

ON ADDITIVITY OF RESONANCE ENERGIES OF
BENZENOID HYDROCARBONS;
THE CONJUGATED CIRCUITS OF RANDIĆ⁽⁶⁾

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ABSTRACT

Resonance energy of a benzenoid hydrocarbon is computed to be the sum of resonance contributed by individual rings making up the molecule. The amount of resonance in a particular ring is assumed to be a function of its location in the molecule but independent of the structure of which it is part. Randić's conjugated circuits⁽⁶⁾ of the first five linear acenes are used to assign numerical values to such individual resonance energies of rings using a graph-theoretical approach. The resulting sums, called additive resonance energies, are shown to have excellent linear correlations with Dewar resonance energies, Randić's resonance energies, A-II resonance energies of Aihara and with Herndon resonance energies. The method represents a novel approach for comparing the stabilities of a set of relatively complex benzenoid hydrocarbons simply by inspection of their topologies.

INTRODUCTION:

Since Dewar⁽¹⁾, more than a decade ago, introduced his his definition of resonance energy, people became attracted to the idea of a "reference structure". Essentially two schools of thought emerged out of this, viz., (i) Hess and Schaad⁽²⁾, who showed that HMO theory with enough and proper parameters lead to results at least as accurate as those of Dewar, and (ii) the "Zagreb group" (Trinajstić et. al.⁽³⁾) and Aihara⁽⁴⁾, who have, independently, used graph-theoretical

methods to obtain results in excellent agreement with those of Dewar.

Two other schools used other approaches: Herndon⁽⁵⁾, using essentially a valence-bond procedure, and Randić⁽⁶⁾ who related resonance energy to the conjugation content of a molecule from the number of conjugated circuits in all its Kekulé valence structures.

In this work Randić's^S resonance energies, RRE, of the first five linear acenes are used to define and compute resonance energies of a wide variety of non-linear acenes using an additive scheme. The values obtained will be shown to have excellent linear correlations with Dewar resonance energies, DRE, Resonance energies calculated by Randić, RRE, Aihara's^S A-II resonance energies, AIIRE, and with those of Herndon, HRE.

POSTULATES AND METHOD OF CALCULATION:

(1) An Additivity Postulate:

A molecule of a benzenoid hydrocarbon is envisaged as a molecular graph composed of subgraphs connected in a particular way. Since in this work only benzenoid hydrocarbons will be considered, the smallest subgraph is a six-cycle one, i.e. a benzene ring. For convenience of illustration each benzene ring is designated as a vertex, ●. Thus naphthalene, e.g., would be represented as ●—●, while phenanthrene as ●—●—●,

and so on, The resulting graphs shall be termed "generating graphs". The assumption is now made that each vertex donates an amount of resonance to the molecule that is only a function of its location in the whole graph (molecule), but independent of the structure of which it is part. Resonance energy of a benzenoid hydrocarbon is then equated to the sum of individual resonance energies contributed by all vertices (rings) making up the total graph. Such sums will be called "additive resonance energies", ARE; thus:

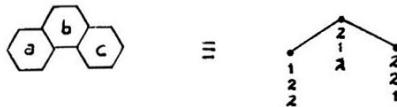
$$\text{ARE} = \sum_i r_i \quad (1)$$

where r_i is resonance energy of a ring, the location of which is given by i .

(2) Assignment of location of a ring:

The linear acenes are taken as models for assigning locations of rings in molecules of non-linear acenes. At this point it is significant to distinguish two types of subgraphs in a benzenoid hydrocarbon, viz., (i) Linear subgraphs: representing vertices (benzene rings) attached linearly. The linear acenes contain only such subgraphs, and ii) Angular subgraphs: representing angular arrangements of benzene rings. Phenanthrene, (I), e.g. contains two linear subgraphs: $\{a, b\}$ and $\{b, c\}$, and one angular graph $\{a, b, c\}$. The location of a particular ring is defined to be the order of the

linear subgraph it terminates. Thus if ring (a) is assigned

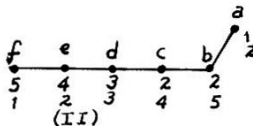


(I)

location 1, then (b) must have a value of $i = 2$ (this is because the order of $\{ab\}$ is 2), and so is ring (c). The ARE of phenanthrene would then be given by $(r_1 + 2 r_2)$.

Had one assigned a value of $i = 1$ for ring (b), both rings (vertices) (a) and (c) would have had locations of 2 and thus leading to the same ARE.

The same situation obtains if ring (c) is given a value of $i = 1$. The molecule of benzo [a] pentacene serves to illustrate the method further. The generating graph of this molecule is shown in (II).



It is immaterial which end of the graph is given a value of $i = 1$. Both sequences shown above lead to an ARE = $r_1 + 2r_2 + r_3 + r_4 + r_5$.

