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CONSERVATION OF MOLECULAR TOPOLOGY
A DEFINITION OF PARITY OF KEKULÉ STRUCTURES
OF CATACONDENSED BENZENOID HYDROCARBONS

Sherif El-Basil

Faculty of Pharmacy, Kasr El-Aini Street, Cairo, Egypt

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ABSTRACT:

A novel approach relating "conservation of molecular topology" during transformations of a set of Kekulé structures and stability is presented. The theory assigns parities to Kekulé structures of benzenoid hydrocarbons which lead to vanishing algebraic structural counts to higher members of linear acenes that were found too unstable to be prepared. Furthermore it explains situations where K (Kekulé count) alone does not lead to correct order of stability among catacondensed benzenoid hydrocarbons (e.g. K(triphenylene) = 9, and K(pentaphene) = 10, but their stabilities are reversed). A novel stability index is introduced that combines both combinational and topological aspects of hydrocarbon stability and was found to be consistent with experimental facts that the existing theories are not.

1) INTRODUCTION

The molecules of the linear acenes fail to exist beyond the sixth ring[1]. In fact hexacene itself is unstable while heptacene has not been prepared[2]. Yet all existing theoretical methods predict sizeable amounts of resonance energies, RE's, for these molecules. Thus for hexacene, e.g. Aihara calculates an AII RE of 0.706 B[3] and graph-theoretical[4] value of 0.778 B. Its topological RE amounts to 0.706 B[5].

Dewar and De Llano computes a value > 2 ev[6]. For a molecule of a linear acene Randić expresses its RE as the sum of values donated additively by all its conjugated circuits[7] and

might be expressed for a linear acene containing i rings[8] as $\{2/(i+1)\}\sum_{x=1}^{i}(i+1-x)R_x$, where R is a conjugated circuit, the value of which depends on its size, x, as computed by Randić[7]. The numbers resulting from these theories even when divided by the number of rings or pi electrons do not predict instability of linear acenes higher than pentacene. A theory that accounts for this peculiar behaviour of the linear acenes and in the meantime consistent with other facts seems desirable.

2) REPRESENTATION OF THE KEKULÉ STRUCTURES AS THEIR SUB-MOLECULES[9]:

A submolecule is a graph resulting when a particular Kekulé structure is transformed into the subspace of its double bonds[9]. Recently the author[10] studied connectivities of these graphs for a wide variety of aromatic hydrocarbons and found a relation between the connectivity of a submolecule and the Kekulé index[11] of its corresponding Kekulé structure for some one hundred cases. Hence a submolecule might be taken to represent the corresponding Kekulé structure. Thus, the fully benzenoid Kekulé structure of naphthalene, e.g. is given by its submolecule, viz.,  and so on.

3) DEGENERATE TRANSFORMATIONS IN A SET OF SUBMOLECULES:

We define a degenerate transformation between two submolecules as one involving only rearranging one edge in the submolecule graph. Thus the two non-equivalent submolecules of naphthalene transform to one another degenerately as follows:

FIG. 1: Degenerate transformation between the two non-equivalent submolecules of naphthalene.

A non-degenerate transformation between two submolecules would necessarily involve the intermediacy of a "different topology". Thus the transformation between the submolecules representing fully benzenoid and least benzenoid Kekulé structures of

phenanthrene passes through an "anthracene topology"; and thus is defined as a non-degenerate transformation:

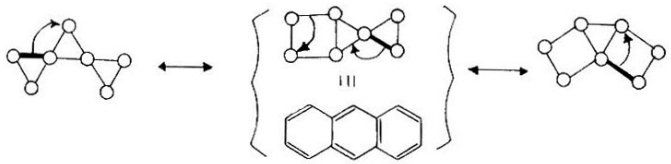

FIG. 2: A non-degenerate transformation between the "most important" and "least important" graphs. The transformation proceeds via an anthracene topology. Edges involved are heavily drawn.

Members of a set of submolecules that transform to one another degenerately (i.e. via rearrangement of only one edge and without the intermediacy of a different topology) are called degenerate.

4) ASSIGNMENT OF PARITY TO INDIVIDUAL SUBMOLECULES BELONGING TO ONE CATACONDENSED BENZENOID HYDROCARBON:

i- Degenerate members are given a parity, p = +1.

ii- Members that do not conserve topology when being transformed to other submolecules of the hydrocarbon that have identical counts of conjugated circuits[7]*, cc, are given p = -1.

iii- A single submolecule with different conjugated circuits count* than the rest of the set is given p=o. Such a "single" submolecule will not be degenerate with other members and will be termed "single" graph.

The method is being illustrated for the pentaphene submolecules. (For convenience the hydrocarbon graph is lightly drawn around its submolecule).

*In corresponding Kekulé structure(s).

