Aromaticity and Conjugation

Milan Randić

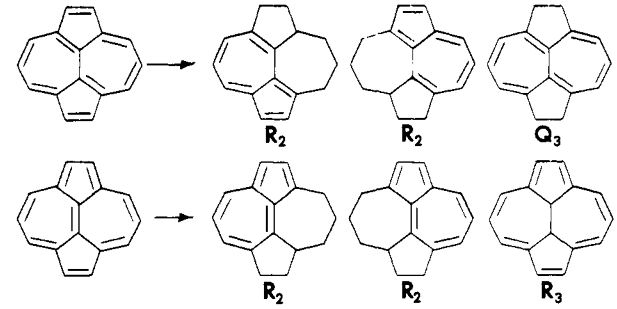
Contribution from the Energy and Mineral Resources Research Institute, Iowa State University, Ames, Iowa 50011. *Received December 4, 1975*

Abstract: A new approach to aromaticity of conjugated hydrocarbons is described. It is based on the concept of *conjugated circuits*, which has been recently recognized as an essential structural element for characterization of conjugated systems (*Chem. Phys. Lett.*, **38**, 68 (1976)). Kekulé structures of a conjugated hydrocarbon are examined and circuits with an alternation of CC double and single bonds enumerated. Systems having only $(4n + 2)$ conjugated circuits are defined as aromatic. Systems having only $4n$ conjugated circuits are considered antiaromatic, i.e., destabilized by the delocalization of π electrons. Finally, systems having both $(4n + 2)$ and $4n$ conjugated circuits are classified as intermediate, showing partial aromatic nature. The approach represents a logical generalization of the famous Hückel $(4n + 2)$ rule, valid rigorously only for monocyclic structures, to polycyclic systems. A brief comparison with several alternative schemes is given and their limitations illustrated.

Difficulties involved in attempts to characterize aromaticity are well known.[1] The simple Hückel $(4n + 2)$ rule, valid only for monocyclic systems,[2] and Platt's perimeter model,[3] an attempt to extend the rule to polycyclic systems, remain frequently used for more general situations without a proper justification and despite recognized deficiencies. This perhaps indicates an intuitive appreciation of the significance of the $(4n + 2)$ π-electron role. We present here an approach to aromaticity in which also a role of $(4n + 2)$ π electrons is dominant. However, it turns out that not the *number* of π electrons is the critical factor, but their *coupling* in conjugated circuits as derived from the Kekulé structures of the system. The approach has lead to a logical generalization of the famous Hückel $(4n + 2)$ rule, valid rigorously only for monocyclic conjugated polyenes, to polycyclic structures. In view of the acclaimed value of the Hückel rule, believed to have been one of the most successful theoretical predictions made in organic chemistry,[4] the approach of a classification of cyclic conjugated π-electron systems developed here seems to be rather interesting mainly because it encloses the polycyclic systems too.

The basis for the approach to aromaticity suggested in this work is the concept of *conjugated circuits*.[5] A polycyclic structure contains various circuits, and an individual Kekulé structure assigns a single or a double bond character to bonds in a circuit. Circuits which have an alternation of the CC single and double bonds are called conjugated circuits. They necessarily are even, and are either of a $(4n + 2)$ or $4n$ type. The notion of conjugate circuits is not so unfamiliar in chemistry; however, it has not been realized that they represent an important structural element. The analysis consists of the *enumeration* of all distinctive conjugated circuits; hence here we have a typical *graph theoretical* scheme. We illustrate the approach with azupyrene, two Kekulé structures of which are decomposed as shown in Scheme I. The remaining two structures are mirror images of the structures shown. Using the designation R_n and Q_n for conjugated circuits of type $(4n + 2)$ and $4n$, respectively, we can summarize the conjugation content of the four Kekulé forms of azupyrene by: $8R_2 + 2R_3 + 2Q_3$. This particular molecule has conjugated circuits of $(4n + 2)$ and $4n$ type.

Scheme I



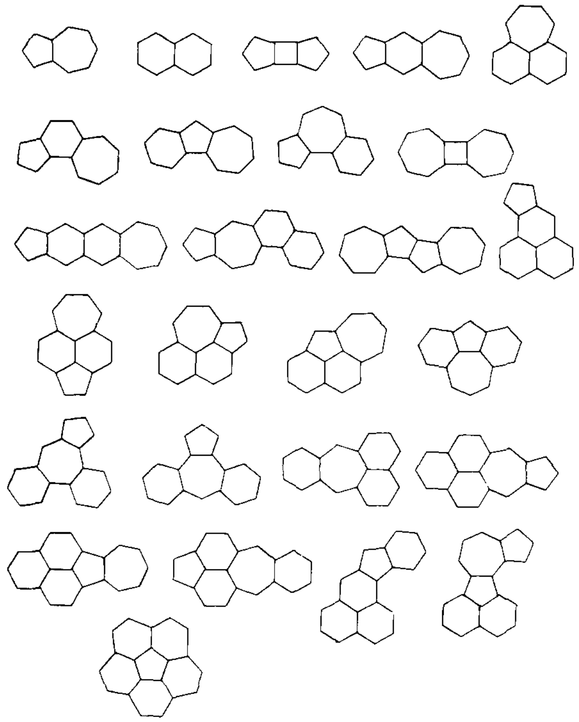
Once we recognized the conjugated circuits in a structure they provide a basis for classification of a system. This allows compounds to be grouped according to a common structural element regardless of their apparent molecular properties. Thus we find benzene and [18]annulene structurally closely related, although they have remarkably different properties.[4] In this way we resolved the difficulty of deciding which molecular property is dominant for a characterization of the elusive aromatic nature of conjugated systems, if indeed there is a single quality which can provide the basis. The strength of our approach is that enormous chemical experience with conjugated hydrocarbons agreeably parallels such a classification in which the conjugated circuits appear as important components.