(3) Resonance energies of individual rings:

RE's of the linear acenes are used to assign numerical values to resonance contributed by a particular ring in a benzenoid hydrocarbon. Empirically r_i , the amount of resonance donated by a benzene ring, the location of which is i , is given by eqn. (2), viz.,

$$r_i = RE(i) - RE(i-1) \quad (2)$$

where $RE(i)$ is resonance energy of a linear acene containing i rings and $RE(i-1)$ is that of a linear acene containing $i-1$ rings. So, e.g., r_5 would be given by $RE(\text{pentacene}) - RE(\text{tetracene})$. Using Randić's RE's eqn. (2) might be written explicitly in the following form:

$$r_i = \frac{2}{i+1} \sum_{x=1}^i (i+1-x) R_x - \frac{2}{i} \sum_{x=1}^{i-1} (i-x) R_x \quad (3)$$

where the first term, it might be shown, is RRE of a linear acene containing i rings, while the second term is that for a linear acene containing $i-1$ rings. R is an index calculated by Randić⁽⁶⁾ making use of DRE's of the first five linear acenes. The value of x indicates the size of the conjugated circuit, thus R_3 , for instance, is characteristic of a conjugated circuit containing 14 pi electrons (such a circuit might take the shape of a phenanthrene or that of an anthracene. The value of R in Randić's work⁽⁶⁾, as well as in this

work, is assumed to be a function of the size of the circuit, but independent of its shape). The following values of R are calculated by Randić⁽⁶⁾: (in ev.)

$$R_1 = 0.869, R_2 = 0.246, R_3 = 0.100, R_4 = 0.041, R_5 = -0.06 \quad (4)$$

The above values of R lead to the following r's (in ev.), (eqn.3).

$$r_1 = 0.869, r_2 = 0.454, r_3 = 0.276, r_4 = 0.183, r_5 = 0.101 \quad (5)$$

Substituting eqn. (3) into (1), one obtains an expression for ARE in closed form:

$$ARE = 2 \sum_i \left\{ \frac{1}{i+1} \sum_x^i (i+1-x) R_x - \frac{1}{i} \sum_x^{i-1} (i-x) R_x \right\} \quad (6)$$

Eqns. (6) and (1) are completely equivalent.

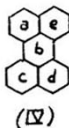
THREE EMPIRICAL RULES:

It sometimes happens in pericondensed systems that a particular ring might assume more than one location, e.g. in the triphenylene derivative, (III), one might assign a value of $i = 3$ for ring (a), as being at the terminus of the anthracene subgraph {c,b,a} or a value of $i = 2$, as



being part of the phenanthrene subgraph {e, a, d} . To avoid ambiguities in assigning locations of rings in pericondensed systems certain empirical rules will be used:

- i) If a ring (vertex) is simultaneously a part of a phenanthrene subgraph, and a linear subgraph, it is given a value of $i = 2$ (as being part of the phenanthrene subgraph).
- ii) If, in a pericondensed system, a ring is located such that it shares a number of its adjacent bonds with those of a subgraph in the total graph, its resonance contribution is reduced by a factor of $(1/n)$, n being the number of bonds in common. Such rings will be called "common rings". The molecule must be viewed as having the minimum number of common rings. Perylene, (IV), serves to illustrate this rule:



One might visualize this molecule as being part of a phenanthrene subgraph, {a,b,c} , plus two common rings, (e) and (d). Alternatively, it might be viewed as two naphthalenes, {a,e} and {c,d} plus a common ring,(b). It is this latter choice that keeps the number of common rings minimum. One assigns the following locations as shown below:



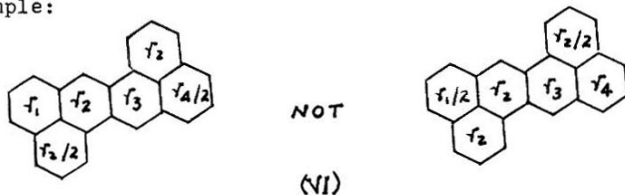
Rings (c) and (d), it is to be observed, have been considered as parts of the phenanthrene subgraphs {a,b,c} and {e,b,d} (c.f. rule i).

Because ring (b), the common ring, shares two of its adjacent bonds with each naphthalene subgraph, its resonance contribution is given by $(r_2/4)$.

