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A GRAPH THEORETICAL APPROACH TO CONJUGATION AND RESONANCE ENERGIES OF HYDROCARBONS

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Abstract—Kekulé forms of conjugated hydrocarbons are examined and an alternative description based on a set of circuits with a formal alternation of single and double bonds rather than traditional set of Kekulé structures offered. The approach is graph theoretical and the analysis consists in enumeration of these unique circuits (called conjugated circuits) and subsequent parametrization when molecular properties are discussed. The concept of conjugated circuits appears close to chemical ideas and was found to directly lead to expressions for resonance energies. A previously briefly outlined scheme on selected benzenoid systems (*Chem. Phys. Letters* **38**, 68 (1976)) has now been extended to larger benzenoid systems, cyclobutadiene-containing systems and several benzocyclooctatetraenes, and large number of non-alternant hydrocarbons. While in benzenoid hydrocarbons only circuits of $(4n+2)$ size arise in cyclobutadienes also conjugated circuits of $4n$ type arise indicating the origin for a lesser stability of these molecules. In polycyclic non-alternant systems some compounds have only conjugated circuits of $(4n+2)$ size, and distantly resemble benzenoids. Others have conjugated circuits of $(4n+2)$ and $4n$ kind and should subsequently be expected to show a greater dissimilarity with benzenoid systems. A representative molecule of the first kind is azulene and a discrimination of non-alternants in *azulenoids*, i.e. those having only $(4n+2)$ conjugated circuits, and *non-azulenoids* (others) has been suggested. Resonance energies of both classes of compounds are examined and the decomposition of the conjugation into circuits of different size is used as the basis for an independent estimate of resonance energies, of the quality of SCF MO calculations. An impressive agreement of the simple graph theoretical approach and fairly elaborate iterative calculations is found, which in the majority of cases is within only few hundredths of an eV. In contrast to usual empirical curve-fitting procedures the parameters involved have simple structural significance. There are some formal similarities between the graph theoretical approach based on the concept of conjugated circuits and a VB semiempirical variant developed by Herndon. The congruence only reveals the combinatorial foundations of the Kekulé structures on which the two approaches are based. Similarities and differences (of a conceptual nature) of the two closely related schemes are discussed, and combined they offer a useful method for discussion of conjugated systems, qualitatively and quantitatively of a predictive power and accuracy associated with SCF MO calculations. Combinatorial basis of the graph theoretical scheme however offer additional interesting connections between properties, such as resonance energies, of different molecules. These follows from the expressions for resonance energies which have not been previously considered.

Recent applications of Graph Theory to organic chemistry[1] brought to light several interesting relationships between the structural data as supplied by the Kekulé valence formulas, and molecular features as reflected in MO calculations. Since the *connectivity* of a molecular graph is analytically represented by the adjacency matrix,[2] which for conjugated hydrocarbons is identical to the Hückel matrix,[3] it appears that the application of the graph theory to conjugated hydrocarbons is nothing but disguised HMO. This is not the case. Graph Theory features a part of *combinatorial theory*, hence it enumerates possibilities, characterizes and classifies systems according to some structural property. It essentially manipulates with integers, is concerned with sequencing structures of systems as well as generating structures with certain prescribed qualities. Graphs become convenient representations of relationships between the elements considered and are of great advantage when the number of combinatorial possibilities is large. In problems with few combinatorial possibilities one may intuitively resolve the situation not necessarily realising that one deals with some aspects of the Graph Theory. This completely parallels the situation in problems with few symmetry properties which may be well resolved without explicit use of the Group Theory. It is in the study of systems with large combinatorial possibilities that graph theoretical approaches offer a more systematic treatment.

Graph Theory can lead to general numerical results, but these are derived through correlations with data (theoretical or experimental) from other sources. A direct use of eigenvalues and eigenvectors of the adjacency matrix of a molecular graph of conjugated hydrocarbon implies a special correlation. Since Hückel energies and HMO have been found to be of limited value, such a special correlation is rather limited in use. However, one may correlate certain graph theoretical quantities with data from more accurate SCF MO calculations. Not only that one finds correlations of impressive accuracy but also conceptually novel views on conjugation, resonance energy and aromaticity follows. Namely, graph theoretical schemes are distinguished from other schemes based on empirical correlations in that the derived expressions allow a direct structural interpretation of the parameters involved. Comparison of the results for different molecules may reveal novel connections and common combinatorial components.

Besides the adjacency matrix, its characteristic polynomial, eigenvalues and eigenvectors, Graph Theory considers various other properties of a system which are associated with the *connectivity* of the system. In particular various subgraphs derived by fragmentation of the structure are of special interest. These include as a special case Kekulé structures and structures obtained by their superposition. Similarly, rings and circuits portray another kind of component of interest in the characterization of graphs of molecular skeletons. A search for various components, their enumeration and characterization provides an important aspect of application of Graph Theory to molecular structures. In such considerations one is interested to discern certain structural elements which allow some ordering of different structures. Once a set of structures has been ordered one may use chemical intuition to search for molecular properties that follow approximately the same order. Here the graph theoretical analysis ends and chemical application begins. It is important to realize that a step from graph theoretical analysis to assignment of numerical values to parameters which appear in the scheme represents a jump. Purely mathematical quantities and concepts now receive certain physical interpretation and dimension.

In this paper we will examine conjugation in hydrocarbons from a graph theoretical point of view. In particular we will closely examine individual circuits in polycyclic conjugated hydrocarbons and will consider how each of the Kekulé valence structure distributes the formally single and double CC bonds along a circuit. It follows that only few among all possible circuits have a regular alternation of the formally single and the double bonds. The analysis consist in discerning and subsequent *enumeration* of such regular circuits—which we call *conjugated circuits*.[4] The conjugated circuits represent a new structural concept—and as chemical intuition suggests, may play an important role in the characterization of selected properties of conjugated molecules. In the recent preliminary communication[4] it has been shown that conjugated circuits lead to simple expressions for the resonance energies (RE) of benzenoid hydrocarbons. Not only that RE of many fused benzenoid hydrocarbons could be predicted with a remarkable accuracy with as few as four derived parameters, but the parameters used have a simple interpretation.[6] Moreover, the analysis has pointed to unsuspected relations among RE of different molecules. For example RE of phenanthrene equals sum 3/5 of the RE of benzene and naphthalene and 2/5 of anthracene. Results of this kind, which are of combinatorial origin, have not been perceived in the long history of quantum chemical calculations abundant with MO data. However, the Graph Theory should not be judged solely on its capability to simulate selected numerical results from experiments or from other theoretical models. The qualitative ideas and conceptualism outlined in this paper may turn out to be more significant than the numerical results.

Conjugated $(4n+2)$ *circuits*. We will illustrate the approach and the concept of conjugated circuits using the example of phenanthrene. There are five Kekulé structures for this molecule (Table 1). The three fused benzene rings give rise to circuits of 6, 10 and 14 carbons. For each separate Kekulé structure all different circuits are examined and those which formally contain an alternation of CC single and double bonds are registered. We use a symbol R_n for a circuit of $(4n+2)$ size. The result of such an analysis is summarized in Table 1. The concept of conjugated circuits provides an alternative viewing of the conjugation content usually summarized by the set of all Kekulé valence forms. Notice that for all the Kekulé forms of phenanthrene, except the last, the number of conjugated circuits is equal to the number of fused benzene rings. In order to maintain this useful relation of an equal number of conjugated circuits for each Kekulé form one of the conjugated circuits in the last valence structure should be eliminated. A closer look of the connectivity in phenanthrene reveals that not all circuits in this structure are independent. For example the molecular perimeter can be obtained from a superposition of circuits of smaller size:

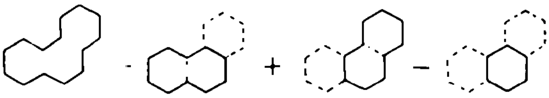
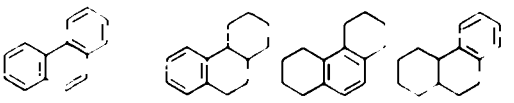
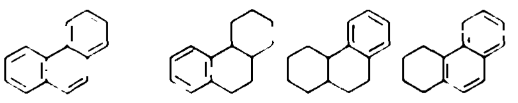
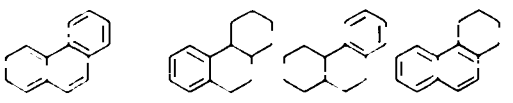
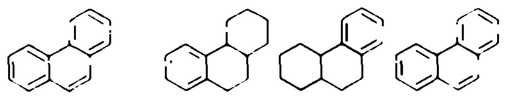
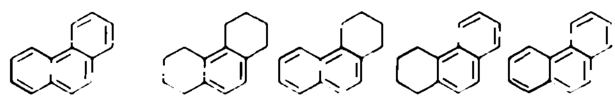