The notion of circuits and their relevance to characterization of such molecular properties as resonance energy is not new. It has been realized for some time that they are an important structural element. For example, Marcus[6] considered self-returning random walks in a molecule. He finds useful additivities of heats of combustion and resonance energies of sets of conjugated compounds in which the count of closed paths coincides. By many years he anticipates some of the more recent graph theoretical schemes[6] discussing aromaticity in conjugated compounds. However, neither he nor the more recent studies discriminate between conjugated circuits and other circuits, which is the basis of our own approach. Hence, in such schemes the contributions of the conjugated circuits are obscured with interference of many other circuits devoid of conjugation, and in our view irrelevant for characterization of molecular properties associated with delocalized π-electron networks.

Aromaticity Postulate

It is commonly accepted that all benzenoid hydrocarbons are aromatic. Therefore, a good starting point is a characterization of aromaticity of benzenoid systems. A comprehensive and rigorous definition of benzenoid systems as such is, however, not trivial.[7] A formal fusion of benzene rings produces structures like triangulene, which have no Kekulé formula, or alternatively may lead to closed rings of fused benzenes as in corannulenes, for which it is not apparent whether they may be viewed as derivatives of annulenes rather than benzene. When these unusual structures are excluded from consideration a close examination of benzenoid systems reveals only the presence of conjugated circuits of $(4n + 2)$ size.[5] *It seems, therefore, that aromaticity and conjugated $(4n + 2)$ type circuits are equally typical of benzenoid systems and the association may be more fundamental.* It has already been found

Table I. Fully Aromatic Systems Containing Only (4n + 2) Conjugated Circuits



that conjugated circuits discriminate among nonalternants, which can be classified as *azulenoid* and *nonazulenoid*, depending on the presence of only (4n + 2) conjugated circuits, such as in azulene, or a presence of conjugated circuits of (4n + 2) and 4n type.[5] A superficial examination of the two nonalternant groups only strengthens an intuitive recognition that systems having (4n + 2) conjugated circuits have more pronounced aromatic characteristics. Hence, it is the *conjugation,* not the *number,* of π electrons which seems to be the essential structural element. So we are led to propose an *Aromaticity Postulate:* "Systems which possess only (4n + 2) conjugated circuits are aromatic."

The postulate proclaims a system as *aromatic* or *not aromatic.* Hence, properties of those compounds which are classified as aromatic should be taken as representative manifestations of aromaticity. Such an approach does not single out one property as dominant, and permits variations known to exist between aromatic systems. Notice that *not aromatic* compounds could (and many do) have similar properties to aromatic systems. The postulate only implies that properties of not aromatic conjugated systems should not be a *standard* for discussion of aromaticity. The approach leaves out any reference to a relative aromatic nature and only establishes whether or not a compound is qualified to be labeled *aromatic.* For a discussion of relative qualities of compounds already classified as aromatic, some of the available aromaticity indices may prove useful.[1,8]

Since aromaticity has been closely linked to the Hückel rule it is useful to generalize the rule so that it comprises all systems which are postulated aromatic. Hence we propose a *generalized Hückel rule:* "Conjugated systems having *only* (4n + 2) conjugated circuits in their Kekulé valence structures provide a generalization of Hückel systems for polycyclic structures."

Such a formulation leaves a close parallelism between the Hückel rule and aromaticity, which is desirable from a historical point of view. Table I shows systems which qualify as aromatic. Important structural differences are to be noticed. In particular it can be seen that the aromaticity postulate does not discriminate between alternants and nonalternants. So we find azulene, besides naphthalene, as a representative aromatic system, in full agreement with chemical experience. Many of the compounds in Table I are azulene derivatives, but in addition there are other molecules of diverse constitutional forms. It is of some interest to find among aromatic compounds the cyclohepta[*def*]fluorene for which MO calculations, which included electron-electron interaction, indicated that it has either a triplet ground state or a low lying thermally excitable triplet state.[9] Attempts to prepare this molecule have been until now without success.[10] This molecule and few others, like acenaphthylene, are characterized by the presence of an essential CC double bond (the central CC bond), which then does not participate in the conjugation with the rest of the molecule. As far as our analysis goes we cannot differentiate this system from a 14π-electron annulene and an isolated CC double bond. Similarly, perylene conjugation shows that here we have two naphthalene parts separated by essentially single bonds. Effect of pertubation of two conjugated fragments is beyond the scope of the present scheme, but in contrast to the theoretical approach to cyclohepta[*def*]fluorene the consideration of conjugated circuits would suggest a partitioning of the molecule into a 14π-electron perimeter and a central CC double bond as a more natural basis for a pertubation treatment than considering the resulting alternant biradical derived by suppressing the coupling of central π electrons, although the latter is useful for correlating suspected triplet ground states of the two systems.

