was then evaporated and the residue was washed with pentane and filtered. The solid was dissolved in ethyl ether and the solution was filtered. Concentration of the filtrate followed by cooling gave 1.2 g (49%) of dark red crystals of the metallocycle **22**.

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Kekulé Index for Valence Bond Structures of Conjugated Polycyclic Systems[1a]

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Abstract: Individual formal valence structures of conjugated hydrocarbon systems have been characterized by an index K, called the Kekulé index, which relates a given set of molecular orbitals to orbitals localized on pairs of adjacent carbons. The localized orbitals can be associated with valence bond structures in a simple and unique way. It is then shown that for systems built from condensed benzene rings the valence structure with the largest values of the Kedulé index corresponds to Kekulé-type valence structures with the largest number of formal benzene Kekulé-type formulas, *i.e.*, to structures for which the empirical Fries rule predicts the greatest stability. The Kekulé index orders different valence structures in a series which should qualitatively indicate relative importance of the individual structures. The approach can be extended also to excited formal structures as discussed for naphthalene. Application of such analyses to a number of alternate polycyclic conjugated systems confirms an intuitive extension of the Fries rule to systems constructed from rings of various sizes.

Despite considerable computational difficulties which make the application of complete VB calculations to large conjugated systems impractical, the method nevertheless has its attractive features and has proved useful for qualitative discussions of organic systems. The results of VB calculations would be of considerable interest as they would indicate the relative weights of different Kekulé-type structures. The valence bond method which forms another basis for description of molecules and bonding has been conceptually closer to chemical ideas and has been found useful even at the very crude qualitative level avoiding actual computations and limited to operating with a few well-selected valence bond structures. It seems desirable to be able to use the language of the valence bond model at a somewhat quantitative level whenever that can be achieved without going into tedious and impractical VB computations. In this paper we consider this problem and describe an approach to arrive at some indication of the relative weights of different Kekulé-type structures although this is accomplished in a somewhat indirect and intuitive way. We associate with individual valence structures an index derived by projecting the given molecular orbitals (HMO or SCF) on a space spanned by functions which characterize individual CC double bonds, selected corresponding to individual formal valence structures of the conjugated system considered. We interpret the results as a measure of overlap between the HMO or SCF wave function and one characterizing the valence structure under the examination. The index thus constructed does not represent a true overlap between an MO description and a VB wave function of the considered conjugated hydrocarbon. The evaluation of the genuine index of overlap between MO and VB wave functions is much more involved and cumbersome. It has been considered, but it appeared that the calculation seemed not sufficiently practical and did not appear to be of compensating value.[2] Although the present approach is not directly connected with VB wave functions, it may nevertheless be associated with individual valence structures, and perhaps represents the simplest intuitive measure of the relative weights of individual VB structures. In fact, we do not deal with any one Kekulé structure directly at all: we take the double bonds in a chosen Kekulé structure *one by one*, and find their overlap with each of the occupied MO's. The point about any Kekulé structure is that it represents a form of pairing of *all* the electrons at the same time. Instead we have been finding something like the sum of bond orders (or double bond characters) of the "double bonds" of a Kekulé structure, when using an MO wave function. This gives something like the importance of a Kekulé wave function within the MO wave function. The argument for the importance of this new index is therefore rather empirical, and as will be demonstrated, it gives sensible results. One may interpret the results to indicate the relative importance of various Kekulé-type formal valence structures: the larger the index the more important the contribution of that particular structure in the total wave function. Such an interpretation is supported by the result that the valence structures with the largest number of benzene Kekulé structures are those with greatest Kekulé index, in complete agreement with the empirical Fries rule.[3]

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[1] (a) Supported in part by the National Science Foundation (Grant 14012X). (b) On leave from Department of Chemistry, Faculty of Science and Mathematics, University of Zagreb, Zagreb, Croatia.

[2] C. A. Coulson, University of Oxford, England, unpublished results, private communication, 1972.

[3] K. Fries, *Justus Liebigs Ann. Chem.*, **454**, 121 (1927); K. Fries, R. Walter, and K. Schilling, *ibid.*, **516**, 248 (1935).