Table 1. Decomposition of the five Kekulé structures of phenanthrene into circuits with an alternation of the single and the double CC bond. In order to make the individual circuits visible only one such circuit is shown at the time

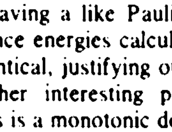
	$3R_1$
	$2R_1 + R_2$
	$2R_1 + R_2$
	$2R_2 + R_1$
	$R_1 + 2R_2 + (R_3)$

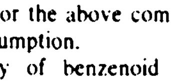
If we now assign the single and the double bond character to the perimeter as implied in the last Kekulé form it becomes apparent that conjugated circuits R_1, R_2 and R_3 are *linearly dependant*. In other words one of the conjugated circuits depicts a duplication of the information on conjugation contained in the particular Kekulé valence structure and can be justifiably eliminated. In view of the subsequent correlation of conjugated circuits and RE in benzenoid hydrocarbons where large circuits generally make little contribution it is plausible to resolve the problem of linear dependance of by excluding the largest circuits involved.

A search for conjugated circuits and their enumeration demands a list of all the Kekulé valence structures of a molecule. While these are not difficult to derive for systems built from a few condensed rings, the situation becomes somewhat involved for larger molecules. For example there are 50 Kekulé structures in ovalene,[7] and a systematic and an efficient construction procedure is desirable in such instances. It appears that the question of obtaining all the Kekulé forms for (larger) molecules has not been considered in the literature. To facilitate an examination of conjugated hydrocarbons, an algorithm which closely follows a recently reported scheme for the enumeration of all Kekulé structures[8] has been developed and adopted for a computer use.[9]

In Table 2 we list the decomposition of the conjugation for selected benzenoid hydrocarbons having several fused benzene rings in terms of conjugated circuits. It represents a continuation of a similar table of the preliminary report[4] which contains the same results for smaller benzenoid hydrocarbons.

We assume—at this stage of the development of the scheme—that circuits involving more than two rings (R_3, R_4, R_5) are equivalent even if they differ in a shape. The validity of this assumption can be evaluated by comparing resonance energies of molecules that differ only by the shape of conjugated circuits, but not in their number. Such are for instance the two isomers of dibenzanthracene shown below





We will refer to such molecules as *isoconjugate systems*.[10] As will be seen later such isoconjugate systems arise also among non-benzenoid hydrocarbons. One can trace their origin to the presence of a non-equivalent bond having a like Pauling bond order. The SCF MO resonance energies calculated for the above compounds are identical, justifying our assumption.

Another interesting property of benzenoid hydrocarbons is a monotonic decrease of the number of larger conjugated circuits in the decomposition of the conjugation. Generally the coefficients of various R_n in the derived expressions for circuit decompositions decrease with n. One can view the first coefficient in such an expression as a measure of the benzenoid character of the system—an index of expected similarity with benzene.[11] Also since the numerical parameters adopted for reproducing RE of benzene, naphthalene, anthracene and tetracene:[4]

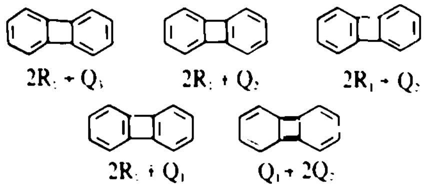
$$R_1 = 0.869\,\mathrm{eV};\quad R_2 = 0.246\,\mathrm{eV};\quad R_3 = 0.100\,\mathrm{eV}$$
$$R_4 = 0.041\,\mathrm{eV}$$

decrease with the size of the conjugated circuit it follows that for the discussion of the RE of conjugated hydrocarbons the dominant role is played by the smaller conjugated circuits R_1 and R_2. This may be viewed as an alternative formulation of the finding of Herndon[12] who in his Resonance-Structure Theory concludes that for benzenoid hydrocarbons it is not necessary to include higher contributions than those from five pairs of double bonds in calculating RE. However, for larger molecules an accumulation of the contributions from R_3 and R_4 conjugated circuits make a significant contribution to RE which should not be overlooked.

Perylene, zethrene and related higher homologs make a special class of structures. For them the number of conjugated circuits contained in all Kekulé structures is *smaller* than the number of fused benzene rings. As we see from the decomposition of the conjugation in conjugated circuits in such molecules the conjugation is in fact confined to *isolated* fragments of the structure. The two naphthalene moieties in perylene are separated by "essentially" single bonds. The central ring in perylene does not participate in *any* conjugate circuit, it is devoid of *any* conjugation, and can be viewed, as Clar has been advocating,[11] as an *empty* ring. It may be useful to refer to systems such as perylene as *conjugation-deficient* systems. The difference between the number of conjugated circuits found in such molecules and the number expected from the number of fused rings indicates the degree of the deficiency present.

Resonance energies are calculated from expressions showing the number of conjugated circuits of different size using the parameters derived from linear acenes.[4] They are shown in the last column of Table 2.

Non-benzenoid alternant hydrocarbons. In benzenoid hydrocarbons only conjugated rings of (4n + 2) size occur which signify the pronounced stability of these molecules. The extension of the approach to non-benzenoid alternant hydrocarbons to be examined now introduces conjugated circuits of 4n size, besides those of (4n + 2). As a consequence, the stability of such systems in somewhat reduced. We will illustrate the situation on biphenylene. There are five Kekulé forms for this hydrocarbon



Below each Kekulé form we indicate the number of conjugated circuits present in it. Here R_r again stands for conjugated circuits of size (4n + 2) and Q_n stands for conjugated circuits of size 4n. The summation of the contributions of the individual Kekulé forms gives for biphenylene: $8R_1 + 2Q_1 + 4Q_2 + Q_3$. For a selection of cyclobutadienes and benzocyclooctatetraenes the results of the decomposition of the molecular conjugation into the circuits components is shown in Tables 3 and 4 respectively.

The derived expressions giving the amount of conjugated circuits in a molecule can again serve as the basis for a discussion of RE of these systems. This requires a selection of numerical values for the parameters R_n and Q_n which have to be taken from another source. In contrast to reported RE for benzenoid systems the calculated resonance energies for non-benzenoid systems

Table 2. Decomposition of conjugation contained in Kekulé structures of benzenoid hydrocarbons into linearly independent conjugated circuits of size $(4n+2) \equiv R_n$

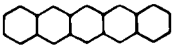
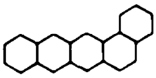
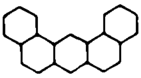
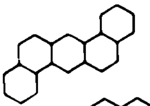
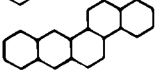
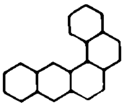
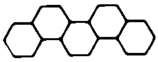
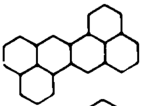
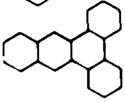
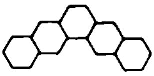
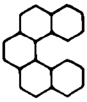
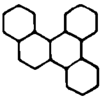
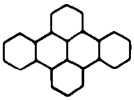
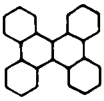
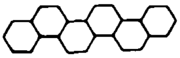
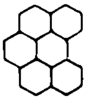
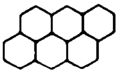
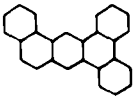
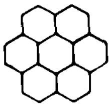
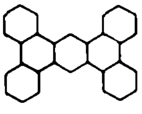
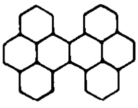
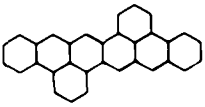
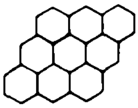
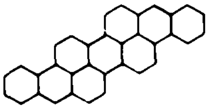
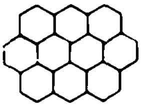
		RE (eV)
	$(10R_1 + 8R_2 + 6R_3 + 4R_4 + 2R_5)/6$	1.883
	$(22R_1 + 12R_2 + 7R_3 + 3R_4 + R_5)/9$	2.543
 	$(36R_1 + 16R_2 + 6R_3 + 2R_4)/12$	2.991
 	$(30R_1 + 18R_2 + 6R_3 + R_4)/11$	2.830
	$(40R_1 + 20R_2 + 5R_3)/13$	3.084
	$(24R_1 + 12R_2)/9$	2.646
	$(42R_1 + 14R_2 + 5R_3 + 3R_4 + R_5)/13$	3.120
	$(26R_1 + 16R_2 + 5R_3 + 2R_4 + R_5)/10$	
	$(40R_1 + 20R_2 + 5R_3)/13$	
	$(46R_1 + 18R_2 + 5R_3 + R_4)/14$	
	$(76R_1 + 24R_2 + 14R_3 + 6R_4)/20$	
	$(96R_1 + 34R_2 + 12R_3 + 2R_4)/24$	
	$(75R_1 + 42R_2 + 9R_3)/21$	
	$(42R_1 + 26R_2 + 12R_3 + 4R_4)/14$	
	$(24R_1 + 18R_2 + 12R_3 + 6R_4)/10$	