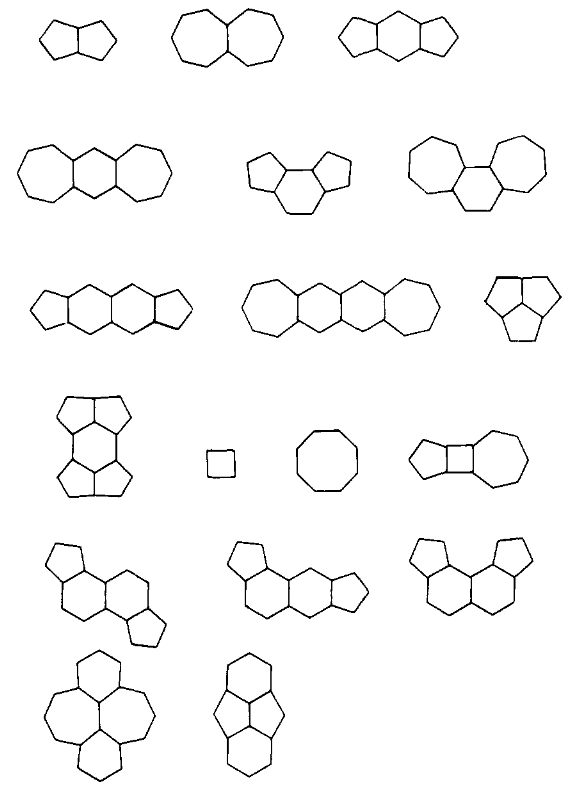
The aromaticity postulate and the Hückel rule can now be extended to situations when *only* 4n conjugated circuits are present: "Systems having only 4n conjugate circuits are antiaromatic and represent generalized Hückel 4n systems."

Such systems are expected to take one of the possible polyolefinic forms. Hence, molecules like pentalene, heptalene, and *s*-indacene, as well as cyclobutadiene accordingly are expected to appear in a less symmetrical geometry characterized by a marked alternation of bond lengths. Examples of antiaromatic systems are shown in Table II.

Systems Which Contain (4*n* + 2) and 4*n* Conjugated Circuits

A large number of conjugated hydrocarbons contain both (4n + 2) and 4n conjugated circuits. Such molecules represent an *intermediate* class of compounds. Their aromatic features, associated with the (4n + 2) conjugation, will be attenuated by the contributions of an antiaromatic nature arising from 4n conjugated circuits. Contradictory assertions regarding their aromatic nature have been made for a number of these molecules. In such situations one should speak of a *partial* aromatic character. The relative magnitudes of aromatic and antiaromatic conjugation will determine the overall molecular properties. Here it is important to have a *measure* of the two distinctive *kinds* of contributions of an opposing nature. For estimating the relative contributions we suggest a partition of the resonance energy (RE) into parts associated with (4n + 2) and 4n conjugated circuits, respectively. Here we face a problem of arriving at a relationship between the graph theoretical parameters, which only signify the number of circuits of various size, and a quantum chemical concept of resonance energy, which is a result of certain approximate quantum mechanical calculations. One proceeds by searching for a *correlation* between the two quantities, and as has been shown[5] a normalized expression for conjugated circuits, obtained by dividing the total decomposition of the conjugation in various contributions of (4n + 2) and 4n type by the number of Kekulé valence formulas of the system, correlates quite well with theoretical RE's. One can view the normalized expressions for conjugation as expressions for the resonance energy of the

Table II. Fully Antiaromatic Systems Having Only $4n$ Conjugated Circuits in Their Kekulé Valence Structures



systems and by selecting some standard molecules derive the numerical contributions to the RE from conjugated circuits of different size. We have adopted[5] benzene, naphthalene, anthracene, and tetracene as standards and used SCF MO calculated resonance energies[11] to fix the values for the parameters R_n and Q_n:

$$\text{benzene} \quad (2R_1)/2 = 0.869 \text{ eV}$$

$$\text{naphthalene} \quad (4R_1 + 2R_2)/3 = 1.323 \text{ eV}$$

$$\text{anthracene} \quad (6R_1 + 4R_2 + 2R_3)/4 = 1.600 \text{ eV}$$

$$\text{tetracene} \quad (8R_1 + 6R_2 + 4R_3 + 2R_4)/5 = 1.822 \text{ eV}$$

One can now formally solve the above system of linear equations and obtain the following numerical values for the graph theoretical parameters R_n: $R_1 = 0.869$; $R_2 = 0.246$; $R_3 = 0.100$; and $R_4 = 0.041$ eV. The corresponding values for parameters characterizing contributions arising from $4n$ conjugated circuits can be derived, except for a sign, from a plot of R_n against circuit size[5] following similar considerations of π-electron energetics of [n]annulenes.[12] The following values were derived:[5] $Q_1 = -1.60$; $Q_2 = -0.45$; $Q_3 = -0.15$; and $Q_4 = -0.06$ eV. In this way the symbols R_n and Q_n, which were introduced as *designations* for conjugated circuits, i.e., purely mathematical quantities, become quantities with a dimension (eV) and have attributed some numerical values. A comparison between the present approach to conjugation and resonance structure theory of Herndon,[13] which is a semiempirical variant of the VB method, shows furthermore that the parameters R_n and Q_n simply correspond to certain molecular integrals originating from definite permutations of π electrons within circuits of the corresponding size. Hence the current scheme has a close relationship with the particular VB method and is capable of simulating a quantum mechanical calculation with a Kekulé structure basis. Alternatively, one may say that the reason that the semiempirical structure resonance scheme gives sensible results is because it properly accounts for the presence of intrinsic conjugated circuits—in a similar way that the basis for the success of the HMO method is its correct account of the connectivity of the conjugated system as defined by the adjacency matrix.