Definition of the Kekulé Index

We derive the Kekulé index (K) in the following way. Let the $2N$ π electron of a conjugated molecule be described by N orthonormal molecular orbitals. The

$$|\phi_1\rangle,\ |\phi_2\rangle,\ \cdots\ |\phi_N\rangle \tag{1}$$

orbitals are ordered by increasing orbital energies. The ground state of the molecule is described by the above orbitals, each of which is doubly occupied. Projection in this space is made with the operator P

$$\hat{P} = \sum_{j=1}^{N} \hat{P}_j \tag{2}$$

where

$$\hat{P}_j = |\phi_j\rangle\langle\phi_j| \tag{3}$$

is the projection operator in the space spanned with orbitals ϕ_j.[4] Consider another function $|L_i\rangle$. Its projection on the space defined by the above set of orbitals $|\phi_j\rangle$ is $\hat{P}|L_i\rangle$. The magnitude of this projection, a scalar quantity designated as $k(L_i)$, is

$$k(L_i) = \left\{\sum_{j=1}^{N} \langle\phi_j|L_i\rangle^2\right\}^{1/2} \tag{4}$$

If $|L_i\rangle$ is normalized then

$$0 \leqq k(L_i) \leqq 1 \tag{5}$$

Let us now describe the same molecule with another set of N normalized orbitals

$$|L_1\rangle,\ |L_2\rangle,\ \cdots\ |L_N\rangle \tag{6}$$

For each of the orbitals $|L_i\rangle$, we can calculate the magnitude of the projection on the original basis $k(L_i)$. If a totality of orbitals (6) represent a particular model of bonding then we can take the arithmetic mean of the individual $k(L_i)$ to characterize the model.

$$K(L) = \frac{1}{N}\sum_{i=1}^{N} k(L_i) \tag{7}$$

It can be easily verified that the $K(L)$ satisfy the same bounds as the $k(L_i)$. One expects that in proportion as $K(L)$ approaches 1, the orbitals $|L_1\rangle$, $|L_2\rangle$, $\cdots$ $|L_N\rangle$ will be able to give an equivalent description of the system as close as the original basis set.

To derive the Kekulé index we have to specify the nature of the orbitals $|L_i\rangle$. Valence structures of a conjugated hydrocarbon are given as a set of pairs of carbon atoms μ and ν between which are localized C=C double bonds. A simple linear combination

$$(2 + 2S_{\mu\nu})^{-1/2}\{|\chi_\mu\rangle + |\chi_\nu\rangle\} \tag{8}$$

where χ_μ and χ_ν are $2p_z$ carbon atomic orbitals and $S_{\mu\nu}$ is the corresponding overlap integral describes the double bond localized on atoms μ,ν in such a valence structure.[7] Similar linear combinations correspond to other pairs of carbon atoms which are formally double bonded. The Kekulé index is then given as the averaged overlap between the initial set of molecular orbitals and selected linear combinations (8) which correspond to a particular Kekulé-type valence structure of the molecule. The explicit expression for $K(L)$ is obtained if one adopts an LCAO representation of initial molecular orbitals. If

$$|\phi_j\rangle = \sum_{\rho=1}^{2N} c_{j\rho}|\chi_\rho\rangle \tag{9}$$

one obtains the following expression for $K(L)$

$$K(L) = \frac{1}{N}\sum_{(\mu,\nu)\epsilon\mathrm{L}}(2 + 2S_{\mu\nu})^{-1/2}\left\{\sum_{j=1}^{N}\left(\sum_{\rho=1}^{2N} c_{j\rho}(S_{\mu\rho} + S_{\nu\rho})\right)^2\right\}^{1/2} \tag{10}$$

If all the overlap integrals are assumed equal, as is frequently the case in π-electron calculations, or if the overlaps are neglected the above expression for the Kekulé index can be reduced to a simpler form. In the latter case a particularly simple form emerges

$$K(L) = \frac{1}{2N}\sum_{(\mu,\nu)\epsilon\mathrm{L}}(q_\mu + q_\nu + 2p_{\mu\nu})^{1/2} \tag{11}$$

which in cases of alternant hydrocarbons further reduces to

$$K(L) = \frac{1}{2N}\sum_{(\mu,\nu)\epsilon\mathrm{L}}(2 + 2p_{\mu\nu})^{1/2}$$

Here q_μ and q_ν are the π-electron charge densities on atoms μ and ν and $p_{\mu\nu}$ is the corresponding bond order. From the above expression for $K(L)$, we see that the Kekulé index is given as an average of a quantity which can be interpreted as a function of the total charge in the μ,ν bond where the summation is made over all double bonds of a particular valence structure of the considered conjugated hydrocarbon.

Results

The calculated values of the Kekulé index depend, for a given valence structure of a molecule, on the choice of molecular orbitals used. We have considered Hückel MO's,[8] and in a number of cases also various available more elaborated SCF MO's.[9] In Table I the Kekulé index for individual valence structures of several benzenoid polycyclic systems is shown. In all cases considered the valence structure with the largest number of Kekulé benzene formulas has the largest index. This suggests that the Kekulé indices can be used to supplement and bring a quantitative explanation of the empirical Fries rule, which says that the most stable Kekulé-type structures are the ones with the maximum number of benzenoid rings. Strictly, the Fries rule speaks only about the most favored valence structure and says nothing about the relative importance of other valence structures. One may attempt to extend the rule also to other structures, but a formalistic generalization in which one would order the structures accord-

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[4] Projection operator has been used by V. Bonačić and J. Koutecký [*J. Chem. Phys.*, **56**, 4563 (1972)] in their analysis of nonuniqueness of the Hartree–Fock solutions of the Pariser–Parr–Pople model for alternate hydrocarbons, and others (see, for instance, ref 5 and 6).

