid hydrocarbons, BH'^{s}, using numbers derived from conjugated circuits[5], cc, contained in them. Randić and Wilkins[6] ordered alkane graphs using molecular path-codes as parameters for entries in sequences to be ordered. One common feature to all the above schemes is the use of some sort of molecular parameters (sets of vertices, size of conjugated circuits, or path codes) to design a particular sequence of numbers characteristic of the structures (graphs) to be ordered (compared). In this paper we present a novel approach of ordering structures without resort to computing sequences of numbers with subsequent application of Muirhead's inequalities, but rather via constructing a special hierarchical series of the graphs to be ordered. The value of the variable will turn out to be a function only of the "location" of the graph in the hierarchy regardless of its molecular parameters. As it will be shown the study of the underlying structure of hierarchical relationships may be more rewarding than the use of just a single molecular parameter to derive an order. The individual Kekulé structures of BH'^{s} will be used as our substrates to illustrate the approach.

2) POSING THE PROBLEM:

Almost a decade ago a group of graph theorists deviced an MO-VB parameter, called, Kekulé index, K(L) to order a set of Kekulé structures which for BH'^{s} takes the form given by eqn. (1)[7]

$$K(L) = \frac{1}{2N} \sum (2+2\ P_{ij})^{\frac{1}{2}} \qquad (1)$$

Where 2N is the number of pi-electrons in the BH; and P_{ij} is bond order between atoms i and j. Recently the author[8] calculated connectivity indices[9], χ_A's, of the submolecules[10] representing the individual Kekulé structures using eqn. (2)

$$\chi_A = \left\{ \sum (m_i m_j)^{-\frac{1}{2}} \right\}^{-1} \qquad (2)$$

where m_i is degree of i th vertex while the summation in both eqns. is taken over all (i,j) edges of the submolecule graph. Over some hundred cases[8] values of K(L) of Kekulé structures paralleled connectivities, χ_A's, of the corresponding submolecules. Problems, however, arose in certain cases, thus K(L) values of phenanthrene Kekulé structures are 0.913, 0.906, 0.900 and 0.897, while the values of χ_A's of the corresponding submolecules are (eqn. 2): 0.2966, 0.2934, 0.2899 and 0.2912. The position of the last structure is not the same as deduced by the two parameters. Similarly triphenylene Kekulé structures generate the following K(L) sequence: 0.907, 0.904, 0.901, 0.898 and 0.895 while the corresponding submolecules yield the following sequence of χ_A values: 0.2287, 0.2277, 0.2264, 0.2247 and 0.2287. Again the trouble lies in the last structure; where the VB quantity, χ_A, predicts a similar weight to it as the fully benzenoid Kekulé structure (first structure). These structures are shown in Fig. 1, while their K(L) and χ_A values are listed in Table 1. Are these just discrepancies? counter examples? or is there a particular scheme that relates to the connectivities of these submolecules through which we might

forecast a difference in ordering sequence? The answer is particularly interesting since Kekulé structures are just the "right substrates" that illustrate the link between MO and VB theories[11] reflected in values of K(L)'s and χ_A's.


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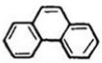
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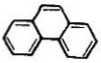
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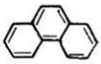
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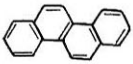
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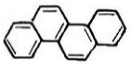
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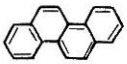
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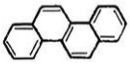
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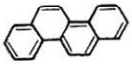
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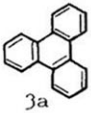
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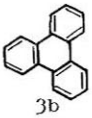
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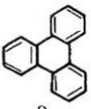
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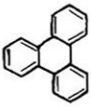
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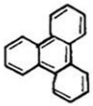
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4f


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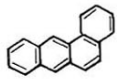

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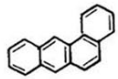

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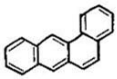

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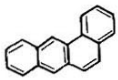

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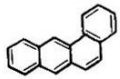

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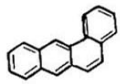

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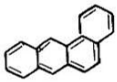

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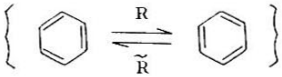

FIG. 1:

Kekulé structures studied in this work. Numbers correspond to Table 1.