We return now to the question of an estimate of the relative contributions of $(4n + 2)$ and $4n$ conjugated circuits to the resonance energy of the system. Let symbol RE$(4n + 2)$ and RE$(4n)$ represent a summation of all contributions of conjugated circuits of a same type, respectively. The total RE is then given as: RE = RE$(4n + 2)$ + RE$(4n)$. For example, in the case of azupyrene we have:

$$\mathrm{RE} = (8R_2 + 2R_3 + 2Q_3)/4 = 0.467 \text{ eV}$$

$$\mathrm{RE}(4n + 2) = (8R_2 + 2R_3)/4 = 0.542 \text{ eV}$$

$$\mathrm{RE}(4n) = (2Q_3)/4 = -0.075 \text{ eV}$$

The quantities RE$(4n + 2)$ and RE$(4n)$ reflect the relative role of the opposing tendencies, which we can associate with aromatic and antiaromatic nature of the compound. As a convenient measure of the two competing contributions we take:

$$A = [\mathrm{RE}(4n + 2) + \mathrm{RE}(4n\}]/[\mathrm{RE}(4n + 2) - \mathrm{RE}(4n)]$$

i.e., RE/(RE$(4n + 2)$ − RE$(4n)$), in which both RE$(4n + 2)$ and RE$(4n)$ appear symmetrically. Notice that for the particular parametrization of R_n and Q_n which we adopted RE$(4n + 2)$ is always positive and RE$(4n)$ is always negative. The reciprocal of A gives the difference between the relative contributions of $(4n + 2)$ and $4n$ conjugated circuits (normalized to the total RE), but the A is a more suitable index as it avoids singularities associated with RE approaching zero. The particular index attributes positive fractions to conjugated molecules having positive RE (i.e., stabilized by delocalization), while negative fractions belong to systems where $4n$ contributions prevail. Extremes 1 and −1 correspond to fully aromatic and fully antiaromatic systems. The scale conveniently allows the results to be read as percentages.

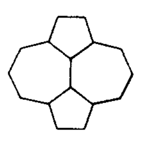
In many cases one can determine the sign of A, i.e., whether the aromatic or antiaromatic nature will prevail, *without* numerical calculations and a need for adoption of a particular numerical set of parameters for R_n and Q_n. It is generally accepted that RE contributions in annulenes decrease in absolute magnitude with ring size[12]

$$\mathrm{RE}(R_n) > \mathrm{RE}(R_{n+1}) \quad \text{and} \quad \mathrm{RE}(Q_n) < \mathrm{RE}(Q_{n+1})$$

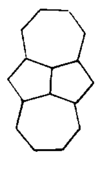
and

$$|\mathrm{RE}(Q_n)| > |\mathrm{RE}(R_n)| > |\mathrm{RE}(Q_{n+1})| > |\mathrm{RE}(R_{n+1})|$$

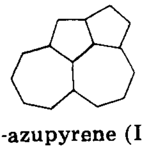
With the above general assumptions and decomposition of the conjugation into various R_n and Q_n circuits it is frequently possible to determine the relative RE among related structures, and hence deduce the relative order of aromaticity. We illustrate the situation on selected pyrene isomers shown below



azupyrene (I)
$(8R_2 + 2R_3 + 2Q_3)/4$



dicyclohepta[*cd*, *gh*]pentalene (II)
$(8R_2 + 2R_3 + 2Q_2)/4$



as-azupyrene (III)
$(6R_2 + 2R_3 + 2Q_2 + 2Q_3)/4$

Table III. Conjugated Systems Having Both (4*n* + 2) and 4*n* Conjugated Circuits: Cyclobutadiene Containing Alternants with a Prevalent (4*n* + 2) Conjugation

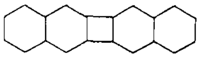
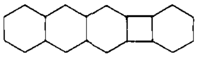
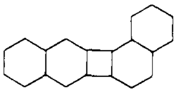
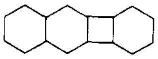
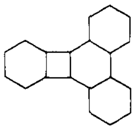
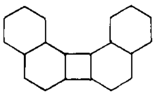
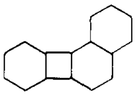
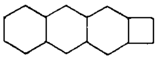
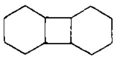
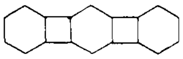
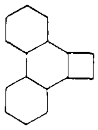
	RE, eV	RE(4*n* + 2), eV	RE(4*n*), eV	% *A*
	1.800	2.381	−0.587	60.6
	1.569	2.194	−0.625	55.6
	1.407	2.322	−0.914	43.5
	1.220	1.878	−0.658	48.1
	1.341	2.513	−1.272	35.4
	1.047	2.366	−1.319	28.4
	0.968	2.165	−1.197	22.3
	0.376	1.280	−0.904	17.2
	0.360	1.390	−1.030	14.9
	0.357	2.073	−1.716	9.4
	0.296	1.858	−1.562	8.6

Table IV. Conjugated Systems Having Both (4*n* + 2) and 4*n* Conjugated Circuits: Cyclobutadiene Containing Alternants with a Prevalent Antiaromatic 4*n* Conjugation

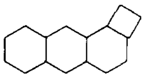
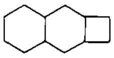
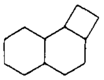
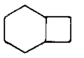
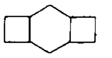
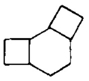
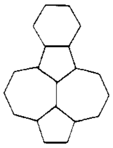
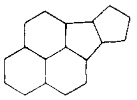
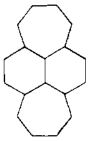
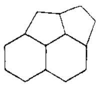
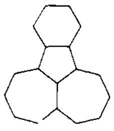
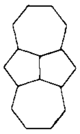
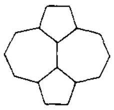
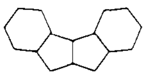
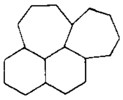
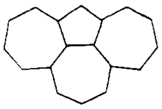
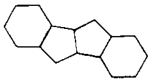
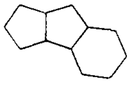
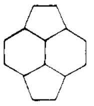
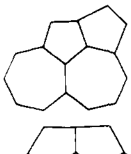
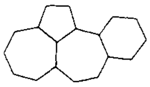
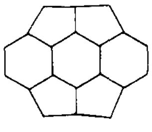
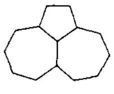
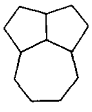
	RE, eV	RE(4*n* + 2), eV	RE(4*n*), eV	% AA
	−0.050	1.480	−1.530	1.7
	−0.108	0.992	−1.100	5.2
	−0.349	1.141	−1.490	13.3
	−0.787	0.579	−1.366	40.5
	−1.343	0.557	−1.900	54.6
	−2.524	0.396	−2.920	76.1