[5] O. E. Polansky and G. Derflinger, *Int. J. Quant. Chem.*, **1**, 379 (1967).

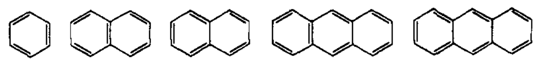
[6] W. England and K. Ruedenberg, *Theor. Chim. Acta*, **22**, 196 (1971).

[7] The characterization of the Kelulé structures by linear combinations of atomic orbitals joined by double bonds has been also considered (neglecting the overlap in the normalization) by J. Čižek and J. Paldus, *J. Chem. Phys.*, **53**, 821 (1970).

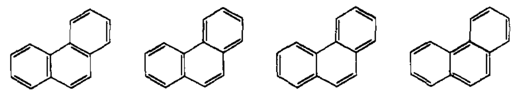
[8] C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations," Pergamon Press, Oxford, 1965; A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Vol. I and II, Pergamon Press, Oxford, 1965.

[9] M. J. S. Dewar and N. Trinajstić, *Czech. Collect. Chem. Commun.*, **35**, 3136, 3484 (1970).

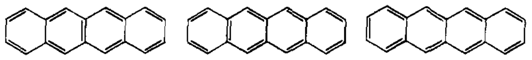
Table I. Kekulé Index for Benzenoid Hydrocarbons



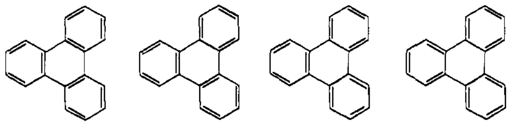
HMO	0.91287	0.917	0.903	0.912	0.900
SCF-MO	0.91287	0.939	0.898	0.933	0.894



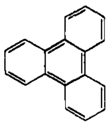
HMO	0.913	0.906	0.900	0.897
SCF-MO	0.931	0.913	0.895	0.890



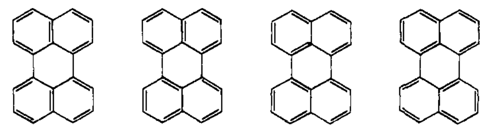
HMO	0.909	0.908	0.898
SCF-MO	0.937	0.925	0.890



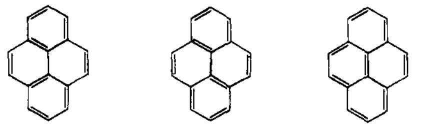
HMO	0.907	0.904	0.901	0.898
SCF-MO	0.918	0.911	0.903	0.896



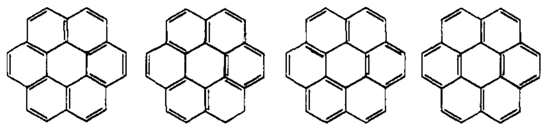
HMO	0.895
SCF–MO	0.896



HMO	0.907	0.902	0.898	0.898
SCF-MO	0.933	0.915	0.896	0.896



HMO	0.905	0.905	0.896
SCF-MO	0.919	0.919	0.887



HMO	0.905	0.900	0.895	0.895
SCF-MO	0.932	0.914	0.897	0.897

HMO	0.890	0.890
SCF-MO	0.879	0.879

ing to the number of Kekulé-type benzene rings does not indicate adequately the relative prominence of the corresponding valence structures. One can expect that the Kekulé index introduced here is a more reliable measure of the relative importance of various valence structures as it is a function of totality of bond orders and may be related to the mean bond order. A compound is, however, more aromatic if the mean bond order is greater.[10] So at least ordering of valence structures according to K will parallel that regularity observed for polycyclic benzenoid aromatic compounds and the concept of nonequivalency of the rings in regard to aromaticity, if the ideas of local aromatic properties is extended to individual valence bond structures.[11,12] The results in Table I indicate, indeed, that the parallelism between the Kekulé index and the number of benzene-type rings is not always maintained; the most striking example is coronene where two structures with the lowest K index have four and one Kekulé benzene rings, respectively, while the valence structures with two and three benzene rings have larger K indices. On the other hand, there are molecules where several structures have the same number of benzene valence formal rings yet the structures are nonequivalent. The K indices in such situations differ (phenanthrene, triphenylbenzene, etc.). Only structures with the same number of equivalent C—C and C=C bonds, regardless of their relative position, *i.e.*, whether they lead to larger or smaller number of benzene-type rings, will give the same K index (coronene, perylene).