3) HIERARCHICAL SEXTET DIAGRAMS:

We propose here the construction of a particular hierarchy depending only on the permutation of double bonds in Kekulé structures, thus letting a, b, c, ...
be a set of Kekulé structures belonging to some BH so that b is obtainable from a by exchanging positions of double and single bonds in just one sextet in a; and similarly c is obtainable

from b when double and single bonds of one sextet in b switch positions, and so on. The resulting diagram will be called "hierarchical sextet diagram". Such templates are being shown in Figs. 2-6 for phenanthrene (1a-1d), chrysene (2a-2e), triphenylene (3a-3e), hexahelicine (4a-4l) and benz [a] anthracene (5a-5g).

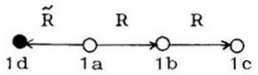

FIG. 2:

Phenanthrene hierarchical sextet diagram cc = 3 (o), cc = 4 (•).

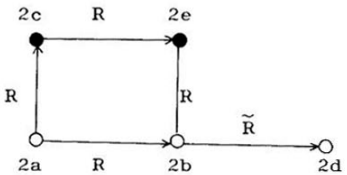

FIG. 3:

Chrysene sextet diagram, cc = 4 (o), cc = 5 (•).

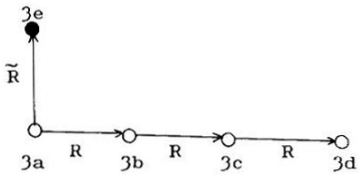

FIG. 4:

Triphenylene sextet hierarchy, cc = 4 (o), cc = 7 (•).

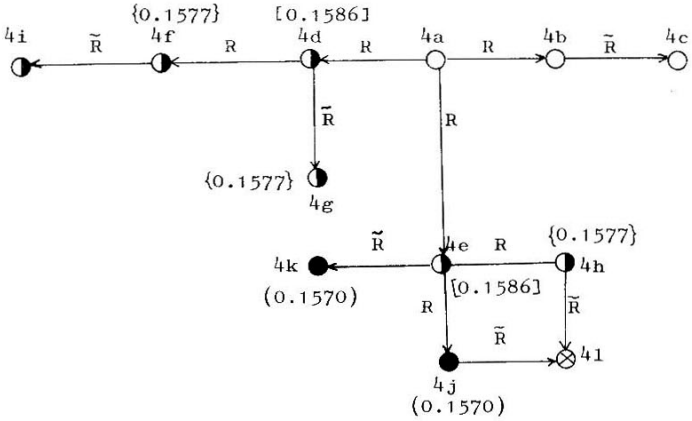

FIG. 5:

Hexahelicene sextet hierarchy, cc = 6 (o), cc = 7 (•), cc = 8 (•), cc = 9 (⊗).

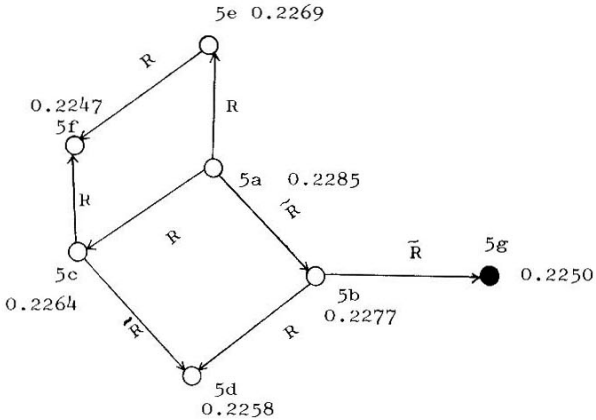

FIG. 6:

Benzanthracene hierarchy, cc = 4 (o), cc = 6 (•).