Table V. Conjugated Systems Having Both (4*n* + 2) and 4*n* Conjugated Circuits: Nonalternants with Prevailing Contributions from Aromatic (4*n* + 2) Conjugation

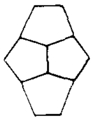
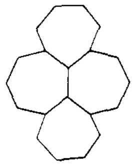
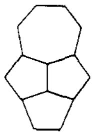
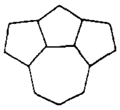
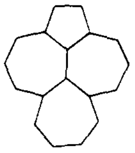
	1.127 86.9%		0.883 50.0%
	0.902 83.4%		0.640 47.6%
	0.832 77.6%		0.325 43.9%
	0.467 75.7%		0.480 36.5%
	0.835 72.6%		0.195 34.5%
	1.080 63.6%		0.180 18.3%
	0.767 63.0%		0.125 16.6%
	0.770 61.6%		0.148 4.6%
	0.228 53.1%		0.028 4.2%

together with the decomposition of the conjugation. The difference between I and II arises from a change in size of antiaromatic circuits, I being more aromatic, having larger 4*n* circuits which are less effective in screening the dominant aromatic components. The difference between II and III arises not only due to an increase in antiaromatic contributions, but also by a decrease in the dominant aromatic content. So without numerical information we deduce for relative resonance energies and a relative aromaticity: azupyrene > dicyclohepta[*cd*,*gh*]pentalene > *as*-azupyrene. The particular numerical values for R_n and Q_n adopted in ref 5 give for RE and *A* the following values: 0.475, 0.325, 0.125 eV; and 75.7, 43.9, 16.6%, respectively.

A considerable degree of aromaticity of azupyrene was attested,[14] based on the similarity of spectral data to that of *azulene* and *pyrene*. Such qualitative characterizations are supported with the quantitative approach advocated here. Notice also that azulene and pyrene remain valid aromatic standards in our scheme. A methyl derivative of *as*-azupyrene has also been synthetized some time ago and found stable and "deserving the designation aromatic".[15,16] The apparently elusive isomer, until recently not available,[16] is expected to show intermediate stability; hence the difficulty of synthesis does not necessarily point to a lack of aromatic character.

A selection of conjugated systems belonging to the intermediate class, i.e., possessing both conjugated circuits of (4*n* + 2) and 4*n* type, is shown in Tables III–VI. The partitioning of the resonance energy, the corresponding RE, and associated aromatic character *A* shown are based on the numerical pa-

Table VI. Conjugated Systems Having Both $(4n+2)$ and $4n$ Conjugated Circuits: Nonalternants with Dominating Antiaromatic Conjugation Associated with $4n$ Conjugated Circuits

	−1.075 91.5%	$(2R_3 + 10Q_2)/4$
	−0.325 76.5%	$(2R_4 + 10Q_3)/4$
	−0.505 50.6%	$(4R_2 + 6Q_2 + 2Q_3)/4$
	−0.155 17.3%	$(6R_2 + 4Q_2 + 2Q_3)/4$
	−0.005 2.0%	$(4R_2 + 6Q_3 + 2Q_4)/4$

rameters of ref 5. For many of the molecules shown the decomposition of the conjugation in $(4n + 2)$ and $4n$ circuits will be found in ref 5. From the available decomposition of the conjugation A is easily derived by making a quotient and changing the sign of the negative contribution in the denominator. For example, the explicit expression for azupyrene becomes

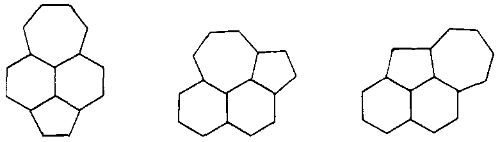
$$A = (8R_2 + 2R_3 + 2Q_3)/(8R_2 + 2R_3 - 2Q_3) = 0.757 \text{ or } 75.5\%$$

Other theoretical and experimental sources could equally be employed for determining the values for the parameters R_n and Q_n. This will somewhat change the present numerical values for the aromaticity index. One does not, however, expect that the relative magnitudes will be strongly affected in such reconsiderations.

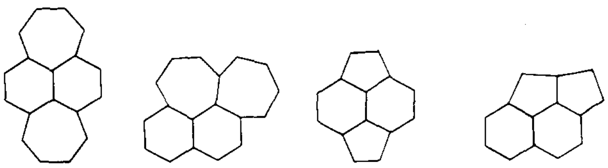
Intermediate aromatic systems all have an aromatic and an antiaromatic component. Hence, *all* such molecules will possess some aromatic quality. A more practical use of the adjective *aromatic* is to associate with it a particular threshold of intensity following from the presence of the $(4n + 2)$ conjugated circuits. The zero on our scale appears at such a convenient reference point: positive A values indicate a predominant aromatic character, negative A values (or a symbol AA for *a*nti*a*romatic) show greater similarity with olefinic compounds. In view of the limitations of any numerical scheme, one may allow some latitude of A values close to zero (positive and negative) and consider such compounds as *nonaromatic*, i.e., neither aromatic nor antiaromatic.