The results in Table I also provide the possibility for a closer comparison of the relative magnitudes involved, whether several valence structures of one molecule are considered, or similar valence structures in different molecules are related. For instance, in phenanthrene the difference between the two highest K values is more than twice than the difference in triphenylene. To what extent such comparisons will be revealing remains to be seen. One may, for example, speculate about the factors which are responsible for the relative stability of various valence structures having equal number of formal benzene Kekulé rings. The results of Table I (*e.g.*, triphenylene) suggest the higher relative stability to be associated with condensed rings with C=C at the fusion site.[13] A different tendency appears when conjugated hydrocarbons involves small rings (Tables III and IV). For conjugated systems having cyclobutadiene rings Kekulé structures corresponding to the largest value of K index are those with C=C double bonds exocyclic to the small rings.[14]

When the Kekulé indices obtained from Hückel MO are compared with those based on more elaborate SCF MO wave functions one observes that in the latter case a wider range of magnitudes results. This is an interesting result and may be related to an argument for a justification of the empirical Fries rule itself. As suggested some time ago[15] the changes of the bond orders when one goes from simple Hückel calculations to more sophisticated SCF MO calculations imply certain valence structures have more weight when the molecule would be described by the VB method. The accompanying changes in bond orders always favor valence structures with the greatest number of Kekulé benzene ring formulas, in accordance with the Fries empirical formulation.

Generally the K indices decrease with the size of a molecule. The decrease along the series naphthalene,

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(10) W. Kemula and T. M. Krygowski, *Tetrahedron Lett.*, 5136 (1968).

(11) E. Clar, *Tetrahedron*, **5**, 98 (1959); **6**, 355 (1959); E. Clar, C. T. Ironside, and M. Zander, *ibid.*, **6**, 358 (1959); *J. Chem. Soc.*, 142 (1959).

(12) J. Kruszewski, *Soc. Sci. Lodz. Acta Chim.*, **16**, 77 (1971).

(13) This again fully parallels the situation concerning the molecule as a whole, not the individual VB structures. For rings formally aromatic it is characteristic that bonds of these rings belonging simultaneously to the aromatic system have a bond order greater than bonds of these rings, which link the aromatic systems (ref 12).

(14) M. Randić and Lj. Vujisić, *J. Org. Chem.*, 37, 4302 (1972).

(15) M. Randić, *J. Chem. Phys.*, **34**, 693 (1961).

anthracene, naphthacene, and pentalene (we consider the largest K values of each molecule) parallels the decrease of the mean bond order for these molecules (0.6220, 0.6041, 0.5936, and 0.5720, respectively). Thus the same factors which are responsible for the trend in bond orders will be important for determining the decrease in the magnitude of the Kekulé index. It is dangerous to speculate on the origin of the observed trends as various factors depend on the size of a molecule. For instance, the number of neglected nonneighboring interactions of the Hückel model will vary monotonically with molecular size. It is interesting then to observe the near constancy of the first K index obtained with SCF treatments which take into account some nonnearest neighbor interactions.

We may briefly summarize the results of Table I as follows. The ordering of valence bond structures according to the Kekulé index parallels the following structural features. (1) Valence structures with smaller number of conjugated C=C bonds on periphery have larger K, (2) between structures with an equal number of conjugated peripheral C=C bonds those with larger number of benzene-like rings have larger K, and (3) if there is an equal number of peripheral C=C and an equal number of benzene-like rings the structures will have almost equal K values. However, the structure with more fused sites of benzene-like rings will have somewhat larger K.

This summary is based on the data for over 30 condensed benzene ring systems, several of which for illustrative purpose are shown in Table I. More details and extensive documentation for the remaining molecules are presented elsewhere.[16]

Finally, a practical aspect of the simple rules for ordering valence bond structures, regardless of its relation to the Kekulé indices, is that they can form a *basis for a convention* on assignment of an index to individual valence bond formulas. In view of revival of interest in VB calculations[17] a need for classification and enumeration of all or selected valence structures will be more in demand. The above scheme (points 1–3) represent a possible answer and appears sufficiently simple and straightforward. In addition, as discussed, it has some intuitive support. Should it happen that two or more valence structures are found which the present scheme does not distinguish and yet they present nonequivalent structures (*i.e.*, they have different number of distinctive C—C and C=C bonds) and therefore should have different K indices, the actual K values can be used to extend the above rules to encompass previously nonapplicable cases.