Table 2. (*Contd.*)

	RE (eV)
	$(86R_1 + 28R_2 + 12R_3 + 5R_4 + R_5)/22$
	$(64R_1 + 48R_2 + 27R_3 + R_4)/20$
	$(192R_1 + 48R_2 + 26R_3 + 12R_4 + 2R_5)/40$
	$(140R_1 + 90R_2 + 46R_3 + 4R_4)/35$
	$(100R_1 + 40R_2 + 10R_3)/25$
	$(60R_1 + 48R_2 + 36R_3 + 24R_4 + 12R_5)/20$
	$(158R_1 + 108R_2 + 66R_3 + 24R_4 + 4R_5)/40$
	$(200R_1 + 160R_2 + 110R_3 + 26R_4 + 4R_5)/500$

appear generally in substantially lesser accord when the results of different authors are compared. We have adopted as a source for correlation the SCF MO calculations of Dewar and Gleicher[14] since primarily in that work more than a dozen benzocyclobutadienes have been reported. Systematically shifted numerical values due to a different scale adopted do not necessarily cause concern when comparing different sources. Discrepancies of a more troublesome kind concern the relative magnitudes of selected molecules. For example, Dewar and Gleicher[14] reported very close magnitudes for RE of anthra(b)cyclobutadiene and phenenthro(1)cyclobutadiene. In contrast Herndon and Ellzey[15] found the difference in the RE of the same pair of molecules to be an order of magnitude larger. In the present work we are concerned with a presentation of an *alternative route* to derivation of RE, and the above differences and their origin are outside the scope of our theme. The prime result of our graph theoretical approach are the expressions for RE based on the concept of conjugated circuits. The actual numerical values for RE will depend on a selection of parameters R_n and Q_n occuring in expressions representing the decomposition of the conjugation. In order to avoid proliferation of empirical parameters, particularly as we are here primarily interested in illustrating the scheme, we have adopted R_n values already used in benzenoid systems.[4] The following values for Q_n are assumed (all in eV):

$$Q_1 = -1.60 \qquad Q_2 = -0.45 \qquad Q_3 = -0.15 \qquad Q_4 = -0.06.$$

These values, except for the sign, are estimated from a plot of R_n against N, the number of carbon atoms in the ring (circuit). In this way we simulated the dependance of RE of annulenes on the size of the ring.[16] In Fig. 1 the derived RE are plotted against the RE values of SCF MO treatment of Dewar and Gleicher. The resulting correlation indicates strongly the validity of the analysis presented here. Namely, the correlation shown in Fig. 1 involves three quite independent sources and quite distinctive kind of data: (1) the conceptually novel notion of conjugated circuits; (2) the numerical parametrization based on linear acenes; and (3) assumption on a general decrease of (4n + 2) annulene stability and an increase of 4n annulene stability with increase in the size of the ring. Yet, when so derived Re are plotted against an SCF MO resonance energies a very satisfactory comparison is found. The figure demonstrates that a linear relation between the SCF MO and graph theoretical results exists. It shows that the currently adopted parameters are plausible although a possibility of other sets of parameters satisfying the linear correlation cannot be excluded.

Table 3. Decomposition of selected cyclobutadienes in conjugated circuits of (4n + 2) and 4n type. SCF MO resonance energies are those of Dewar and Gleicher (Ref. 14) and are linearly related to those derived from parameters selected to agree with SCF MO scale as subsequently adopted by Dewar and de Llano (Ref. 25). (see Fig. 1).

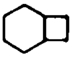
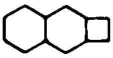
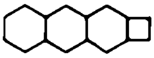
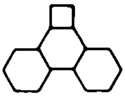
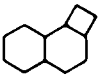
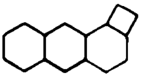
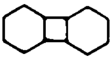
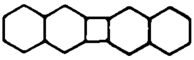
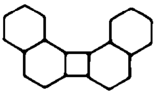
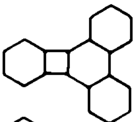
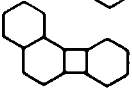
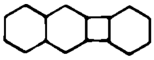
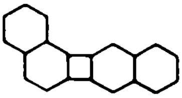
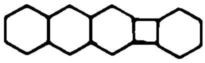
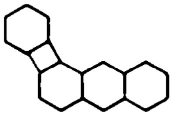
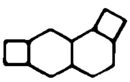
Molecule	Circuit decomposition	Resonance Energies (eV) SCF MO	 This work
	$(2R_1 + 2Q_1 + 2Q_2)/3$	0.830	−0.790
	$(4R_1 + 2R_2 + 2Q_1$ $+ 2Q_2 + 2Q_3)/4$	1.968	−0.105
	$(6R_1 + 4R_2 + 2R_3 + 2Q_1$ $+ 2Q_2 + 2Q_3 + 2Q_4)/5$	2.843	0.380
	$(18R_1 + 4R_2 + R_3 + 8Q_1$ $+ 2Q_2 + 2Q_3 + Q_4)/9$	2.739	0.297
	$(6R_1 + 2R_2 + 4Q_1$ $+ 2Q_2 + Q_3)/5$	1.667	−0.348
	$(10R_1 + 6R_2 + 2R_3 + 6Q_1$ $+ 2Q_2 + Q_3 + Q_4)/7$	2.430	−0.049
	$(8R_1 + 2Q_1 + 4Q_2$ $+ Q_3)/5$	2.610	0.362
	$(24R_1 + 12R_2 + 2Q_1$ $+ 4Q_2 + 5Q_3 + 2Q_4$ $+ Q_5)/10$	4.707	1.794
	$(32R_1 + 12R_2 + 8Q_1$ $+ 8Q_2 + 5Q_3)/13$	4.401	1.500
	$(38R_1 + 8R_2 + 2R_3$ $+ 8Q_1 + 10Q_2 + 3Q_3$ $+ Q_4)/14$	4.637	1.241
	$(16R_1 + 4R_2 + 4Q_1$ $+ 6Q_2 + 2Q_3)/8$	3.515	0.69
	$(14R_1 + 4R_2 + 2Q_1$ $+ 2Q_2 + 3Q_3 + Q_4)/7$	3.671	1.08
	$(26R_1 + 12R_2 + 4Q_1$ $+ 6Q_2 + 6Q_3 + Q_4)/11$	4.602	1.41
	$(20R_1 + 8R_2 + 4R_3$ $2Q_1 + 4Q_2 + 3Q_3$ $+ 3Q_4 + Q_5)/9$	4.516	1.57
	$(24R_1 + 10R_2 + 4R_3$ $+ 6Q_1 + 8Q_2 + 2Q_3$ $+ Q_4)/11$	4.302	0.92
	$(6R_1 + 2R_2 + R_3$ $10Q_1 + 6Q_2 + 3Q_3)/7$		1.90

Table 3. (*Contd.*)