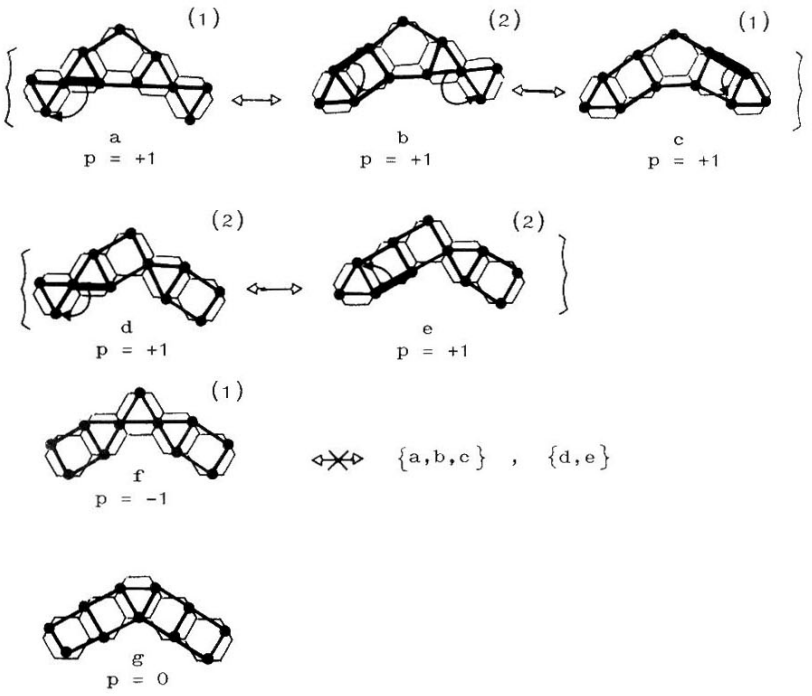

FIG. 3: Degenerate, ⟷, and non-degenerate, ⤫, transformations of pentaphene. Only graph g contains 9 cc, the rest only five. Thus g is a "single" graph whose parity is zero.

Members {a ⟶ f} have cc = 5 while g has 9 cc .
Numbers above individual graphs are their multiplicities; e.g. there are two equivalent Kekulé structures* of b (b and its mirror immage) and so on.

*Graphs (a-g) are non-equivalent while b and its mirror immage are equivalent.

5) AN INDEX OF STABILITY, S:

For a catacondensed benzenoid hydrocarbon a stability index, S. is defined by eqn. 1,

$$S = K. \sum_{i=1}^{K'} n_i p_i \qquad (1)$$

where K is the total number of Kekulé structures n_i is multiplicity of i th submolecule and p_i, its parity. The summation is being taken over all non-equivalent Kekulé structures K'. Thus for pentaphene we have:

$S = 10\ (1 + 2x1 + 1 + 2x1 + 2x1 - 1 + 0x1) = 7$

6) THE LINEAR ACENES:

One peculiar feature that is very particular only to linear acenes is the fact that for a linear acene containing i rings only one pair among its (i+1) submolecules "conserve topology" when transformed to one another. This is shown in Fig. 4 for heptacene.

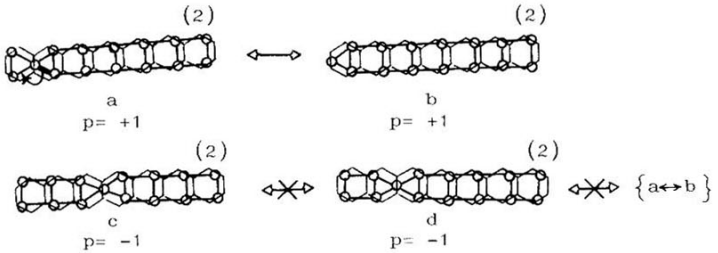

FIG. 4: Degenerate and non-degenerate submolecules of heptacene. All graphs contain 7 cc .

All members have identical cc counts. According to eqn. 1, heptacene has no stability (S=0), which is consistent with

experimental findings[2, 3]. Observe that only a and b are degenerate. Thus to go from a to d, e.g., would necessitate replacing heptacene topology with benz [a]hexacene, Fig. (5).

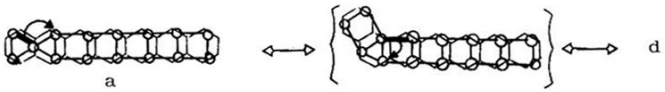

FIG. 5: A non-degenerate transformation of heptacene.

7) RESULTS AND DISCUSSION:

Table 1 outlines stability indices for 17 catacondensed hydrocarbons and their RE's based on conjugated circuits counts[7]. Balaban-Harary duals[12] are used to represent the hydrocarbons. (The hexagons are replaced by vertices and then connecting adjacent ones). The merits of our stability index, S, becomes clear from inspection of table 1:

i- Linear acenes have decreasingly lower S's as the number of their rings increases. The formalism predicts no stability for heptacene which is consistent with experimental facts[3].

ii- Heptacene and both hydrocarbons 9 and 10 have 8 Kekulé structures and almost identical RE's yet the two latter isoconjugates are far much more stable; as reflected in values of S.

iii- The above observation is not limited to a comparison between a linear and a non-linear acene: thus pentaphene, 11, has K=10 while triphenylene, 12, has only K=9, yet their RE's are very similar (in fact RE(12) is slightly greater than RE(11), a fact reflected in their respective S values).

iv- Similarly hydrocarbons 13 and 16, both having K=13 yet RE(16) > RE(13); which is again consistent with values of S.