It is instructive to compare different compounds among themselves and include in such considerations the corresponding decomposition of the conjugation. For instance several nonalternants show quite a high aromaticity index, which is not the case with cyclobutadiene containing compounds of Table III. This is primarily due to the absence of small $4n$ conjugated circuits in the former, in particular, absence of Q_1 contributions. A close comparison of the information in Tables III–VI also shows that the aromaticity index does not necessarily parallel RE. For instance, one can compare pyracyclene and azupyrene; the RE of the former is almost twice as large as that of the latter,[17] but both are of comparable aromatic content as measured by A, pyracyclene being less aromatic. The lack of benzene-like conjugation (R_1 circuits) in azupyrene leaves the system relatively poor in RE. In contrast the naphthalene nucleus in pyracyclene supplies the system with considerable RE. On the other hand the contributions of antiaromatic Q_3 circuits are larger for the latter, leaving pyracyclene significantly less aromatic.

One can compare several compounds having a common aromatic component and follow a decrease in the aromatic nature as the number of aromatic conjugated circuits decrease and the number of antiaromatic conjugated circuits grows. Formally the common nucleus is perturbed by additional conjugated circuits; eventually the role of $4n$ antiaromatic circuits becomes more and more apparent. For instance, in the example shown the common nucleus is $(4R_1 + 2R_2)$ (i.e., naphthalene) and the variable additional component is indicated. Notice that the decomposition of the conjugation allows in this example to establish the relative aromaticity without actually using the numerical values for R_n and Q_n, except for the general assumption on the trends involved. (The number of Kekulé structures is the same for all the molecules and was ignored.)



$6R_3 \quad > \quad 4R_3 \quad = \quad 4R_3$



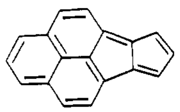
$> \; 6Q_4 \; > \; 3Q_3 + 3Q_4 \; > \; + 6Q_3 \; > \; 2Q_2 + 3Q_3 + Q_4$

Comparison with Other Aromaticity Criteria

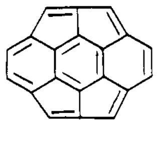
We will confine the discussion to comparisons of our predictions with selected approaches in the literature and will consider only those aromaticity criteria which are of *structural* origin, i.e., based on structural information on the system, such as the number of π electrons, number of rings and their size, number of Kekulé valence forms, parity of Kekulé structures, and generally on *molecular connectivity* and quantities derived from such information. Such a comparison is more meaningful, since all such approaches have the same structural information on a disposal. Schemes which use molecular properties, such as bond lengths, ring currents, specific reactivity, etc., for the basis of characterization of aromaticity need also to be closely examined, but the different nature of such comparisons is better left for a separate study.

Besides the Hückel rule, which strictly applies to monocyclic polyenes, several attempts to characterize the aromaticity solely from the structural information have been presented in the literature. In particular we will discuss the following: (1) scheme of Platt,[3] which employs π-electron periphery and makes an emphasis on the *number* of electrons; (2) scheme of Volpin,[18] which attempts to characterize cata-condensed fused rings, again using the *number* of electrons as a critical factor; and (3) scheme of Craig,[19] who considers *symmetry* properties of MO and VB approximated descriptions of conjugated π systems. These schemes in many instances provide a useful indication of the aromatic nature of a molecule. However, despite some success one is disturbed with failures in other instances when the predictions are in an apparent contradiction with chemical experience. This strongly suggests that they embrace *some* of the structural features responsible for aromaticity, but *fail* to recognize the essential factor. As we have seen, *conjugated circuits* represent the crucial structural component for discussion of aromaticity. The prime purpose of the following discussion is not to refute the above-mentioned structural aromatic criteria, the limitations of which have been generally recognized; rather we are interested in illuminating the role of various structural elements contained in these approaches and show some parallelism or lack of similarity with the criteria advocated here.

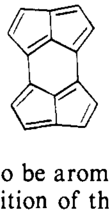
In Platt's approach the molecular periphery and the number of π electrons, rather than conjugation, are emphasized. Such a scheme improperly assigns the decisive role to the *largest* (or one of the largest) circuits, while the current approach suggests just the opposite. That Platt's model in numerous instances makes correct predictions is due to some parallelism among the number of circuits of different sizes. However, neglect of the important smaller conjugated circuits does lead to errors in Platt's scheme in some situations. Thus pentalenophenalene, with a 16π-electron periphery, is predicted nonaromatic according to Platt's criterion.



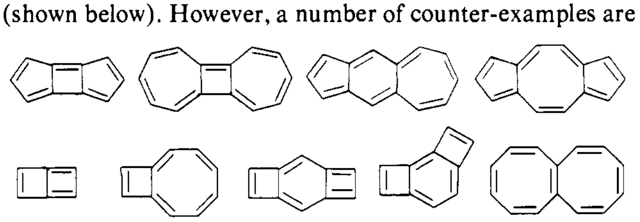
The decomposition of its conjugation, however, gives: $(8R_1 + 4R_2 + 4Q_2 + 4Q_3)$ and is classified as intermediate. Moreover, *any plausible* assumption on the relative magnitudes of the parameters R_n and Q_n will predict a *positive* RE, hence a prevailing aromatic character. The numerical parameters of ref 5 give: RE = 0.883 eV; and A = 50.1%. Although the large circuits are not crucial in dictating the molecular properties associated with aromaticity, their role should not be neglected. In some cases the larger conjugated circuits make a major contribution to the resonance energy. For example, for coranene the expression for RE is: $(8R_1 + 4R_2 + 6R_3 + 8Q_2 + 28Q_3)/9$. The negative contributions of Q_3 circuits reduce RE to a low value and resulting small aromaticity (A = 4.6%).



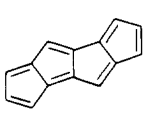
Another example where Platt's model disagrees with our prediction is shown below. The system has a 14π-electron periphery, hence expected to be aromatic according to Platt's approach. The decomposition of the conjugation, however, reveals only $4n$ conjugated circuits, suggesting a fully antiaromatic compound.