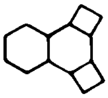
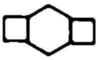
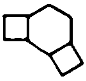
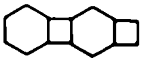
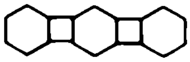
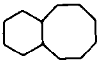
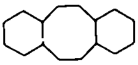
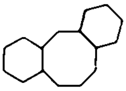
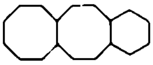
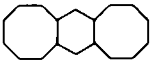
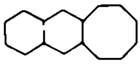
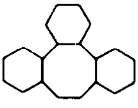
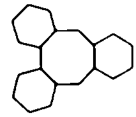
Molecule	Circuit decomposition	Resonance Energies (eV) SCF MO	This work
	$(6R_1 + 2R_2 - R_3 + 15Q_1 - 4Q_2 + 2Q_3)/9$		-1.84
	$(2R_1 + 2R_2 - 4Q_1 + 2Q_2 - 2Q_3)/4$		-1.49
	$(2R_1 - R_2 + 8Q_1 - 4Q_2)/5$		-1.92
	$(15R_1 + R_2 - 2R_3 + 6Q_1 + 10Q_2 - Q_3)/7$		-0.11
	$(28R_1 + R_2 + 3R_3\ 8Q_1 + 16Q_2 + 4Q_4)/12$		0.356

Table 4. Expressions for Resonance energies of selected benzocyclo-octatetranes in terms of conjugated circuits R_n and Q_n

	$(2R_1 + 2Q_2 + 2Q_3)/3$
	$(8R_1 + 2Q_2 + 4Q_3 + Q_4)/5$
	$(4R_1 - 2Q_2 - 4Q_3 - 2Q_4)/4$
	$(4R_1 + 2R_3 - R_4 - 6Q_2 - 2Q_3)/5$
	$(2R_1 + 2R_4 - 4Q_2 - 4Q_3)/4$
	$(4R_1 + 2R_2 - 2Q_2 - 2Q_3 - 2Q_4)/4$
	$(24R_1 + 2Q_2 - 6Q_3 - 3Q_4 - Q_5)/9$
	$(10R_1 - 2Q_2 - 6Q_3 - 5Q_4 + Q_5)/6$

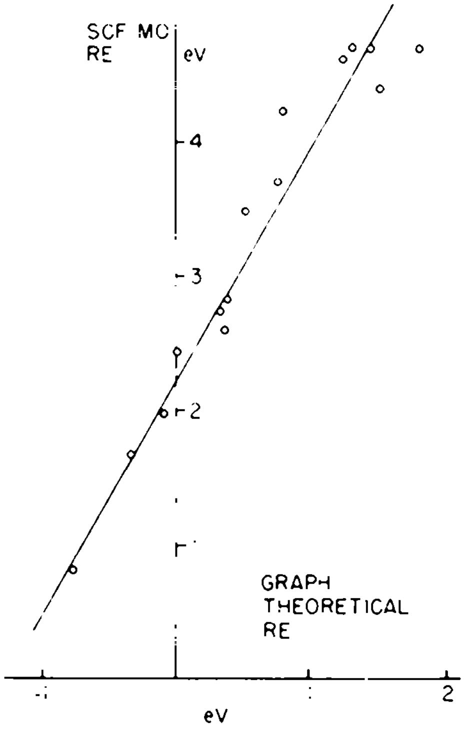
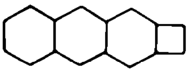
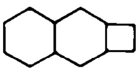


Fig. 1. A comparison between the SCF MO resonance energies obtained by a Pariser–Parr–Pople type calculation (Dewar and Gleicher) and those derived from the graph theoretical decomposition of conjugation with parameters suited to simulate subsequently adopted scale (Dewar and de Llano) where positive RE correspond to structures stabilized by pi-electron delocalization and negative RE correspond to structures which are destabilized by interacting pi-electrons and tend to localize CC double bonds.

The stability of molecules containing 4n rings has been the subject of several theoretical studies.[16] A number of graph theoretical approaches uses the concept of the parity of a Kekulé structure.[17] It is assumed that structures of opposite parity make opposite contributions to the stability of the system.[18] The concept of conjugated circuits allows finer discussions of the contributions of individual Kekulé structures by facilitating an estimate of the relative importance of different valence forms. Moreover, by examining the number of conjugated circuits of different size a meaningful comparison of different systems is possible. For instance, it was suggested on the basis of qualitative HMO calculations[18] that anthra(b)cyclobutadiene 1, a linear fusion of cyclobutadiene to anthracene, will be slightly more stable than naphtho(b)cyclobutadiene 2, a similar fusion of cyclobutadiene to naphthalene:


1


2

The analysis of the conjugation in terms of (4n + 2) and 4n conjugated circuits provides a *quantitative* estimate for the difference in stability as measured by RE, of the accuracy associated with SCF MO calculations. Namely from the corresponding expressions for RE (Table 3) of the two compounds one easily derives for the difference:

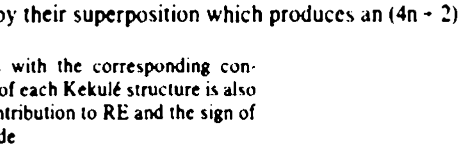
$$((2R_1 + 3R_2 + 4R_3) - (Q_1 + Q_2 + Q_3) + 4Q_4)/10 = 0.47\ \mathrm{eV}.$$

Notice a fractional increase of the contributions of (4n + 2) conjugated rings and simultaneous decrease of the negative role of 4n conjugated circuits (except for negligible effect of Q_4). So as the result of the two trends which support each other considerable stabilization of 1 relative to 2 follows.

The conjugated circuits are suitable for a quantitative discussion of the contributing role of individual Kekulé structures. By substituting numerical values for R_n and Q_n a partial contribution of each Kekulé form to the RE can be directly derived. For example, the five Kekulé valence structures of biphenylene shown previously give 1.59 eV; 1.29 eV (twice); 0.14 eV; and −2.50 eV respectively. When these contributions are divided by the number of Kekulé forms, normalized portions follow which simply add to the total RE. For a selection of non-benzenoid hydrocarbons these are shown in Table 5. We see that individual Kekulé structures make considerably different contributions to the RE of a molecule, some even appear with negative contributions. The derived partial contributions to RE for each structure allow these to be ordered according their role to the overall stabilization of the molecule. It is interesting that the results point to limits of application of the empirical Fries rule, found valid for benzenoid systems, to non-benzenoid conjugated hydrocarbons. Fries pointed that the dominant role among the Kekulé valence structures belong to the structure with the greatest number of formal benzene rings, i.e. in our terminology, to the valence structure with the largest number of R_1 conjugated circuits. When one compares the first two structures in Table 5 one sees that the most important structure has less benzene rings R_1 than the next structure in the sequence.

Observe that frequently one can make conclusions on the relative contributions to RE without resorting to numerical evaluations involving R_n and Q_n parameters. It is sufficient to assume some regularity in trends of change of the parameters with circuit size, such as monotonic decrease of absolute magnitudes with n. Thus, in fact we can order the Kekulé valence structures of biphenylene and argue about their relative importance without envoking numerical data. It is interesting that in many instances an intuitive scheme based on projection of MO results on constructed combinations of orbitals to represent individual valence structures gives numerical parameters—called Kekulé indices[30]—which form a basis for a same or closely related ordering of valence structures.

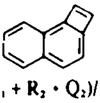
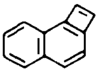
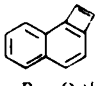
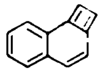
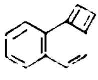
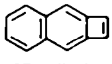
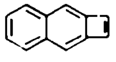
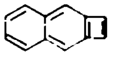
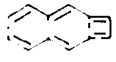
Another important result of Table 5 is illustrated in naphthocyclobutadienes. *The sign of parity does not necessarily imply the sign of the contribution to the RE.* The concept of parity of valence structures has been introduced into the resonance theory by Longuet-Higgins and Dewar[17] in order to extend some conclusion valid for benzenoid systems to non-benzenoid systems. The relative parity is deduced from a distribution of CC double bonds in two structures under comparison and depends on the number of permutations required to transform one of the structures into another. It is then generally assumed that the same parity also indicates a similar role of the two structures. Recently it has been recognized, however, that tacitly assumed compatibility of parities based on pairwise determinations does not hold for some molecular topologies,[9] e.g. structures having three odd-membered fused rings. Even more disturbing is finding that some of the valence structures of the *same* parity may make *opposite* contributions to the molecular resonance energy. As the absolute sign for parity we select the most important structure, i.e. one having the largest positive contribution to RE, and assign its parity as positive. This determines the signs of all the remaining parity labels. It follows from our considerations that a structure with a *positive* parity need not necessarily make a *positive* contribution to RE, hence may destabilize the system. The situation has not been recognized in current discussions of RE of conjugated systems which are based on the algebraic count of the Kekulé forms alone.[17] Naphthocyclobutadienes provide example of structures for which the simple mending of the resonance theory is not adequate. A more striking example of discrepancy between the sign of a contribution to RE of individual Kekulé forms and the parity type gives another cyclobutadiene derivative:



Conjugation contents:	$(3R_1 + 2Q_3)/13$	$(R_2 + 2Q_1 + 2Q_2)/13$
Partial RE:	0.166 eV	−0.277 eV

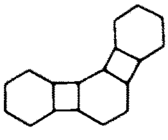
Both structures are of the same parity, as can be verified by their superposition which produces an (4n + 2)

Table 5. Kekulé structures for naphthocyclobutadienes with the corresponding contributions to the expressions for resonance energy. Parity of each Kekulé structure is also shown as (+) or (−). Notice that the sign of the partial contribution to RE and the sign of parity do not always coincide

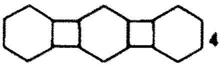
				
$(R_1 + R_2 + Q_2)/5$	$(2R_1 + Q_1)/5$	$(R_1 + R_2 + Q_1)/5$	$(R_1 + Q_1 + Q_3)/5$	$(R_1 + Q_1 + Q_2)/5$
0.134 eV (+)	0.038 eV (+)	−0.116 eV (+)	+0.176 eV (−)	−0.236 eV (−)
				
$(2R + Q_2)/4$	$(R_1 + R_2 + Q_3)/4$	$(R_1 + R_2 + Q_1)/4$	$(Q_1 + Q_2 + Q_3)/4$	
0.312 eV (+)	0.242 eV (+)	0.120 eV (+)	−0.550 eV (−)	

ring,[21] yet their contributions to RE are of opposite sign and quite sizable. In fact the two structures represent the most positive and the most negative structure respectively, when the contributions to RE are examined. Any plausible selection of the numerical magnitudes for the parameters R_n and Q_n will not change the situation. In view of this finding satisfactory correlations reported between the RE and algebraic count of the structures remain intriguing if shown sufficiently general.

The decomposition of the conjugation in circuit components allows a meaningful comparison between different structures. For example the relative stability of linearly and angularly fused conjugated rings has been considered in the literature and it was speculated[22] that the latter has a greater stability. A count of conjugated circuits for the structure shown does not support such an assertion:


3

$(28R_1 + R_2 12Q_1 - 20Q_2 - 4Q_3)/13$


4

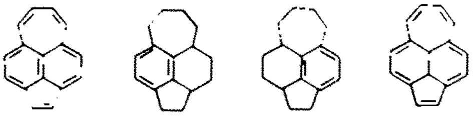
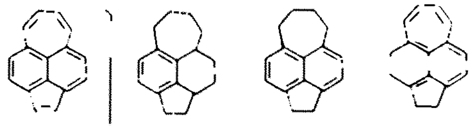
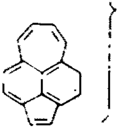
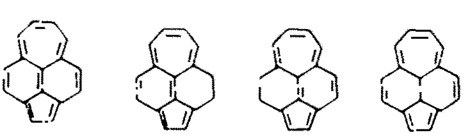
$(28R_1 + R_2 + 3R_3 - 8Q_1 - 16Q_2 + 4Q_3)/12$

The linear isomer has a larger positive contributions and fewer negative contributions than the angular isomer, hence will be more stable when judged by the amount or RE. An argument to the opposite was based on consideration of a single, albeit the most dominant, Kekulé form. A simultaneous absence of formal double bonds in both four membered rings makes the most dominant structure in 3 prominent, in particular as in 4 a formal presence of a double bond in one of the 4-membered rings cannot be avoided. However a neglect of the role of other structures may be quite misleading. The overall count of conjugated circuits shows that 3 has 12 cyclobutadiene rings compared with only 8 in 4. One can argue that though 4 has no valence structure in which a double bond is not also in a 4-membered ring it equally has no valence structure with both 4-membered rings being formally represented as cyclobutadienes. The lack of such energetically unfavorable structures appears it has more than offset the relative contribution of the most dominant structure in 3. Repeatedly it emerges that *conjugated circuits*, not fragments such as individual bonds or rings, or alternatively individual Kekulé forms, represent the essential structural element when discussing properties of conjugated hydrocarbons. In this way no dilemma of neglecting an individual structure because it is "quinoid" or associated with a "known instability of cyclobutadiene" arises. If a situation occurs making such considerations desirable one is now in a position to avoid arbitrary decisions and screen all structures in order to select those making the dominant contributions.

Non-alternant hydrocarbons. As a further test of the generality of the approach, an application of the scheme to the class of non-alternant hydrocarbons appears proper. It is justified by the encouraging results of the analysis of benzenoid systems and cyclobutadienes.

Non-alternant hydrocarbons occupy a special position in chemistry of conjugated molecules. They are of constant interest to theoretical chemists as well as a challenge to experimental research. A number of these molecules and numerous derivatives were synthetized in recent years.[23] A limited number of theoretical calculations were also reported for them.[24] Hence, an extension of the enumeration of conjugated circuits in these systems is of considerable interest. Valid conclusions on the stability of such systems can be expected from the subsequent numerical predictions of RE. For an ample number of non-alternants the reported RE disagree which would make the problem of selecting empirical parameters difficult. Fortunately, as will be seen, there are no new empirical parameters to arise and in the

Table 6. Decomposition of the four Kekulé valence structures of acepleiadylene into conjugated circuits. Notice that in this example only conjugated circuits of (4n + 2) size arise

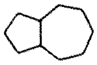
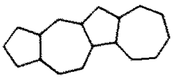
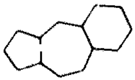
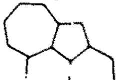
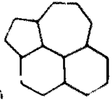
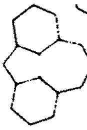
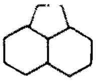
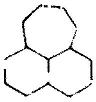
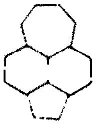
	$2R_1 + R_3$
	$R_1 + R_2 + R_3$
 symmetrically equivalent case	$R_1 + R_2 + R_3$
	$3R_3$
Total:	$4R_1 + 2R_2 + 6R_3$

continuation of our exposition we retain the parameters already used for the discussion of RE in benzenoid systems and cyclobutadienes. It should be emphasized, however, that the particular selection for the numerical values for R_n and Q_n may be revised in the future when a larger number of molecules considered here are reconsidered by a more reliable theoretical model than presently available. Currently, the calculations[25] of Dewar and de Llano offer a sufficiently large basis of molecular forms to provide a test for other schemes. The same source has also been used by Herndon and Ellzey[15] for discussion of the resonance-structure theory and the selection of parameters involved there. There are other theoretical models worthy of attention, e.g. the approach of Hess and Schaad,[26] a modified Hückel scheme in which however a judicious selection of reference structures is introduced to yield reliable predictions of relative stabilities of conjugated systems. In view of frequent confusion of graph theoretical schemes with the HMO model, the adoption of parametrization which simulates an SCF MO calculation appears desirable. In addition, since the complexity of iterative calculations even of semi-empirical SCF MO method is considerable application of graph theoretical scheme which is simple and transparent may point to inconsistencies and possible or probable errors in the reported results, so provides a test on the source of data itself.

The presence of odd membered rings in non-alternants does not introduce difficulties. Conjugated circuits are necessarily even, as they imply an alternation of bond type. In comparison with conjugation decomposition in alternant hydrocarbons there is an important difference which signifies non-alternants: the number of independent conjugated circuits is always smaller than the number of fused rings. We illustrate the situation on cyclohept(fg)acenaphthylene **5** with the resulting decomposition: $4R_1 + 2R_2 + 6R_3$ (Table 6). The reduction in the number of conjugated circuits is directly related to the presence of the so called essential single bonds, and more generally to constraints on the assignment of bond types imposed by the fusion of odd membered rings. For instance, bonds *cis* to central CC bond in **5** *always* have the same bond type. In other words some (degree of) freedom of assignment of bond character is lost in these systems. One can refer to such molecules as "conjugation-deficient", like perylene and zethrene, since here again conjugation is reduced in comparison with the isocyclic *alternants* having the same number of CC double bonds.