In Table II are listed Kekulé indices for several nonalternant hydrocarbons. The improvement on going from HMO to SCF MO calculations is more pronounced here, as illustrated in the case of acenaphthylene and pyracyclene, for which a comparison is made. This is not suprising in view of the fact that the results of Hückel theory are usually appreciably better for alternant hydrocarbons than for nonalternants.[18]

Table II. Kekulé Index for Nonbenzenoid Nonalternant Hydrocarbons

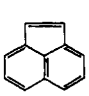
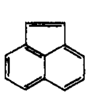
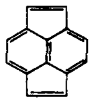
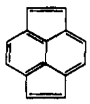
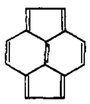
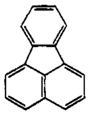
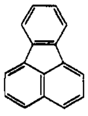
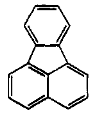
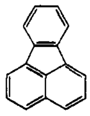
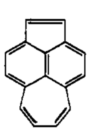
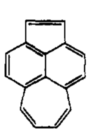
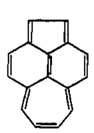
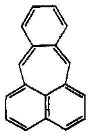
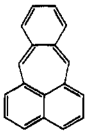
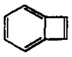
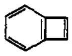
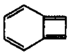
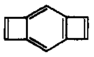
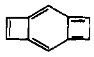
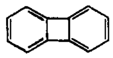
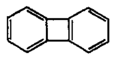
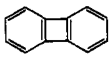
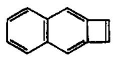
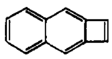
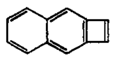
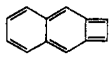
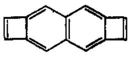
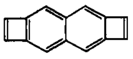
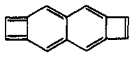
					
HMO	0.912	0.904	0.918	0.910	0.861
SCF-MO	0.945	0.913	0.944	0.893	0.834
					
HMO	0.906	0.903	0.900	0.897	
					
HMO	0.9015	0.9014	0.8900	0.909	0.905

Table III contains results for polycyclic systems involving six- and four-membered rings (alternants). The results of Tables II and III display the same characteristic already noticed when rings of different size are fused, namely that the structures with the largest K indices are those with the largest number of exocyclic C=C bonds. The Fries rule is not applicable to systems presented in Tables II and III, and we consider in the next section the extension of the Fries rule to a wider family of polycyclic conjugated molecules.

Table III. Kekulé Index for Nonbenzenoid Alternant Hydrocarbons

					
HMO	0.941	0.905	0.832	0.894	0.882
					
HMO	0.918	0.906	0.895	0.865	
					
HMO	0.925	0.922	0.894	0.860	
					
HMO	0.936	0.914	0.880		

An Extension of the Fries Rule

In order to formulate a rule which may be considered as an extention of the Fries rule to a wider class of conjugated systems, we will examine in some detail how the Kekulé index of a larger system is related to the indices of the molecular fragments. In some molecules two or more nonequivalent structures with respect to symmetry of the molecule may have the same value for the Kekulé index. This occurs because the effective symmetry used in calculating the K indices is sometimes higher than the molecular symmetry. Therefore the relative orientation of distant fragments represented by the same

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(16) A. Graovac, I. Gutman, M. Randić, and N. Trinajstić, *Croat. Chem. Acta*, in press.

(17) R. Mc Weeny, *Proc. Roy. Soc., Ser. A*, **223**, 306 (1954); **227**, 288 (1955); J. C. Shug, T. H. Brown, and M. Karplus, *J. Chem. Phys.*, **35**, 1873 (1961); **37**, 330 (1962); **38**, 1749 (1963); M. Simonetta and E. Heilbronner, *Theor. Chim. Acta*, **2**, 228 (1964); M. Simonetta, E. Gianinetti, and I. Vandoni, *J. Chem. Phys.*, **48**, 1579 (1968); J. J. C. Mulder and L. J. Oosterhoff, *Chem. Commun.*, 305, 308 (1970); W. J. van der Hart, J. J. C. Mulder, and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, **94**, 5724 (1972).

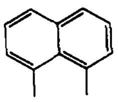
(18) J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, "Valency Theory," Wiley, London, 1965, p 285.

Figure 1. Schematic representation of coupling of two fragments leading to the same K index.

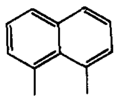
Figure 2. Schematic representation of linking molecular fragments to produce the same K index.

valence structures may not bring a change in calculated K index. That the effective interaction is of higher symmetry than the actual problem suggests is not uncommon in the molecular problems. For instance, the existence of excessive degenerate eigenvalues occurs often in the Hückel approach, and it has been traced to higher symmetry of the associated graphs.[19]

Consider a fragment of a molecule which has two or more possible Kekulé structures (A, B, $\cdots$). For example, in perylene such a fragment is represented by



A



B

In a molecule belonging to the point group D_{mh} the number of such fragments is n, where $n \geqslant 2$ is an integral multiple or a divisor of m. The Kekulé index of the molecule is a sum of the indices of all fragments, which is self-evident from the definition of K (eq 10 and 11). The first possibility to be considered is that the fragments have the same (partial) K index, *i.e.*, $K(\mathrm{A}) = K(\mathrm{B})$, which would be illustrated by perylene. For $n = 2$ we have two nonequivalent structures of the molecule with the same K index (Figure 1). It is not difficult to see that the similar situation arises also in cases with $n > 2$. The second possibility which may produce different valence structures having the same K index arises from cases with $K(\mathrm{A}) \neq K(\mathrm{B})$. Here the cases $n = 2$ and $n = 3$ are of no interest as they correspond to alternative labeling of the fragments. When $n = 4$ there are two nonequivalent arrangements of fragments with the same K index (Figure 2).