Pyrene, (V), illustrates the rule still further:



Resonance contributions are shown inside rings. If there is a choice of which ring to be considered "common", the one of higher location is selected. Zethrene, (VI), is an example:

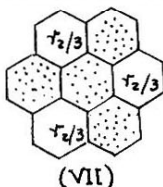


iii) The Triphenylene subgraph:

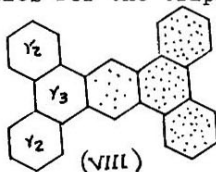
The particular structure of triphenylene leads to an

induced sextet in its central ring which imparts an extrastability that amounts to 0.4 rings⁽⁷⁾ as suggested by magnetic measurements⁽⁷⁾. Therefore whenever a triphenylene subgraph could be factored out of the total graph an additional factor of $0.4 r_2$ is (empirically) added to its ARE. For triphenylene itself its ARE is, therefore, $(r_1 + 3r_2 + 0.4 r_2)$.

If, furthermore, two triphenylene subgraphs share together their central ring a factor of $0.4 r_2$ is added to each system. Coronene, (VII), is such an example:



The undotted rings share the central ring of the dotted triphenylene system making another triphenylene. Thus ARE (coronene) = $(r_1 + 3r_2 + 0.4 r_2) + (3 \times \frac{r_2}{3} + 0.4 r_2)$. The same applies for the triphenylene derivative (VIII).



Thus ARE (VIII) = $(r_1 + 3r_2 + 0.4r_2) + (r_3 + 2r_2 + 0.4r_2)$.

RESULTS:

Table 1 shows the hydrocarbons studied in this work , their circuit decomposition⁽⁶⁾ divided by the number of their Kekulé valence structures, their additive resonance energies, ARE'^s, and the corresponding values of Randić'^s resonance energies⁽⁶⁾, RRE'^s. The table also lists available values of Dewar resonance energies⁽¹⁾, DRE, Aihara'^s A-II resonance energies⁽⁴⁾, AIIRE, and Herndon's resonance energies⁽⁵⁾, HRE.

Least-squares analysis of the data leads to the following linear eqns. ; correlation coefficients being shown in parentheses:

$$\text{RRE} = 1.2766 \text{ ARE} - 0.2911 ; (0.9930) \quad (7)$$

$$\text{DRE} = 1.2722 \text{ ARE} - 0.3448 ; (0.9921) \quad (8)$$

$$\text{AIIRE} = 0.3100 \text{ ARE} + 0.0178 ; (0.9823) \quad (9)$$

$$\text{HRE} = 1.2459 \text{ ARE} - 0.2648 ; (0.9906) \quad (10)$$

Figs. 1-4 are plots of eqns. 7-10.

DISCUSSION OF RESULTS

The method represents a novel topological method of computing resonance energies of benzenoid hydrocarbons using only a pencil and a paper approach. The method might be viewed as an extension of Clar's belief that the individual rings in a benzenoid hydrocarbon have different aromaticities.⁽⁸⁾ This very concept is embodied in eqn. (6), where ARE'^s are

Fig. 1: Correlation of Randic's resonance energies⁽⁶⁾, RRE, with ARE's, equ. (7)

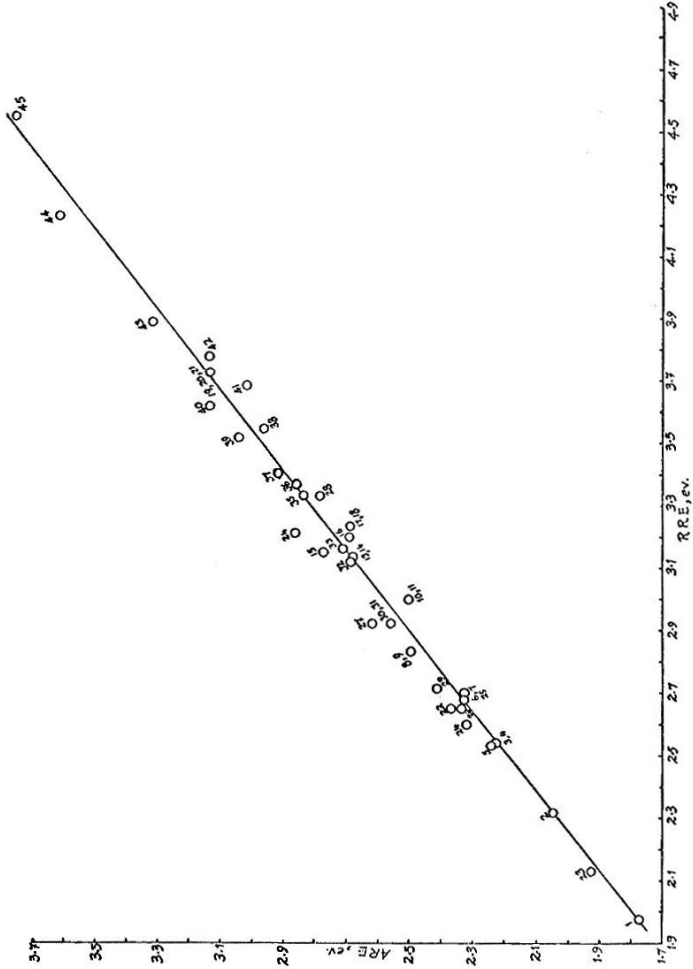


Fig. 2: Correlation of Dewar's resonance energies⁽¹⁾, DRE, with ARE's, equ. (8)