Another interesting result of the decomposition of

Table 7. Decomposition of selected non-alternant systems which have only conjugated circuits of (4n + 2) type (azulenoids). A comparison of calculated resonance energies is shown for Dewar and de Llano SCF MO method, Herndon and Ellzey resonance-structure model and here outlined graph theoretical scheme. Several SCF MO resonance energies have since been revised (Ref. 31) and are indicated by an asterisk

Compound	Decomposition	Resonance energies (eV) SCF MO	Resonance theory	This work
	Azulene $2R_2/2$	0.26	0.34	0.246
	$(4R_2 + 2R_4)/3$	0.39 0.40	0.45	0.355
	Benzazulene $(2R_1 + 2R_2 + 2R_3)/3$	0.84 0.82 0.85	0.78	0.810
	Cycloheptacenaphthylene	1.15 1.19*	1.18	1.215
	Naphthazulene $(4R_1 + 4R_2 + 4R_3)/4$	1.15 0.99*		
	Cycloheptfluorene $2R_3/2$	−0.08 0.12*	0	0.100
	Acenaphthylene $(4R_1 + 2R_2)/3$	1.34	1.35	1.323
	Pleiadene $(3R_1 + 3R_2)/3$	1.21 1.12*	1.35	1.115
	Acepleiadylene $(4R_1 + 2R_2 + 6R_3)/4$	1.45 1.52*	1.01	1.142

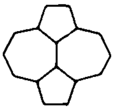
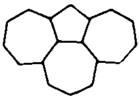
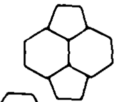
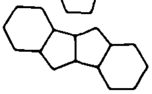
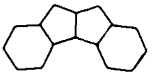
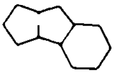
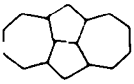
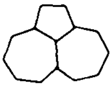
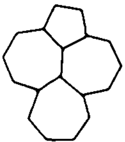
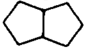
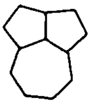
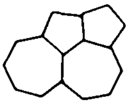
conjugation in cycloheptacenaphthylene 5 is the appearance of conjugated circuits only of (4n + 2) size. A list of other non-alternants which are also characterized by the presence of rings only of (4n + 2) size is given in Table 7. There are, however, numerous other non-alternants which contain both, (4n + 2) and 4n, types of conjugated circuits (Table 8). The situation is analogous to that found for alternant hydrocarbons where the first class correspond to benzenoid systems, while the second class, having conjugated circuits of both types, includes cyclobutadienes, cyclo-octatetraenes and other alternant non-benzenoids. So one can expect the two classes of non-alternants (Tables 7 and 8 respectively) to show considerably different properties. Hence a differentiation among the two kinds of non-alternants seems prudent and we propose to classify all non-alternants into:

(1) those having only (4n + 2) conjugated circuits;

(2) those having in addition to or instead of (4n + 2) circuits, also 4n type conjugated circuits.

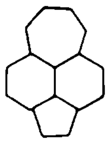
The most common representative of the first class is

Table 8. Decomposition of conjugation for selected non-alternant systems for which conjugated circuits of (4n + 2) and/or 4n type also arise (non-azulenoids). Calculated resonance energies are also shown and correspond to semi-empirical SCF MO (Dewar and de Llano, and (•) corrected values due to Dasgupta and Dasgupta) and the graph theoretical scheme here developed. The alternative graph theoretical scheme assumes all Q_n to be zero. All energies are in eV

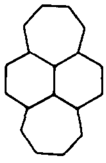
Compound	Conjugation	Resonance energies				
		SCF	Graph theoretical			
			(1)	Diff.	(2)	Diff.
	Azupyrene $(8R_2 + 2R_3 + 2Q_3)/4$	0.69 0.563•	0.475	0.088	0.524	0.021
	Azulenoheptalene $(6R_2 + 4Q_3 + 2Q_4)/4$	0.42 0.204•	0.195	0.009	0.369	-0.165
	Pyracyclene $(4R_1 + 2R_2 + 6Q_3)/4$	0.84 0.767•	0.770	−0.017	0.992	−0.225
	Dibenzpentalenes $(8R_1 + 2Q_2 + 4Q_3)/5$	1.27	1.080	0.190	1.390	−0.120
	$(4R_1 + 2Q_2 + 4Q_3 + 2Q_4)/4$	0.60	0.480	0.120	0.869	−0.269
	Benzpentalene $(2R_1 + 2Q_2 + 2Q_3)/3$	0.44	0.180	0.260	0.579	0.239
	Acepntalene $6Q_2/3$	0.30	-0.900	0.600	0	-0.300
	Dicycloheptpentalene $(8R_2 + 2R_3 + 2Q_2)/4$	0.68 0.369•	0.325	0.044	0.542	0.173
	Aceheptylene $(4R_2 + 2Q_3)/3$	0.52 0.81•	0.233	0.577	0.327	0.483
	$(4R_2 + 6Q_3 + 2Q_4)/4$	0.25	-0.005	0.30	0.246	0.004
	Pentalene $2Q_2/2$	0.01	0.450	0.46	0	0.01
	Aceazulene $(4R_2 + 2Q_2)/3$	0.56	0.033	0.527	0.327	0.233
	as-Azupyrene $(6R_2 + 2R_3 + 2Q_2 + 2Q_3)/4$	0.61 0.600•	0.125	0.475	0.419	0.181

undoubtly azulene, so that the term *azulenoids*—like benzenoids—suggests itself. The other class accordingly is refered to as *non-azulenoids*.

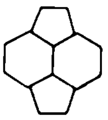
The suggested differentiation of non-alternants analogous to that of alternants was not previously recognized or even suspected. Its use is illustrated on seemingly related structures of cycloheptacenaphthylene **5**; dicycloheptanaphthalene **6**; and cyclopentacenaphthylene **7**:



5



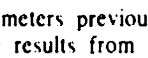
6



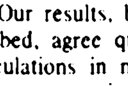
7

Until recently only **5** was known and its properties suggested the aromatic character of the system.[27] In contrast attempts to synthetize **7** have failed.[28] Bergman and Agranat[29] suspected this not to be fortuitous. Using analogies they looked upon the compounds **5**–**7** as "naphthologs" of azulene, heptalene and pentalene respectively, supporting the notion of the distinctive character of the compounds. The decomposition of these compounds in conjugated circuits (Tables 7 and 8) fully supports their view, as we see that the compounds belong to different classes of non-alternants.

From the expressions for decomposition of the conjugation into contributions from conjugated rings of different size a numerical prediction of RE follows. For selected *azulenoid* (non-alternant) hydrocarbons for the purpose of comparison also, RE as evaluated from the SCF MO method are given as well as the predictions of the Structure-Resonance model. Our results, based on the parameters previously described, agree quite well with the results from other calculations in numerous instances. A few deviations however are noticeable, including among others cycloheptfluorene, pleiadiene, and acepleiadylene. It is probably premature to speculate about the importance of other factors beyond the connectivity which may play some role (assumptions such as equal weighting of structures, and the disregard of the shape of conjugated circuits) since the prevailing agreement for RE of numerous benzenoid, non-benzenoid, and also non-alternant hydrocarbons suggests the scheme has a general validity. An influence of other factors should not however be dismissed outright, even if they are not going to remove the present discrepancies in particular cases. Their importance is reflected in situations when systems are isoconjugate (i.e. have a same circuit composition), yet the compounds show considerably different properties. For instance *s*-indacene **8** has been synthetized[30] while its asymmetrical isomer **9** is still unknown:



8



9

Both molecules have only two Kekulé structures, but while for *s*-indacene the two structures are *equivalent*, this is not the case for the asymmetrical form. So possibly not only the *size* but also the *shape* of a conjugated circuit may have an influence.