4) RESULTS AND DISCUSSION:

Table 1 lists $K(L)'^{s}$, $\chi_A'^{s}$ and conjugated circuits, cc'^{s} for 33 Kekulé structures shown in Fig. 1.

Notwithstanding the fact that conjugated circuits estimate molecular resonance energies of BH'^{s} quite accurately, it seems they do not reflect identical orders of individual Kekulé structures to those predicted by K(L) values. For example 4d and 4e of hexahelicene contain identical cc'^{s} yet neither their $K(L)'^{s}$ nor $\chi_A'^{s}$ of their corresponding submolecules are identical. Also 4g and 4h constitute an isoconjugate pair whose $K(L)'^{s}$ are different. More interestingly are deviations in χ_A values from the order predicted by the Kekulé indices. Such values of $\chi_A'^{s}$ are placed in parentheses in Table 1. As it becomes clear from Figs. 2-6, the value of χ_A of a submolecule depends on the locations of the corresponding Kekulé structure in the derived sextet hierarchy relative to highest value of χ_A. Consider, e.g. phenanthrene hierarchy, Fig. 2, we observe χ_A (1a) $>$ χ_A(1b) $>\chi_A$ (1c) which is the same as we expect from relative locations of these graphs relative to one another. Structure 1d has the lowest K(L) but its χ_A is larger than χ_A (c). This is consistent with positions of the points on the diagram, thus both 1b and 1d are adjacent to 1a while 1c is one point further. Hence χ_A (1d) is expected to be greater than χ_A (1c) which is the case. The same situation obtains with triphenylene sextet

hierarchy (Fig. 4) thus 3e is "closer" to 3a than 3c is, thus we expect χ_A (3a) to be greater than χ_A (3c) which is true. Such deviation in relative ordering of Kekulé structures are not, therefore, discrepancies between MO, K(L), and VB, (χ_A), quantities, but they reflect a very particular discipline of sextet rotations in the Kekulé pattern of the BH. With more involved hierarchical relationships one must restrict comparison of "point-locations" on the diagram to graphs with identical numbers of cc's. Thus a set of points representing Kekulé structures whose cc numbers are identical will predict relative values of χ_A's of the corresponding submolecules just from their locations on the hierarchical diagram. Hexahelicene (Fig. 5) illustrates this concept, thus points 4a-4c correspond to Kekulé structures containing six cc's each.

Values of χ_A's of their submolecules progressively decrease on going to the right on the hierarchy a⟹b⟹c. Structures d-i contain seven circuits each. We observe that points with "equivalent" locations lead to submolecules with identical χ_A's. Thus d and e are both adjacent to a so they are located the same distance away from the same point, and hence χ_A's of their submolecules are identical (χ_A = 0.1586), similarly h, g and f are all located two points away from a, their χ_A's are also identical, (0.1577). Points k and j representing structures containing eight circuits each and occupy equivalent locations on the diagram, whence their χ_A's are identical (0.1570). One should, therefore, no longer be disappointed to find out that while 4d and 4e contribute identical

weights to the total state eigenvector of hexahelicene (from the view point of cc), yet their Kekulé indices are not identical. Frequently, isoconjugate structures, such as {4d, 4e} and {4g, 4h} occupy equivalent positions in the hierarchical series, these points correspond to Kekulé structures containing identical cc patterns and whose submolecules will have identical connectivity indices. However identical χ_A's does not always mean isoconjugate structures, e.g. k and j which have identical positions and χ_A's do not correspond to isoconjugate Kekulé structures. One last case, that of the non-fully benzenoid hydrocarbon benz [a] anthracene might explain the method further and illustrate some of its apparent shortcomings. Investigation of Table 1 raises two questions: 5a and 5b contain identical cc's, $(3\ R_1 + R_2)$, yet different K(L)'s, and, why χ_A (e) is greater than χ_A (c) while their K(L) values predict the opposite order. Inspection of sextet hierarchy, Fig. 6, answers to these questions only partially. While e and b are adjacent to a yet their positions are not exactly equivalent (because of cyclic connections with other members) but at least we conclude that χ_A (e) must be greater than χ_A (d) (e is closer to a than d). This is true. Points f and d are both 2-edges away from a but f is connected to c and e while d is linked to c and b since χ_A (b) > χ_A (e) we might conclude that χ_A (d) > χ_A (f).