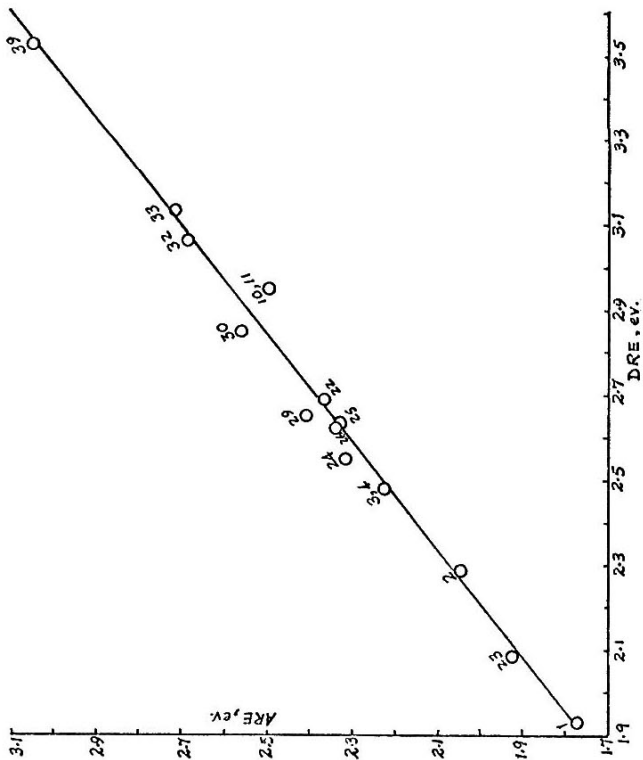


Fig. 3: Correlation of Aihara's resonance energies⁽⁴⁾,
 AIIRE, with ARE's, equ. (9)

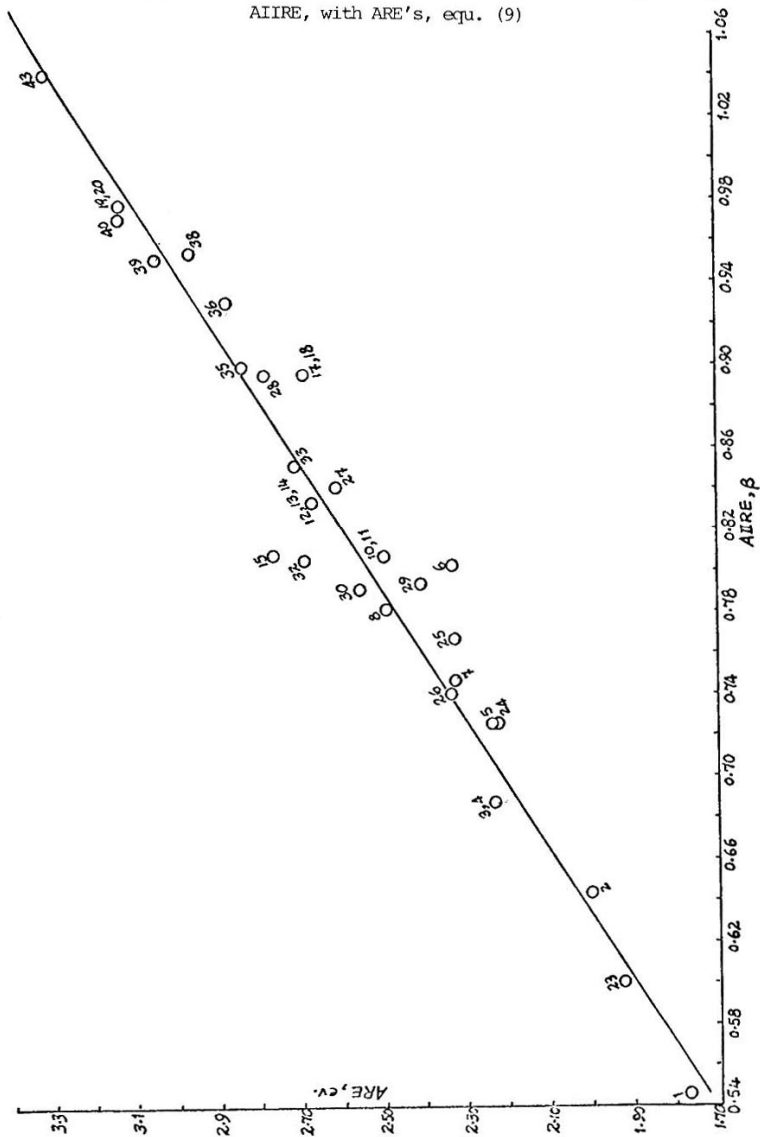
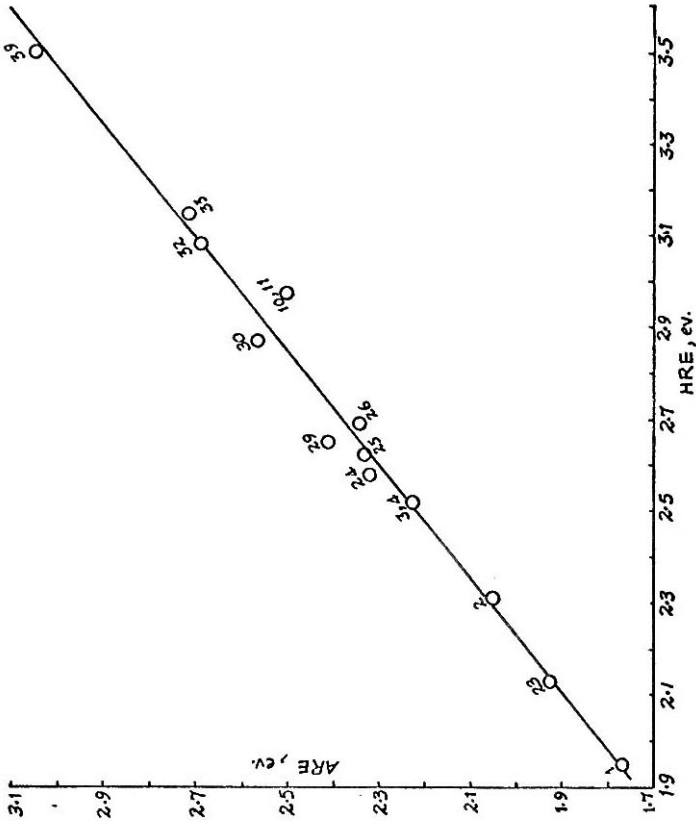