Resonance energies of non-azulenoid hydrocarbons are shown in Table 8. For a number of molecules quite good agreement with the results of the SCF MO calculation is found. However, for a number of cases the agreement is not impressive and even poor. It appears that confidence in the particular set of numerical parameters R_n and Q_n is not fully justified, particularly in view of the comparison in Fig. 1 which only demonstrates that a *linear* relation between the SCF MO and the graph theoretical results exists. It remains to be seen if another set of parameters could produce a better agreement. In particular Q_n parameters may require a re-evaluation. It may happen that the negative contributions of Q_n are exaggerated and that future investigations point to their less dramatic role.[14] Alternatively, the data in Table 8 may be used for an independent estimate of the graph theoretical parameters in a similar manner that the resonance energies of benzene, naphthalene, anthracene and tetracene were used to determine the now adopted $R_1 - R_4$ values. However, it appears that the reported SCF MO resonance energies are to some extent internally inconsistent—if we presume that the expressions for RE derived by counting conjugated circuits are valid and that the discrepancy of our predictions and those from SCF MO results are solely due to deficiency in selected numerical values for R_n and Q_n. Thus the ratio of the RE of acepentalene and pentalene is independent of a selection of Q_2 and is equal to 2. The discrepancy of the Dewar and de Llano values is too great to be ascribed to computational fluctuations. Similarly several differences in RE of the molecules in Table 8 should allow estimates of various combinations of Q_n parameters. The difference $(Q_3 - Q_2)$ can be determined from the pair of structures: azupyrene-dicycloheptpentalene and aceheptylene-aceazulene. The ratio of the respective differencies in RE is independent of Q_n and should be 3/4. The Dewar and de Llano initial results give an inconclusive answer: approx. 0/0, while the revised values of Dasgupta and Dasgupta give approx. 4/5. Part of the discrepancies in Table 8 are also due to parameters R_n involved. The values adopted for benzenoid hydrocarbons which have lead to impressive agreement for benzenoid and also for azulenoid hydrocarbons do not fully conform to requirements of SCF MO results for non-azulenoids. This can be seen by combining some of the expressions for RE so that the resulting expression does not depend on Q_n parametrization. From RE of benzpentalene and as-acepyrene one can in this way derive an estimate of $(3R_2 + R_3 - R_1)$. The graph theoretical values give for the above expression -0.31 eV, while SCF gives $+0.56$ eV, the disagreement which suggest that the currently available data is insufficient for a proper re-evaluation of the parametrization.

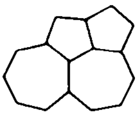
In order to illustrate a possible effect of selection of a different parameter we included in Table 8 also RE derived by assuming $Q_2 = Q_3 = Q_4 = 0$, which represents the extreme situation in which anti-aromatic contributions are negligible. We see that the above assumption improves substantially agreement in some cases, and destroy the previously obtained agreement in others. Neither of the two selections of the parameters is superior to the other—the definitive assignment has to await an accumulation of a larger body of reliable data on this kind of compound. It is true that some revised SCF calculations show better agreement with the current graph theoretical analysis.[11,12] For instance the revised

RE for dicycloheptpentalene is only 0.37 eV, which is much closer to our estimate of 0.325 eV than the originally reported value of 0.68 eV. Similarly, revised values for dicyclopentaheptalene (azupyrene), pyracyclene and dicycloheptazulene are in very good agreement with our derived magnitudes. On the other hand, in some instances the discrepancies persist and the revised values do not show better agreement (e.g. aceheptylene and aceazulene).

Few non-alternants, like pentalene, when decomposed into conjugated circuits, show only a presence of 4n rings. These "pentalenoids"[11] are expected to be of little importance in the chemistry of pi-delocalized systems in view of the negative RE and associated instability.

DISCUSSION

A qualitative examination of Kekulé forms of a system frequently may give an insight into the nature of a conjugated compound and point to differences between seemingly related structures. Thus Anderson, Masada, and Montana[15] recognized an ambivalent nature of azupyrene, while Trost and Bright considered alternative valence forms as dominant for pyracyclene.[16] Such discussions can be easily embraced by descriptions based on the concept of conjugated circuits and supplemented by a quantitative characterization. Non-alternant conjugated systems have intrigued chemists in particular in relation to the question of their aromatic character, and not infrequently opposite claims have been proposed for a particular compound. Attempts to a characterization of compounds as aromatic and non-aromatic include also several purely structural schemes, i.e. schemes based solely on the information supplied by the set of Kekulé structures of a compound, or the molecular connectivity. The most notable such schemes are those of Platt[17] and Craig.[18] Platt considered separated (4n + 2) pi-electron shells on the molecular periphery. The scheme can explain the aromatic character in some condensed benzenoid hydrocarbons (e.g. pyrene, coronene) and non-alternants such as acepleiadylene, to which the Hückel rule does not apply. Craig, on the other hand, considers symmetry properties of selected Kekulé forms, and arrives at acceptable answers in some cases, but also to ambiguities in a few instances. Both these approaches only illustrate the insufficiency of a scheme which somehow arbitrarily insists on characterizing a molecule on incomplete data. For example, pentalenoheptalene **10**, is *non-azulenoid* according to our classification, while acepleiadylene (Table 6), naphthazulene **11**, and cycloheptaacenaphthylene **12**, all isoelectronic with the former and all *azulenoid*, have the same number of peripheral pi-electrons: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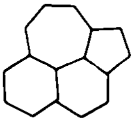
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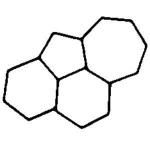

12

(for Kekulé forms of these compounds see ref. 39). The concept of conjugated circuits and the decomposition of Kekulé structures into contributions of (4n + 2) and 4n type appear to discriminate well the differences among conjugated systems. In particular this appears to be more important in non-alternants where the distinction between the two kinds of systems is less apparent. Current interest in the chemistry of non-alternants, and in particular those we have classified as *non-azulenoids*, (the field opended by Hafner and Schneider[40] in the late 1950s by synthesis of methyl derivatives of aceheptylene and aceazulene), makes our contribution timely. We hope that the approach proves useful not only for the discussion of resonance energies and stabilities but also other molecular properties. There are some indications that indeed this may be the case. Particularly relevant may be the considerations of proton magnetic resonance and ring currents in conjugated systems. Yamaguchi and Nakajima[41] considered the diamagnetic susceptibilities of a ring in compounds **5–7** and found calculated magnetic anisotropies of **5**, which is azulenoid to be positive, that for **6** and **7**, which are non-azulenoids to be negative. The question of bond fixation—a measure of the localization of the pi-electron system[42]—is another property discussed for conjugated systems. It may prove of significance that molecules **6** and **7** show a greater double bond fixation than the azulenoid **5**. To what extent this finding proves general remains to be seen, however it is plausible to expect azulenoid and non-azulenoid compounds to show a different degree of bond fixation.

The future applications of the concept of conjugated circuits may show additional examples of molecular properties that reflect the inherent presence of (4n + 2) conjugated circuits and an attenuation of their impact due to counter-contributions from 4n conjugated circuits. The recent extension of such considerations to aromaticity[5] has lead to a nice systematization of abundant data on conjugated systems and clarified ambiguities in many instances. It is shown there that in discussion of aromaticity it is useful to partition RE into contributions arising from (4n + 2) conjugated circuits and those arising from (4n) conjugated circuits. So two molecules with an approximate resonance energy may have considerably different constitution in terms of conjugated circuits and show different aromatic character, which is predominantly determined by (4n + 2) conjugated circuits only.

Relation to the Structure-Resonance model. There are two different aspects that need be considered when making a detailed comparison between the here proposed scheme for evaluation of RE and the results of the Structure-Resonance model of Herndon. As will be seen the numerical results for RE here reported could be exactly those obtained with Herndon's Structure-Resonance approach. They are different because: (1) we use somewhat different parametrization; and (2) we do not neglect terms arising from higher contributions. On the other hand the emphasis in our method is on graph-theoretical content of the problem, while Herndon developed a semi-empirical variant of VB approach, i.e. a quantum mechanical scheme. We will first discuss the differences in the numerical results and parametrization, and will provide a justification for our connotation of the importance of all contributions appearing in the expressions for RE.