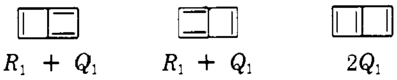
Volpin considered a less general family of cata-condensed conjugated systems which may be prone to some structural characterization. He suggested a generalization of the Hückel rule as follows: "A system will be aromatic if the *number* of π electrons in it equals $4n + 2$." Since in cata-condensed systems all electrons are on the molecular periphery, the above may be viewed as a special case of Platt's criterion. On the other hand such systems may be viewed as bridged annulenes and if they fulfill the Hückel rule, it was thought to have no eigenvalue equal to zero in the HMO scheme, and hence have a close shell structure typical of aromatic systems. According to Volpin the following are examples of aromatic systems (shown below).



However, a number of counter-examples are known of cata-condensed rings with $(4n + 2)$ π electrons which possess nonbonding MO's within the Hückel method and hence cannot be aromatic. An example is shown below.[20]

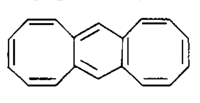


The limitations of such extensions of the Hückel rule have been recognized[21] and procedures for testing whether a system (including nonbranched cata-condensed hydrocarbons as a special case) possesses nonbonding levels developed.[22] Our analysis of the above shown examples points to *two* distinctive groups: (1) The conjugation in each molecule in the first group (the first row) involves only $(4n + 2)$ conjugated circuits; and (2) The conjugation in molecules of the second group (the second row) give rise also to $4n$ conjugated circuits. These compounds then classify as *intermediate* in our scheme and the degree of aromaticity will depend on the relative magnitudes of the opposing contributions. This second group includes fused-ring systems with two $4n$ π-electron rings which have overall $(4n + 2)$ π electrons. Among conjugated fused-ring systems these are particularly interesting, and received some attention, in particular: octalene,[23] cyclooctatetraenocyclobutadiene,[24] and the elusive transient butalene.[25] The question of whether they reflect the instability of their component antiaromatic rings or the stability of their overall $(4n + 2)$ π electrons has been the subject of several experimental and theoretical studies.[26] The problem is simply resolved in our approach by examining the relative contributions of the two antagonistic tendencies. For example, in butalene the decomposition of the conjugation gives that shown below, giving for RE = $(2R_1 + 4Q_1)/3$ and pointing to a strong antiaromatic character of the system (AA = 57.6%).



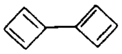
Octalene similarly shows a larger number of antiaromatic conjugated circuits, which in absolute magnitudes make a greater contribution than aromatic conjugated circuits, so that one may conclude that in such systems composed of the fusion of two $4n$ fused rings the antiaromatic conjugation will prevail.

Since most of the compounds used in the discussion of aromaticity of cata-fused systems are somewhat exotic, with the exception of octalene, already shown *not* to be aromatic,[23] another example of a failure of Volpin's $(4n + 2)$ π-electron criterion for cata-condensed systems is provided by dicycloocta[*a,d*]benzene. The four Kekulé structures give for the decomposition of the conjugation: $(2R_1 + 2R_4 + 4Q_2 + 4Q_3)$.



The numerical data suggest that here contributions from antiaromatic $4n$ conjugated circuits prevail, giving for RE = −0.145 eV, and the corresponding antiaromatic index is AA = 13.7%. The conclusion is in full agreement with experiment: the compound is found nonplanar and unrelated to aromatic [18]annulene.[27] A deficiency of the fusion criterion of Volpin, however, is also evident from omission of some aromatic systems which happen to have $4n$ π electrons, an example being biphenylene.

Finally, Craig proposed as a basis for a fundamental distinction among conjugated hydrocarbons symmetry properties associated with MO and VB descriptions of such systems. Such considerations have led to simple rules for determining the aromatic type, and the scheme had some support in the past. It properly distinguishes between benzenoid systems and molecules like pentalene and heptalene. But besides its restrictions to systems possessing a relevant symmetry property it is known that the approach does not always work. In some instances it leads to ambiguities arising from a dependence of the result on the selected Kekulé structure for the molecule. In other examples it gives predictions which are difficult to accept. For instance, according to Craig's rule the molecule shown below should be aromatic.[28] The system is related to cyclobutadiene as is biphenyl related to benzene. A parallelism then suggests that the above structure should not essentially differ from cyclobutadiene, a model antiaromatic molecule. Our scheme attributes to the above system the same conjugation as in two isolated cyclobutadienes. Another example of an incorrect prediction of Craig's rule is octalene,[19] which is not aromatic as the rule implicates. The decomposition of the conjugation in octalene gives $(2R_3 + 4Q_2)$, hence, irrespective of the details of adopted parametrization it points to a dominant role of the $4n$ conjugation.



Concluding Remarks

Conjugated circuits, which form the basis for the outlined discussion of aromaticity, a purely mathematical concept derived from molecular graphs and their decomposition offer a foundation for classification of structures in groups with some common inherent structural features. That selected molecular properties parallel the same classification only reflects their combinatorial origin describable by the same constitutional elements. For a long time bond additivity of various molecular properties has been recognized, but now we see that when resonance energy and aromaticity are considered, a more general additivity scheme—that of additivity of conjugated circuits—appears important. Intuitively one expects that among the multitude of possible circuits contained in conjugated polycyclic structure circuits with an alternation of formally CC single and double bonds may play a special role, and the present work supports such expectations. Fully aromatic and antiaromatic systems as introduced here represent a simple and a logical generalization of the famous Hückel rule to polycyclic compounds. Difficulties with other systems with pronounced ambivalent nature are nicely resolved by realizing their dual character and attempting to dissociate stabilizing and destabilizing contributions. The suggested measure of the partial aromatic character does not necessarily parallel the relative magnitudes of RE. Rather than stability, it measures the degree to which delocalization (stabilizing) contributions are diminished by contributions of an opposing nature, which favor a localized π-electron model. The distinction is important and hopefully the proposed scheme approaches closely what intuitively has been associated with aromaticity of conjugated systems.