5) A RELATION TO CLAR'S SEXTET PATTERNS[12]:

One might construct all Clar's sextet structures from combinations of Kekulé structures whose places are defined on the sextet hierarchical diagram, thus:

a- Members that possess just respective (adjacent) $\varkappa_A$ values lead to graphs with <u>one</u> sextet,

b- Members that are separated by one member in their $\varkappa_A$'s lead to graphs with two sextets. Fig. 7 illustrates this for pairs with adjacent $\varkappa_A$'s of benzanthracene. Thus an ordering of Kekulé structures is made possible from Clar's sextet patterns produced when pairs of Kekulé structures are combined. <u>The resulting order is that of the connectivities of their submolecules</u>. Work comprising some hundred cases will be published elsewhere[14].

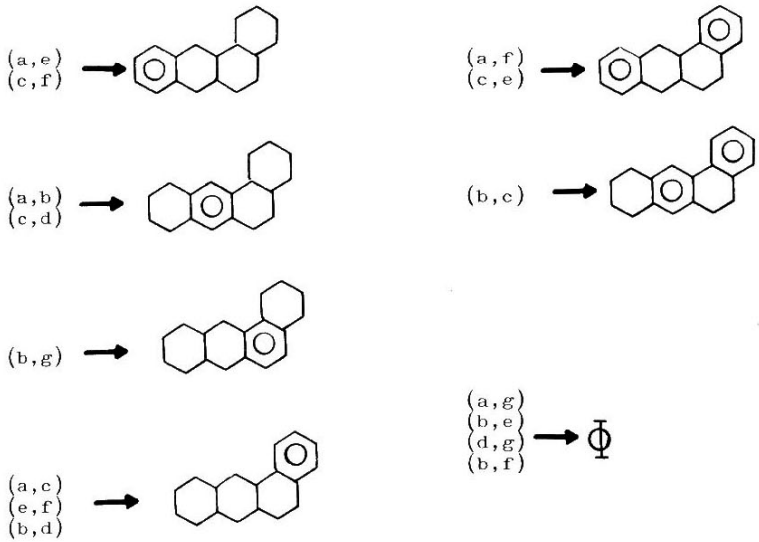

FIG. 7:

Clar's sextet patterns from adjacent and non-adjacent Kekulé structures of benzanthracene.

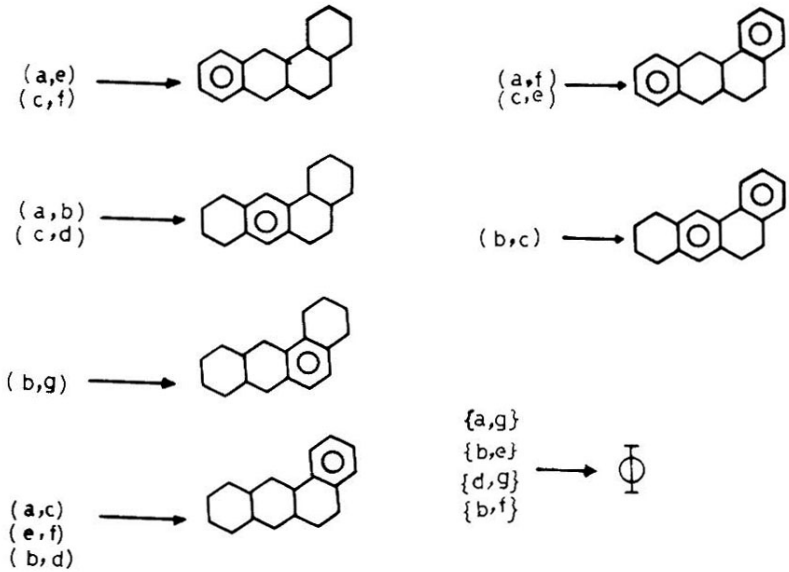

FIG. 7:

Clar's sextet patterns from adjacent and non-adjacent Kekulé structures of benzanthracene.