Fig. 4 : Correlation of Herndon's resonance energies⁽⁵⁾, HRE, with ARE's, equ. (10)



identified as sums of individual Rb^s of the rings composing a molecule. In our treatment the "value" of aromaticity of a particular ring has been related to its location relative to other rings in the molecule but independent of the structure of which it is part.

Graph-Theoretical analysis of data⁽⁹⁾

Investigation of table 1 reveals two main points regarding equalities and non-equalities of two (or more) ARE^s (and the corresponding other RE^s):

(a) If the ARE^s of two (or more) isomeric non-linear acenes happen to be identical, their other estimates of RE^s (by Randić⁽⁶⁾, Dewar⁽¹⁾, Aihara⁽⁴⁾ or Herndon⁽⁵⁾) are also identical or nearly so. Examples are systems (3,4); (8,9), (10,11), (12, 13, 14), (17,18), and (19,20,21). Randić calls such pairs of isomers "isoconjugate systems", as being having the same "conjugation content" from a consideration of their number of conjugated circuits and Kekulé valence bond structures.

The generating graphs of some isoconjugate systems are shown below:



"Generating graphs of some isoconjugate systems".

In the language of graph theory one states the following lemma for such isoconjugate systems:

Lemma 1

Let $G_1(n,m) = (V,E)$ and $G_2(n,m) = (V,E)$ be two generating graphs of order n and size m .

Let $G_1(n,m)$ be factored out into a set of linear subgraphs:

$G_1(n_1, m_1) = (V_1, E_1)$; $G_1(n_1^", m_1^") = (V_1^", E_1^"), \dots$, and similarly for $G_2(n,m)$; being factored into a set of linear subgraphs $G_2(n_2, m_2) = (V_2, E_2)$; $G_2(n_2^", m_2^") = (V_2^", E_2^"), \dots$, where

$$(V_1, E_1) \subset G_1(n,m), \text{ and}$$

$$(V_2, E_2) \subset G_2(n,m),$$

and similarly for other subgraphs.

If the two sets have identical numbers of subgraphs, then:

$$\text{ARE}(G_1) = \text{ARE}(G_2) \quad \text{iff}$$

$$n_1 = n_2 \quad ; \quad n_1^" = n_2^" \quad , \dots \text{ and}$$

$$m_1 = m_2 \quad ; \quad m_1^" = m_2^" \quad , \dots$$

Clearly in a set of generating graphs belonging to an isoconjugate system there is a correspondance between their vertex sets that preserves adjacency. i.e. such graphs are isomorphic.