For the purpose of discussing Kekule indices of different valence bond structures it is important to distinguish between equivalent and nonequivalent C—C and C=C bonds as they would contribute differently to the K value. For instance, in coronene there are four nonequivalent CC bonds (with bond orders 0.7450, 0.5380, 0.5380 (accidently the same four figures), and 0.5219). The last two valence structures for instance have the same number of distinctive CC bonds which produces the same K value regardless of the relative orientation of these bonds, which in one case leads to four benzene formal rings while in the other only one. Actually one can understand the basis for the Fries rule as originally stated from a detailed comparison of valence bond structures and bond order matrix of molecular orbital calculations. Bond orders calculated by the Hückel method show pronounced alternation in magnitudes in particular along the periphery of the conjugated system. This property has for instance been used as a measure of aromaticity.[12,20] Fused rings tend generally to have lower bond orders, which may somewhat obscure the alternative pattern. In the summation of bond order contributions to K over particular VB structure alternation of bond orders allows the possibility of accumulation of an excess of bond orders over the average values, thus increasing the mean bond order. The Kekulé index as defined in the previous section very closely follows the mean bond order (K values are more general and take into account possible variations of charges on atoms forming the bond). From a bond order–bond length correlation an increase in the mean bond order corresponds to tighter bonding, shorter bonds, and an energetically more stable system. Now by examining those structures with the largest number of benzene-like rings and the corresponding bond order matrix it will be seen that the particular distribution of C=C and C—C bonds overlaps with the alternation of larger and smaller bond orders. Thus the parallelism of bond alternation and the distribution of C=C bonds in the valence structure with the largest number of formal benzene rings is a justification for the Fries rule. If the original formalism is extended to other *valence structures* it fails in a number of instances, since formal arrangement of benzene rings is no longer accompanied by similar parallelism in bond order contributions. However, it appears to be possible to extend the Fries rule to *nonbenzenoid systems.* The Fries rule can be rationalized knowing that benzene itself is a stable molecule both in the chemical and thermodynamic sense. We may regard benzene as a member of the annulene series and generalize Fries's rule in terms of the Hückel rule which states that π electrons lead to stabilization of $(4n + 2)$ annulene ring systems, while they destabilize $(4n)$ annulene ring systems. The difference between the two classes of annulenes decreases when n is large enough.[21] Now the generalization of the Fries rule to polycyclic conjugated molecules, which would indicate the most stable Kekulé-type valence structure of the latters, requires examining the number of $(4n + 2)$ and $(4n)$ annulene-like rings. The most stable structure is one with: (a) the maximum number of $(4n + 2)$ annulene-like rings, (b) the minimum number of $(4n)$ annulene-like rings, (c) the smaller $(4n + 2)$ rings are more stable than the larger ones, and (d) the larger $(4n)$ rings are more stable than the smaller ones. The above intuitive generalization of the Fries rule is in fact supported by the results of the present calculations. The generalized rule presents a qualitative summary of the results quantitatively obtained by the projection of the available MO wave functions on the set of localized molecular orbitals constructed for each double bond of the valence bond structures considered. If one wishes to generalize the Fries rule not only to nonbenzenoid conjugated hydrocarbons, but also to individual valence

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(19) U. Wild, J. Keller, and H. H. Günthard, *Theor. Chim. Acta*, **14**, 384 (1969).

(20) A. Julg and Ph. Francois, *Theor. Chim. Acta*, 7, 249 (1967).

(21) For example, M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 685 (1965); T. M. Krugowski, *Tetrahedron Lett.*, 1311 (1970); H. P. Figeys, *Tetrahedron*, **26**, 5225 (1970); R. C. Haddon, V. R. Haddon, and L. M. Jackman, *Fortschr. Chem. Forsch.*, **16**, 103 (1971); I. Gutman, M. Milun, and N. Trinajstić, *Croat. Chem. Acta*, **44**, 207 (1972).