Consider our decomposition of the conjugation for tetracene: $(8R_1 + 6R_2 + 4R_3 + 2R_4)/5$. If one carries the scheme of Herndon to its end one would derive the expression: $2(4\gamma_1 + 3\gamma_2 + 2\gamma_3 + \gamma_4)/5$, which obviously becomes identical on equating $\gamma_n = R_n$. In view of the relatively small magnitudes of R_3 and R_4 one may consider the inclusion of all the terms in the expression for

RE of no great consequence. However, if one is interested first in *expressions* for resonance energies, as we are here, then these additional terms are important. The neglect of higher conjugated circuits results in a lesser discrimination among conjugated systems. The concept of *isoconjugate systems* also becomes unnecessarily obscured and possibly misleading when compounds differ in the number of higher conjugated circuits. By not deriving the expressions for RE earlier analyses have been deprived of useful conclusions. For example, RE of the two naphthazulenes **11** and **12** have been reported in different calculations as follows:

Authors	Compound **11**	Compound **12**
Hess and Schaad[26]	0.52 β	0.51 β
Dewar and de Llano[25]	1.15 eV	1.15 eV
Herndon and Ellzey[15]	1.18 eV	1.18 eV

Despite the identical RE for the two isomers the significance of the result escaped attention. MO schemes, whether one is using the simple HMO or more elaborate SCF MO approach, do not provide a basis for understanding of the coincidental results. In that respect the VB model has a clear advantage, although it appears this has not been exploited in previous applications. Recognition of the conjugated circuits as elementary structural components in the current analysis adds an important conceptual factor to the Resonance-Structure model. From the expressions for RE we see that the two compounds **11** and **12** indeed have *identical* decomposition of the conjugation—so should be expected, within the validity of the correlation between the parameters R_n, Q_n, to have the same RE. It is not so unusual to find different structures having identical decomposition of the conjugation (Table 9).

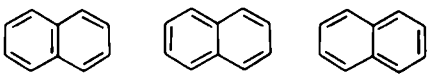
As already pointed out a neglect of higher contributions in the resonance-structure scheme does not introduce appreciable deviations for RE as compared with SCF MO results for *benzenoid systems*. However, the simplification cannot be generalized to non-benzenoids and nonalternants. Consider for example the conjugation in the following compounds:

Compound	Conjugated circuits	Resonance energies Herndon & Ellzey	 Dewar & de Llano
Acepleiadylene	$(4R_1 + 2R_2 + 6R_3)/4$	1.01 eV	1.45 eV
Pyracyclene	$(4R_1 + 2R_2 + 6Q_1)/4$	1.01 eV	0.84 eV

The difference amounts to almost 0.40 eV, which is for instance larger than the RE of azulene. Moreover, a neglect of higher contributions in this case obliterates even the differentiation of *azulenoid* and *non-azulenoid* nature of the compounds considered and may give an impression that the two compounds ought to be closely related.

In order to appreciate a conceptual difference between the resonance-structure theory and the graph theoretical approach we are now going to emphasize differences, rather than similarities of the two schemes. The resonance-structure theory developed by Herndon is a semi-empirical VB scheme, hence its language is that of VB theory and *its parameters are molecular integrals*. Subsequently Herndon and Ellzey demonstrated that VB framework is capable of providing a basis for semi-quantitative discussions of molecular properties of a same quality to that of alternative MO semi-empirical schemes.

Our scheme, as initially developed, has nothing to do with VB theory, or any eigenvalue problem and Hamiltonians. It evolved from the problem of *encoding* individual Kekulé valence structures in terms of quantities which have a structural interpretation. Here one examines molecular skeletons (connectivity) and searches for differences in kind of bonds, distribution of valencies, locations of formal double bonds, kind of rings and their fusion mode etc. A close examination of the Kekulé structures of conjugated systems revealed that such formulas also differ generally in the kind of circuits found. Some circuits show a regular alternation of the bond type having an equal number of the formally single and double CC bonds; others have an irregular sequencing of single and double bonds. A graph theoretical analysis then consists in *recognizing* distinctive circuits and proceeding with an *enumeration* of circuits of different kinds and sizes. So when we examine the three Kekulé forms of naphthalene:

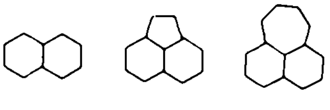
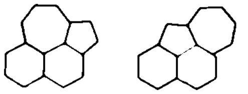
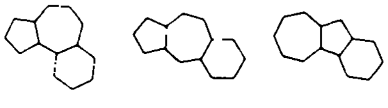
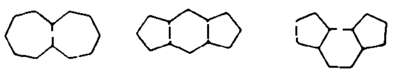
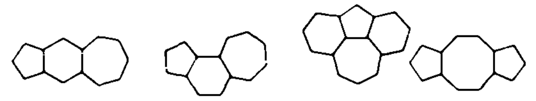
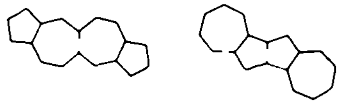


we obtain for the number of regular circuits with alternation of the CC bond type $2R_1$, and $(R_1 + R_2)$ twice, respectively. The coefficients of individual R_n terms provide a source for a *code* of an individual Kekulé form. The symbol R_n has no other hidden meaning besides the simple designation of the size of an $(4n + 2)$ conjugate circuit, i.e. it represents a purely mathematical quantity. At this point the graph theoretical analysis ends.

Chemical intuition however suggests that conjugate circuits—in contrast to circuits which do not support a regular alternation of bond type—also *may have* some deeper physical and chemical *content* and correspond to some molecular property. This however has to be examined. To pursue the possibility one has to employ an *empirical* approach. So one searches for correlations between graph theoretical quantities and experimental or theoretical results which can support the supposition of the intrinsic importance of conjugate circuits. Here one is at liberty in selecting the source. An SCF MO calculation appears to have greater flexibility in simulating experimental results than simple HMO, known to have certain limitations. Besides, such a choice will dispel a notion that the graph theory is but a disguised HMO. In our case it made the comparison with the results of Herndon and Ellzey easier, as these authors also tried to simulate the results of the same source. Notice, that once such a correlation has been established *it attributes a physical meaning to graph theoretical parameters* (R_n and Q_n). They can now be recognized as equivalent to certain molecular integrals associated with permutations of electrons among double bonds.

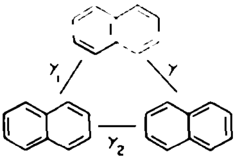
One may say that the reason that the graph theoretical

Table 9. Conjugate systems with an identical decomposition of the conjugation in circuits of (4n + 2) and/or 4n type. In few instances the molecules differ in the number of carbon atoms

	$(4R_1 + 2R_2)/3$
	$(4R_1 + 4R_2 + 4R_3)/4$
	$(2R_1 + 2R_2 + 2R_3)/3$
	$2Q_3/2$
	$2Q_4/2$
	$2R_3/2$
	$(4R_2 + 2R_4)/3$

scheme based on the concept of conjugated circuits gives sensible results is because it mimics a quantum mechanical calculations with a Kekulé structure basis. Alternatively, the surprisingly good predictions of the resonance-structure theory of Herndon and Ellzey are due to the fact that the scheme takes into account correctly the conjugation as contained in various (4n + 2) and 4n conjugated circuits. Such a view, which then points to *why* the results of the resonance-structure theory are so good, presumes that one accepts conjugated circuits as *elementary structural components*. For a conjugated hydrocarbon a set of Kekulé valence forms represents a *basis* for discussion of certain molecular properties. However, a set of conjugated circuits represents an alternative basis and the compatibility between the resonance-structure model and the graph theoretical approach to RE only shows that the two bases are equivalent. We are familiar with superpositions of valence structures and general bond additive schemes, the present work points to even more general superposition and additivity scheme—the *circuit* additivity of conjugation and RE.

An important difference between the two schemes is their formal treatment of the Kekulé valence structures. The conjugate circuits R_n and Q_n are properties associated with a *single Kekulé valence structure*. Permutational molecular integrals γ_n of the resonance-structure theory belong to a *pair of Kekulé valence structures*. Thus for naphthalene one has:[12,14]



The labels γ_n are assigned to edges of a graph constructed in which vertices correspond to the individual Kekulé structures. Graphs arise here as convenient book-keeping for multiple combinatorial possibilities. In contrast, in our scheme actual molecular graphs, representing connectivity among carbons, are examined. In deriving the expressions for RE one can hence consider *n*(*n* + 1)/2 *pairs of structures* and count permutations of CC double bonds, or consider *n structures* and count individual conjugated circuits—these appear as useful alternatives. The congruence of the two schemes is a remarkable demonstration of the combinatorial nature of VB method. One can view the two approaches, the VB scheme of Herndon and Ellzey and the graph theoretical conceptualism here exposed as being of complementary nature, which combined give an important alternative for discussion of conjugated hydrocarbons, and even more general systems, to the prevailing semi-empirical MO schemes.

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