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TABLE 1

Kekulé indices, K(L)'s and conjugated circuits, cc's of Kekulé structures and connectivities, χ_A's of the corresponding sub-molecules as calculated from eqn. 2. Parentheses indicate deviations in χ_A values from the order predicted by the Kekulé indices.

BH-Kekulé structure		cc		K(L)	χ_A
Phenanthrene	1a	$3R_1$	= 3	0.913	0.2966
	1b	$2R_1 + R_2$	= 3	0.906	0.2934
	1c	$2R_1 + R_3$	= 3	0.900	0.2899
	1d	$R_1 + 2R_2 + R_3$	= 4	0.897	(0.2912)
Chrysene	2a	$4R_1$	= 4	0.912	0.2310
	2b	$3R_1 + R_2$	= 4	0.907	0.2291
	2c	$2R_1 + 2R_2 + R_3$	= 5	0.902	0.2285
	2d	$2R_1 + 2R_2$	= 4	0.901	0.2272
	2e	$2R_1+R_2+R_3+R_4$	= 5	0.896	0.2264
Triphenylene	3a	$4R_1$	= 4	0.907	0.2287
	3b	$3R_1 + R_2$	= 4	0.904	0.2277
	3c	$3R_1 + R_3$	= 4	0.901	0.2264
	3d	$3R_1 + R_4$	= 4	0.898	0.2247
	3e	$R_1+3R_2+3R_3+R_4$	= 8	0.895	(0.2287)
Hexahelicene*	4a	$6R_1$	= 6	0.9114	0.1602
	4b	$5R_1 + R_2$	= 6	0.9075	0.1592
	4c	$4R_1 + 2R_2$	= 6	0.9037	0.1583
	4d	$4R_1+2R_2+R_3$	= 7	0.9051	(0.1586)
	4e	$4R_1+2R_2+R_3$	= 7	0.9040	(0.1586)
	4f	$4R_1+R_2+R_3+R_4$	= 7	0.9013	0.1577

TABLE 1: (Cont.)

BH-Kekulé structure		cc	K(L)	χ_A
	4g	$3R_1 + 3R_2 + R_3 = 7$	0.9013	0.1577
	4h	$3R_1 + 3R_2 + R_3 = 7$	0.9001	(0.1577)
	4i	$3R_1 + 2R_2 + R_3 + R_4 = 7$	0.8975	0.1568
	4j	$3R_1 + 2R_2 + R_3 + R_4 + R_5 = 8$	0.8978	0.1570
	4k	$2R_1 + 4R_2 + 2R_3 = 8$	0.8966	(0.1570)
	4l	$3R_1 + R_2 + 2R_3 + R_4 + R_5 + R_6 = 9$	0.8939	0.1561
Benzanthracene*	5a	$3R_1 + R_2 = 4$	0.9112	0.2285
	5b	$3R_1 + R_2 = 4$	0.9083	0.2277
	5c	$3R_1 + R_3 = 4$	0.9071	0.2264
	5d	$2R_1 + 2R_2 = 4$	0.9042	0.2258
	5e	$2R_1 + R_2 + R_3 = 4$	0.9028	(0.2269)
	5f	$2R_1 + R_2 + R_4 = 4$	0.8986	0.2247
	5g	$R_1 + 2R_2 + 2R_3 + R_4 = 7$	0.8960	(0.2250)

*K(L) values are computed using eqn. 1 and HMO bond orders compiled in ref. (13).