If, furthermore, $K_1 = K_2$; K being the number of Kekulé valence-structures; then

$$RE(G_1) = RE(G_2)$$

From table 1, it is seen that hydrocarbons 8,9,10,11 have all identical ARE's yet $RRE(8) = RRE(9) \neq RRE(10) = RRE(11)$. This is to be expected since the conjugation contents of (8) and (9) are different from those of (10) and (11). Thus $K_8 = K_9 = 11$ while $K_{10} = K_{11} = 12$. A better index for comparing stabilities of a set of benzenoid hydrocarbons, would, therefore be $ARE \times K$ rather than ARE. For the above set one has: (in ev.),

$$K_8 ARE_8 = K_9 ARE_9 = 11 \times 2.507 = 27.577 \quad ; \quad RRE_8 = RRE_9 = 2.830$$
$$K_{10} ARE_{10} = K_{11} ARE_{11} = 12 \times 2.507 = 30.084; \quad RRE_{10} = RRE_{11} = 2.991$$

One, therefore, might state the following simple rule :
A set of isomeric benzenoid hydrocarbons having identical values of $(K \cdot ARE)$ will have identical RE's. Throughout the set of 45 hydrocarbons studied in this work no violations to this rule have been observed.

(b) This part of the discussion is concerned with inequalities of ARE's of a pair of isomeric benzenoid hydrocarbons. The amount of resonance contained in two or more graphs of the same order and size might be compared by simply inspection of the order of the linear subgraphs contained in each one; the one with higher order contains the lower amount of resonance, given identical K 's. This

is a natural result of the fact that $r_m > r_n$ for all $m < n$. (c.f. eqn. (3); in fact $r_i \rightarrow 0$ as $i \rightarrow \infty$, a result consistent with the well known fact that as the number of rings in a linear acene increases, its stability goes down⁽¹⁰⁾).

Examples are:

- i) ARE(7) < ARE(8)
- ii) ARE(17) < ARE(19)
- iii) ARE(32) < ARE(34)
- iv) ARE(36) < ARE(38).

The corresponding RE's follow the same pattern, provided identical K^s in each set. If the K^s are different then to compare the stabilities of two or more isomeric benzenoid hydrocarbons one uses $K.ARE^s$. For example compounds 15 and 17 are isomeric yet the former, one might factor out two linear subgraph each of order 3, while the latter contains a linear subgraph the order of which is 4. One, therefore, concludes that $ARE(17) < ARE(15)$, which is indeed true, yet $RRE(17) > RRE(15)$. This latter order is reproduced when $K.ARE$ is used, thus:

$$K_{17}ARE_{17} = 16 \times 2.690 = 43.04 \text{ ev. ,}$$

$$K_{15}ARE_{15} = 15 \times 2.783 = 41.745 \text{ ev. ,}$$

i.e. $KARE(17) > KARE(15)$, which is identical to their order of stabilities.

In this context one states the following lemma:

Lemma 2

Let $G_1(n,m)$ and $G_2(n,m)$ be two generating graphs, such that there exists two subgraphs so that:

$$G_1'(n_1, m_1) \subset G_1(n, m) \quad ,$$

$$G_2'(n_2, m_2) \subset G_2(n, m)$$

Then $ARE(G_1) < ARE(G_2)$ iff

$$n_1 > n_2$$

If, furthermore,

$$K_1 ARE(G_1) < K_2 ARE(G_2) \quad , \quad \text{then}$$

$$RE(G_1) < RE(G_2).$$

Lemmas 1 and 2 make it possible telling relative stabilities in a set of isomeric benzenoid hydrocarbons simply by inspection of: a) their topologies, as manifested in the quantity ARE, and b) their conjugation content, as reflected in the value of K.

The composite quantity, KARE, seems, in all cases studied to be quite adequate for comparative purposes.

Topological analysis of data⁽¹¹⁾

Three main sets are identified in this work:

(i) A set \underline{L} of individual resonance energies donated by individual benzene rings having particular locations in the molecule. It is given by:

$$\underline{L} = \left\{ r_i \mid r_i = \frac{2}{i+1} \sum_x^i (i+1-x)R_x - \frac{2}{i} \sum_x^{i-1} (i-x)R_x, 1 \leq i, x \leq 5 \right\} \quad (11)$$

(ii) A set \underline{A} comprising ARE's, \underline{a} 's :

$$\underline{A} = \{ \underline{a} \}, \quad (12)$$

$$\underline{A} = \bigcup \{ \mathcal{L} \mid \underline{L} \subset \mathcal{L} \} \quad (13)$$

$$\mathcal{L} = \{ r_2, r_3, r_4, r_5, r_{\text{triphenylene}}, r_{\text{pyrene}} \} \quad (14)$$

where the last two values are resonance energies assigned to triphenylene and pyrene respectively. \mathcal{L} might be viewed as the "basis set" for the computed values of ARE's.