The approach also shows that Kekulé forms contain more information than we have credited them with in the past. Hence a neglect of Kekulé forms and valence structure arguments, be it wholly qualitative or semiquantitative, to planar conjugated systems appears unjustified. We anticipate a return of Kekulé forms in everyday chemical language. A revival of interest in VB calculations and a recent development of a semiempirical resonance theory[13,29] are encouraging signs of a trend toward a full recognition of the role of Kekulé structures in chemistry.

References and Notes

(1) I. Agranat, *MTP Int. Rev. Sci.: Org. Chem., Ser. One*, **3**, Chapter 5 (1973).

(2) E. Hückel, *Z. Phys.*, **70**, 204 (1931); **72**, 310 (1931).

(3) J. R. Platt, *J. Chem. Phys.*, **22**, 144 (1954).

(4) F. Sondheimer, *Chimia*, **28**, 163 (1974).

(5) M. Randić, *Chem. Phys. Lett.*, **38**, 68 (1976); *Tetrahedron*, submitted for publication.

(6) R. A. Marcus, *J. Chem. Phys.*, **43**, 2643 (1965); H. Hosoya, K. Hosoi, and I. Gutman, *Theor. Chim. Acta*, **38**, 37 (1975); I. Gutman, M. Milun, and N. Trinajstić, *Croat. Chem. Acta*, **48**, 87 (1976); J.-i Aihara, *J. Am. Chem. Soc.*, **98**, 2750 (1976).

(7) D. Cvetković, I. Gutman, and N. Trinajstić, *J. Chem. Phys.*, **61**, 2700 (1974).

(8) For a review see: J. Kruszewski and T. M. Krygowski, *Acta Chim. Soc. Sci. Lodz.*, **18**, 165 (1973).

(9) P. Baumgartner, E. Weltin, G. Wagniere, and E. Heilbronner, *Helv. Chim. Acta*, **48**, 751 (1965).

(10) K. Hafner (Darmstadt), private communication (1975).

(11) M. J. S. Dewar and C. de Llano, *J. Am. Chem. Soc.*, **91**, 789 (1969).

(12) H. P. Figey, *Tetrahedron*, **26**, 5225 (1970); T. M. Krygowski, *Tetrahedron Lett.*, 1311 (1970); I. Gutman, M. Milun, and N. Trinajstić, *Croat. Chem. Acta*, **44**, 207 (1972); J.-i. Aihara, *Bull. Chem. Soc. Jpn.*, **48**, 517 (1975).

(13) W. C. Herndon, *J. Am. Chem. Soc.*, **95**, 2404 (1973).

(14) A. G. Anderson Jr., G. M. Masada, and A. F. Montana, *J. Org. Chem.*, **38**, 1439 (1973).

(15) K. Hafner, R. Fleischer, and K. Fritz, *Angew. Chem.*, 77, 42 (1965).

(16) H. Reel and E. Vogel, *Angew. Chem.*, **84**, 1064 (1972).

(17) There are some differences in calculated RE for these molecules among different authors. We based the estimate on our own parametrization of R_n and Q_n.

(18) M. E. Volpin, *Russ. Chem. Rev.*, **29**, 129 (1960).

(19) D. P. Craig, *J. Chem. Soc.*, 3175 (1951); *Theor. Org. Chem., Pap. Kekule Symp.*, 25 (1959).

(20) D. A. Bochvar, I. V. Stankevich, and A. V. Tutkevich, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1185 (1969); C. F. Wilcox, Jr., *J. Am. Chem. Soc.*, **91**, 2732 (1969).

(21) A. T. Balaban, *Rev. Roum. Chim.*, **15**, 1251 (1970).

(22) A. T. Balaban, *Rev. Roum. Chim.*, **17**, 1531 (1972); D. Cvetković, I. Gutman, and N. Trinajstić, *Theor. Chim. Acta*, **34**, 129 (1974); *Croat. Chem. Acta*, **44**, 365 (1972); T. Živković, *Croat. Chem. Acta*, **44**, 351 (1972); M. Randić, *Theor. Chim. Acta*, in press.

(23) R. Breslow, W. Horspool, H. Sugiyama, and W. Vitale, *J. Am. Chem. Soc.*, **88**, 3677 (1966); N. L. Allinger and C. Gilardeau, *Tetrahedron*, **23**, 1573 (1967).

(24) G. Schröder and H. Röttele, *Angew. Chem., Int. Ed. Engl.*, 7, 635 (1968).

(25) Efforts for synthesis have been undertaken in few laboratories, e.g., R. Breslow (Columbia University, New York), private communication; J. Clardy (Iowa State University, Ames), private communication.

(26) R. Breslow, *Acc. Chem. Res.*, **6**, 393 (1973); R. G. Bergman, *ibid.*, **6**, 25 (1973); R. Breslow, J. Napierski, and T. C. Clarke, *J. Am. Chem. Soc.*, **97**, 6275 (1975).

(27) J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Am. Chem. Soc.*, **92**, 962, 969, 973 (1970).

(28) R. Zahradnik and P. Čársky, "Organic Quantum Chemistry Problems", Plenum Publishing Co., New York, N.Y., 1972.

(29) W. C. Herndon and M. L. Ellzey, Jr., *J. Am. Chem. Soc.*, **96**, 6631 (1974).