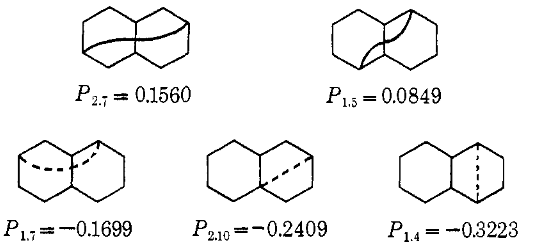
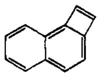
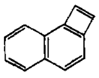
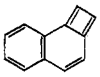
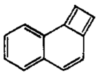
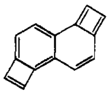
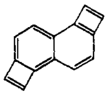
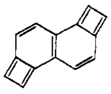
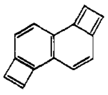
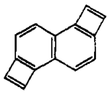
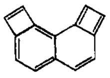
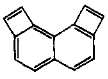
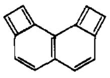
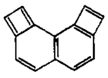
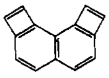
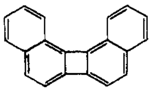
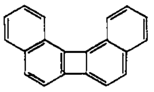
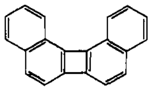
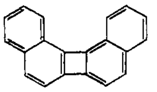
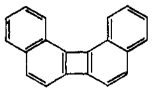
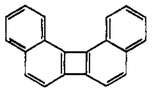
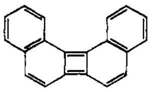
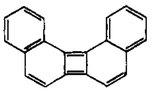
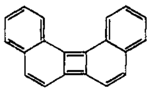


Figure 3. Schematic representation of relevant nonadjacent bond orders of naphthalene.

structures of benzenoid and nonbenzenoid molecules, the Kekulé index introduced in this paper appears to make a plausible basis for such an extension. The absolute magnitudes of individual Kekulé indices listed in Tables I–IV would be affected by adoption of another set of MO wave functions, as illustrated in some cases by comparison between Hückel and SCF functions. However, the relative magnitudes and general conclusions, including the above generalization of the Fries rule, are not expected to change. In some cases, of course, it will be not possible to fulfill all the conditions (a)–(d) in the same Kekulé valence structure. In such cases the best structure is a compromise. Examples of such molecules are given in Table IV.

Table IV. Kekulé Index for Polycylic Hydrocarbons in Which It Is Not Possible to Achieve at the Same Time the Maximum Number of the Benzenoid Rings and Minimum Number of Nonbenzenoid Rings

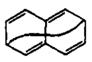
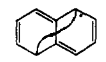
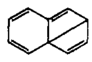
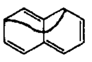
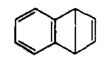
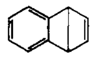
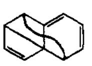
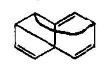
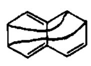
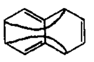
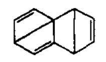
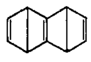
HMO	 0.926	 0.916	 0.860	 0.845	
HMO	 0.8897	 0.8798	 0.8796	 0.8697	 0.8599
HMO	 0.8871	 0.8870	 0.8689	 0.8688	 0.8687
HMO	 0.9088	 0.9080	 0.9071		
HMO	 0.8998	 0.8990	 0.8909		
HMO	 0.8860	 0.8779	 0.8698		

Finally, we would like to mention that in some molecules several of the K indices are interrelated so that one value is the arithmetic mean of two others. For example, in 1,2:7,8-dibenzobiphenylene (Table III) we have: $K_2 = (K_1 + K_3)/2$, $K_5 = (K_3 + K_6)/2$, and $K_8 = (K_7 + K_9)/2$, where K_1, K_2, etc. are the indices of the nine valence structures in decreasing order. These arithmetic relationships follow from the particular distribution of C=C double bonds among the distinctive nonequivalent bond types. If for instance we label the 13 nonequivalent bonds in 1,2:7,8-dibenzobiphenylene we can verify immediately the above relations and find other such relations in other molecules.

Kekulé Indices for Excited Valence Structures

The approach described in previous sections can be extended to so-called excited (nonclassical) valence structures. These are characterized by pairing of nonadjacent π electrons (Dewar structures of benzene, for instance). To illustrate such an extension, in Table V are listed indices for all nonequivalent singly and doubly excited structures of naphthalene. Several interesting points emerge. The ordering of VB structures according to the magnitude of K indicate that some structures with more distant pairing are preferred to those with smaller separations of paired orbitals. This indicates that some caution is necessary when a naive picture is extended to such more complex structures, as an uncritical application may be misleading. However, the actual ordering shown in Table V can be fully understood by closer examination of the bond order matrix of naphthalene. In Figure 3 schematically are shown relevant nonadjacent bond orders of naphthalene. The ordering of valence bond structures almost fully follows the decrease in nonbonded bond orders. The actual contributions of other (adjacent) bond orders may perturb the complete parallism in some instances, in particular if the differences between bond orders are small. Another interesting features is the larger spread of K indices, the difference between the K values of the first and the last valence structure being five to ten times greater than for unexcited structures. The drop of the mean K on going from unexcited to singly excited valence structures is appreciable. A similar change in mean K on going from singly to doubly excited structures is less pronounced. In fact the decrease of K value between the lowest singly excited structure and the highest K value of doubly excited structure is less than the differences between individual K values of either singly or doubly excited structures. This points to some limitations of truncations of included valence bond structures based only on formal recognition of a number of distant coupling of pairs of orbitals. One can expect for larger systems even some overlapping in K values be-