(iii) A set \underline{R} , of actual resonance energies given by:

$$\underline{R} = \{ \emptyset ; \emptyset = b\underline{a} + C \} \quad (15)$$

Where \emptyset is an actual resonance energy (say calculated by Randić, Dewar, etc.); \underline{a} is its corresponding ARE, b is a least squares slope and C is the corresponding constant.

The three sets are related as illustrated below:

$$\begin{array}{ccc}
 \left\{ \begin{array}{c} r_1 \\ \vdots \\ r_5 \end{array} \right\} & \xrightarrow{\Sigma} & \left\{ \begin{array}{c} \overset{\curvearrowright}{a} \\ \vdots \\ \underset{\curvearrowleft}{a} \end{array} \right\} & \xrightarrow{f} & \left\{ \begin{array}{c} \overset{\curvearrowright}{\emptyset} \\ \vdots \\ \underset{\curvearrowleft}{\emptyset} \end{array} \right\} & (16) \\
 \underline{L} & & \underline{A} & & \underline{R}
 \end{array}$$

where $\overset{\curvearrowright}{a}$ represents the highest computed ARE (compound 45). The function Σ is an operator that sums up appropriate values of r_i according to rules i-iii and eqn.(1). (or eqn. (6) using R^s). The results of this operator function on the five values of r is set \underline{A} . The function f multiplies each value of \underline{a} by a constant and then adds a particular constant to the result. Set \underline{R} is thus obtained. Sets \underline{A} and \underline{R} might be viewed as two topological spaces. The function f has the following characteristics:

- 1) f is continuous.
- 2) f^{-1} is also continuous.
- 3) f and f^{-1} are "one-to-one", i.e. each \underline{a} in \underline{A} is related to only one \emptyset in \underline{R} and vice-versa. Isoconjugate systems are counted as one point in the set.
- 4) f and f^{-1} are "onto", i.e. each \underline{a} in \underline{A} and \emptyset in \underline{R} are accounted for. Therefore f and f^{-1} are both bijections and sets \underline{A} and \underline{R} are homeomorphic. The graph of f is given by:


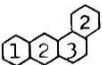

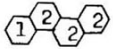
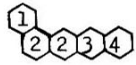
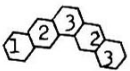
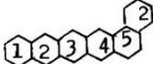
$$\left\{ \langle \underline{a}, b\underline{a} + c \rangle \mid \underline{a} \in A \right\} \quad (17)$$

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Table 1

Resonance Energies and circuit Decomposition* of Benzenoid Hydrocarbons (Numbers inside rings are their locations).

	ARE, ev.	RRE, ev.	DRE, ev.	AIIE, β	HRE, ev.
1  $(10R_1 + 4R_2 + 2R_3)/5$	1.78	1.97	1.93	0.55	1.95
2  $(16R_1 + 8R_2 + 3R_3 + 2R_4)/7$	2.05	2.32	2.29	0.64	2.31
3  $(20R_1 + 10R_2 + 4R_3 + 2R_4)/8$	2.23	2.54	2.48	0.69	2.52
4  $(20R_1 + 10R_2 + 4R_3 + 2R_4)/8$	2.23	2.54	2.48	0.69	2.52
5  $(22R_1 + 11R_2 + 7R_3 + 3R_4 + 2R_5)/9$	2.24	2.54		0.72	
6  $(26R_1 + 16R_2 + 5R_3 + 2R_4 + R_5)/10$	2.33	2.70		0.75	
7  $(28R_1 + 16R_2 + 12R_3 + 7R_4 + R_5 + R_6)/11$	2.34	2.68		0.80	

8		ARE, RRE, DRE, AIIRE, HRE, ev. ev. ev. β ev.
	$(30R_1 + 18R_2 + 6R_3 + R_4)/11$	2.51 2.83 0.78
9		2.51 2.83
	$(30R_1 + 18R_2 + 6R_3 + R_4)/11$	
10		2.51 2.99 2.95 0.81 2.97
	$(36R_1 + 16R_2 + 6R_3 + 2R_4)/12$	
11		2.51 2.99 2.95 0.81 2.97
	$(36R_1 + 16R_2 + 6R_3 + 2R_4)/12$	
12		2.68 3.13 0.83
	$(40R_1 + 20R_2 + 10R_3 + 3R_4 + 2R_5)/13$	
13		2.68 3.13 0.83
	$(40R_1 + 20R_2 + 10R_3 + 3R_4 + 2R_5)/13$	
14		2.68 3.13 0.83
	$(40R_1 + 20R_2 + 10R_3 + 3R_4 + 2R_5)/13$	
15		2.78 3.15 0.87
	$(44R_1 + 30R_2 + 16R_3 + 5R_4 + 3R_5 + R_6)/15$	