Our stability index might thus be viewed as an "algebraic structure count" designed for catacondensed benzenoid hydrocarbons, particularly to compare benzenoid hydrocarbons, especially to compare branched with non-branched ones. Many years

ago Dewar and Longuet-Higgins[13, 14] demonstrated that the simple structure counting rules of resonance have quantitative significance when applied to even alternant systems constructed from rings of $(4n+2)$ atoms and chains. We may now view this opinion as representing only part of the truth. It turns out that both topological as well as combinatorial aspects must be taken into consideration. K reflects the latter character only, while S contains both. The present approach offers for the first time a relation between conservation of molecular topology among a set of submolecules and the stability of the hydrocarbon they represent. A "state" defined by a subset of degenerate submolecules might be thought of as a "bonding MO" that containing a collection of non-degenerate ones as a "antibonding MO" while that containing a "single" graph would then represent a "non-bonding MO". Fig. 6 shows such states for the benzopentaphene, 13 (See TABLE 1).

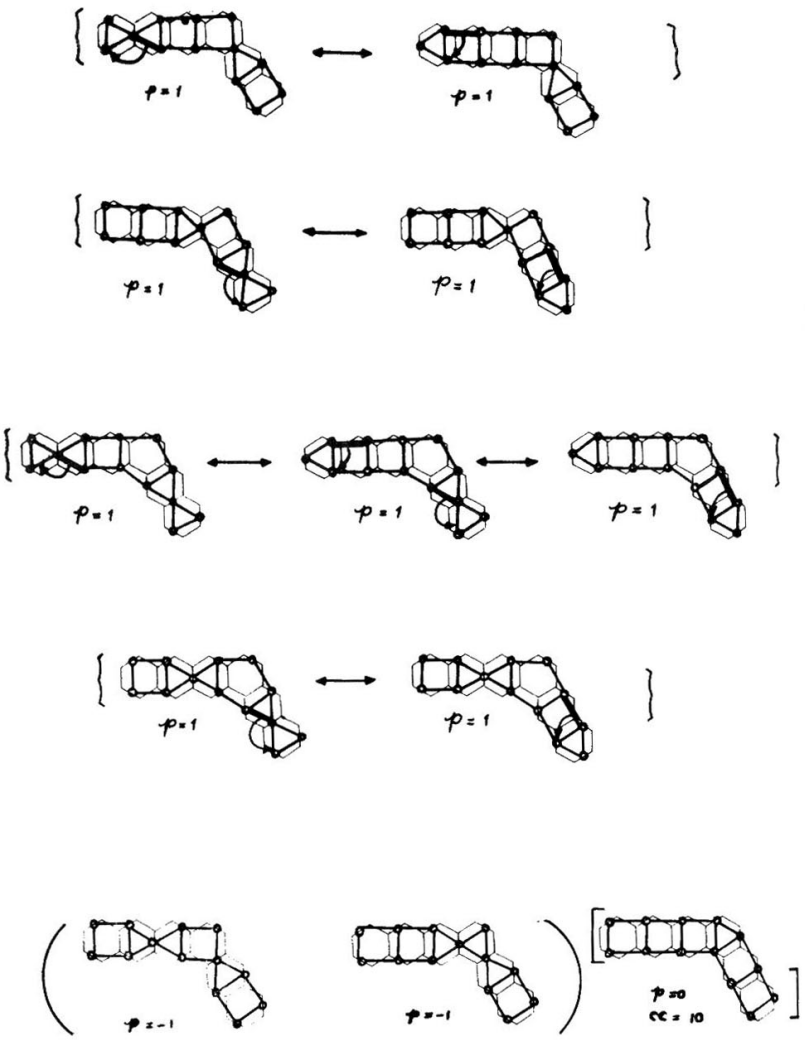

FIG. 6: Bonding,{ },antibonding,( ), and non-bonding,[ ]states of benzopentaphene (13).

TABLE 1

Stability indices, S, (eqn. 1) and RE's of Randić[7] of catacondensed acenes.

No.	Dual graph	K	$n_i p_i$	S	RE(ev)
1		3	3	9	1.323
2		4	4	16	1.599
3		5	3	15	1.782
4		6	2	12	1.883
5		7	1	7	>2
6		8	0	0	>2
7		5	4	20	1.777
8		7	6	42	2.32
9,10		8	8	64	2.54
11		10	7	70	2.70
12		9	8	72	2.71
13		13	8	104	2.94
14,15		12	12	144	2.99
16		13	12	156	3.12
17		13	12	156	3.13

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