Table V. Kekulé Index for Excited Structures of Naphthalene

	Singly Excited	
 0.8762	 0.8581	 0.8567
 0.8463	 0.8376	 0.8237
	Doubly Excited	
 0.8116	 0.7998	 0.7972
 0.7894	 0.7773	 0.7583

tween structures with different number of "long" pairings. Namely, the positive nonadjacent p_{ik} contributions of a more excited structure may more than compensate for a decrease in K index of a particular structure with fewer nonadjacent pairings but in which negative nonadjacent contributions are present.

The application of the outlined procedure to other molecules and their valence structures, including also excited valence formulas, may reveal additional interesting features, despite the admittedly somewhat arbitrary definition of the Kekulé index. An important result of the present work is that the proposed index makes it possible to investigate intimate relations between MO wave functions and VB valence structures. The suitability of this or another index for classification of VB structures should be tested systematically on extensive material. Tables I–IV contain information on some 20 molecules, which are selected for illustrative purposes. However, the conclusions are drawn and tested on altogether some 100 molecules and supplementary tables will be documented elsewhere.[16] The molecules represent a structurally diverse class of compounds: condensed benzene rings, nonbenzenoid alternant, and nonalternate hydrocarbons. Other definitions of an index to relate MO wave functions and VB structures, in fact MO wave functions associated with the latter, are possible.[22] Also "Kekulé solutions" consisting of ethylene-like molecular orbitals which are associated with each double bond of the given Kekulé structure are not the only, and even perhaps not the most opportune form for localized orbitals.[6] Some refinements and modifications can therefore be expected to be stimulated by the present work, and it remains to be seen to what extent they can introduce some novel features and enrich the present analysis.

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(22) Professor J. Koutecký (Freie Universitat Berlin, Germany) [private communication, 1973] considers a mean of bond orders associated with the pairs of carbon atoms connected with double bonds in the Kekulé structures as an alternative index. So modified index is simply related to Kelulé index K, in particular for alternate systems. We average $(1 + p_{ik})^{1/2}$ while modified index is the simple average of p_{ik}, both taken over the same set of paired atoms characterizing the particular valence structure. For neighboring atoms p_{ik} are less than one; therefore the Kekulé index K will always be larger than the simple average value of p_{ik}. For individual p_{ik} contributions the increment is decreasing as p_{ik} increases in the interval of interest. From the monotonic relationship of individual terms which contribute to the sum representing K values or the modification of K, one may expect that essentially the same conclusions would be drawn. The situation may be somewhat different for nonalternate systems and excited valence structures when the simple monotonic behavior between the two schemes may break down.

Acidity of Hydrocarbons. L. Equilibrium Ion Pair Acidities of Thiophene, Benzothiophene, Thiazole, Benzothiazole, and Benzofuran toward Cesium Cyclohexylamide in Cyclohexylamine[1]

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Abstract: Relative equilibrium ion pair acidities have been determined for several heterocyclic compounds by reference to hydrocarbon indicators having colored cesium salts in cyclohexylamine. pK values for the 2 position (on a per-hydrogen basis) relative to 9-phenylfluorene = 18.49 are: thiophene, 38.42 ± 0.06; benzothiophene, 37.05 ± 0.23; benzothiazole, 28.08 ± 0.11; thiazole, 29.50 ± 0.11; benzofuran, 36.84 ± 0.18.

In recent years, there has been considerable interest in kinetic acidities of azolium salts,[2] azoles,[3] and five-membered monoheterocycles.[4] However, inconsistencies frequently exist in the relative rates observed. For example, in EtOH–EtOK, thiophene exchanges faster than furan,[4b] but benzoxazole exchanges faster than benzothiazole.[3a] Additional inconsistencies exist when comparisons are made of relative rates of compounds in different solvent systems. In Me_2SO–*t*-BuOK, 5-methoxythiophene-*2-d* exchanges slower than thiophene-*2-d*,[4a] whereas in MeOD–MeOK the order reverses.[5]

All previous available data relate to kinetic acidities, and because of the biological importance of these and related heterocycles,[2a] measures of equilibrium pK_a's

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