16		ARE, ev	RRE, ev	DRE, ev	AIIE, β	HRE, ev
		2.69	3.20			

$$(50R_1 + 36R_2 + 20R_3 + 7R_4 + 2R_5 + 2R_6 + R_7) / 17$$

17		2.69	3.23		0.89	
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$$(52R_1 + 21R_2 + 13R_3 + 10R_4 + 5R_5 + 2R_6) / 16$$

18		2.69	3.23		0.89	
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$$(52R_1 + 21R_2 + 13R_3 + 10R_4 + 5R_5 + 2R_6) / 16$$

19		3.14	3.72		0.98	
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$$(76R_1 + 40R_2 + 20R_3 + 10R_4 + 4R_5 + 2R_6) / 21$$

20		3.14	3.72		0.98	
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$$(76R_1 + 40R_2 + 20R_3 + 10R_4 + 4R_5 + 2R_6) / 21$$

21		3.14	3.72			
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



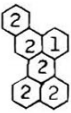



$$(76R_1 + 40R_2 + 20R_3 + 10R_4 + 4R_5 + 2R_6) / 21$$

22		2.37	2.65	2.69		
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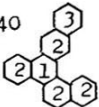
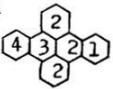
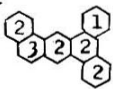


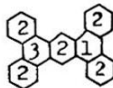
$$(24R_1 + 12R_2) / 9$$

23		1.93	2.13	2.10	0.60	2.13
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$$(12R_1 + 8R_2 + 4R_3) / 6$$

	ARE, ev.	RRE, ev.	DRE, ev.	AIIRE, β	HRE, ev.
24  $(22R_1 + 14R_2 + 7R_3 + 4R_4)/9$	2.32	2.60	2.55	0.72	2.58
25  $(24R_1 + 18R_2 + 12R_3 + 6R_4)/10$	2.34	2.67	2.63	0.77	2.62
26  $(24R_1 + 12R_2) / 9$	2.34	2.64	2.62	0.74	
27  $(34R_1 + 20R_2 + 6R_3)/12$	2.62	2.92		0.84	
28  $(50R_1 + 22R_2 + 3R_3)/15$	2.80	3.28		0.89	
29  $(26R_1 + 5R_2 + 5R_3 + 2R_4)/9$	2.41	2.71	2.65	0.79	2.65
30  $(32R_1 + 14R_2 + 8R_3 + R_4)/11$	2.56	2.92	2.85	0.79	2.87
31  $(32R_1 + 14R_2 + 8R_3 + R_4)/11$	2.56	2.92			

32		ARE, RRE, DRE, AIIRE, HRE, ev. ev. ev. β ev.
	$(42R_1 + 14R_2 + 5R_3 + 3R_4 + R_5) / 13$	2.69 3.12 3.06 0.84 3.08
33		2.72 3.16 3.13 0.85 3.15
	$(42R_1 + 26R_2 + 12R_3 + 4R_4) / 14$	
34		2.87 3.21
	$(46R_1 + 18R_2 + 5R_3 + R_4) / 14$	
35		2.84 3.33 0.90
	$(52R_1 + 28R_2 + 12R_3 + 3R_4 + R_5) / 16$	
36		2.87 3.37 0.93
	$(58R_1 + 22R_2 + 15R_3 + 7R_4 + 5R_5 + R_6) / 17$	
37		2.92 3.39
	$(60R_1 + 48R_2 + 36R_3 + 24R_4 + 12R_5) / 20$	
38		2.96 3.54 0.95
	$(68R_1 + 30R_2 + 8R_3 + 7R_4 + 4R_5 + 2R_6) / 19$	
39		3.05 3.51 3.52 0.95 3.50

	ARE, ev.	RRE, ev.	DRE, ev.	AIIRE, β	HRE, ev.
40 	3.14	3.61		0.97	
$(72R_1+34R_2+12R_3+7R_4+4R_5+R_6)/20$					
41 	3.02	3.68			
$(76R_1+24R_2+14R_3+6R_4)/20$					
42 	3.14	3.77			
$(86R_1+28R_2+12R_3+5R_4+R_5)/22$					
43 	3.32	3.88		1.04	
$(96R_1+34R_2+12R_3+2R_4)/24$					
44 	3.62	4.24			
$(140R_1+90R_2+46R_3+4R_4)/35$					
45 	3.78	4.54			
$(192R_1+48R_2+26R_3+12R_4+2R_5)/40$					

*The slight difference between our circuit decomposition and that of Randić⁽⁶⁾ comes from the fact that the latter neglects contributions from some of the higher circuits ($\geq R_3$); these, however, donate very small, almost negligible, contributions.

Annotations of the Editor:

(1) One of the referees pointed out that the "generating graphs" defined on page 3 of this paper are identically the "characteristic graphs" introduced originally by A.T. Balaban and F. Harary, Tetrahedron 24, 2505 (1968).

(2) The figure captions have been added by the editor.

O.E.P.