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ON THE CHARACTERIZATION OF LOCAL AROMATIC PROPERTIES IN BENZENOID HYDROCARBONS[a]

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Abstract—A generalization of the Kekulé index for composite valence structures provides a quantitative value corresponding to Clar's assessment of benzenoid character of aromatic ring systems. The idea involved is further specialized for the individual local rings in the molecules. Comparison with limited experimental data supports the validity of this approach.

INTRODUCTION

Accumulated experimental evidence supports the idea, introduced by Clar, that individual rings in the same polycyclic benzenoid compounds may have different aromaticity.[1] Accordingly, certain localized benzene-like regions exist in condensed aromatic hydrocarbons. A quantitative measure of the benzene character of such parts in these molecules appears desirable. Despite convincing explanations requiring a concept of isolated pi-electrons sextets little attention has been devoted to further theoretical examination of Clar's hypothesis or to the problem of local aromaticity. Polansky and Derflinger[2] considered Clar's theory of localized benzenoid regions in condensed aromatics and found a justification of Clar's postulate. By means of HMO method they took benzene MO's as the basis for the representation of molecular orbitals of polycyclic bnezenoid systems. They derived an index characterizing the individual rings of a molecule which is determined from the coefficients when the MO's of the system are expanded in sets of MO's of each ring (the latter being taken as orbitals of isolated benzene). Another approach, due to Kruszewski,[3] modifies a procedure which reduces the aromaticity of a system to an index measuring the equalization of its peripheral bonds.[4] Local aromatic properties are in this model characterized by applying the equalization criterion of aromaticity to individual rings. One could similarly extend other aromaticity criteria to a molecular fragment or an individual ring. Such criteria, for instance, consider whether a given cyclic conjugated hydrocarbon will be more or less stable than its open chain analog[5] or than the corresponding classical analog.[6] Such extensions, however, have not been considered as yet, though an explicit mention of aromaticity criteria applied to individual rings in polycyclic systems has been made.[7]

We present here another characterization of the individual rings of polycyclic benzenoid hydrocarbons. The approach may be considered a modification of the recently introduced idea of a Kekulé index, designed to characterize the individual Kekulé valence bond structures.[8] The Kekulé index is derived for individual valence bond structures by evaluating the magnitude of the overlap between the given molecular orbitals of the molecule and functions characterizing the set of CC double bonds specified by the valence bond structure. The index so evaluated does not represent the true overlap between a MO wavefunction and a VB wavefunction of the molecule, because an unusual specification of the VB structure was required to simplify the evaluation. We take successively the contributions corresponsing to individual CC double bonds. Nevertheless, the approach presents an intuitive measure of the relative weights of individual VB structures.

Kekulé index for composite valence structures

If one wishes to consider a Kekulé index for a structure which is a linear combination of two or more valence bond structures this can be accomplished by extending the summation to cover all the structures of interest. The consideration can be restricted also only to a molecular fragment of interest, and if necessary different weights can be given to nonequivalent structures. Such considerations are of interest when examining aromatic systems and also their local properties. According to

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Clar[1] there is no need to consider aromatic sextets confined to isolated monocyclic systems equivalent to sextets shared among two or more rings. In the latter cases the benzene-like character of the rings may be diluted to a large extent. Well defined and localized sextets should be separetely indicated as well as isolated CC double bonds. Clar thus arrived at a characteristic symbolic representation of aromatic systems in which only some rings are fully benzene-like, others share benzene-like character by taking part in accommodating migrating sextets, yet others may have one or two fixed double bonds or even be empty.[1] A few examples of Clar's symbols for selected aromatic molecules are shown in Fig 1. We will refer to such symbolic representations as Clar's structural formulas. Clar's formulas for any benzenoid hydrocarbon can be obtained by a superposition of several well selected Kekulé valence bond structures. A pair of Kekulé structures which only differ in the relative orientation of the three CC double bonds within a single benzene ring, the remaining CC double bonds have the same positions represent a single isolated sextet, n such formally isolated sextets are represented by 2n Kekulé structures. The corresponding index for one of Clar's structures, which we will call Clar index in analogy to the Kekulé index corresponding to a Kekulé structure, will then be given as the mean of the corresponding Kekulé indices, and can similarly be evaluated from available tables of bond orders.[9] For a selection of benzenoid hydrocarbons the values of Clar indices for various Clar's structural formulas are given in Table 1. Several interesting details may be observed. For instance in the case of anthracene there are two nonequivalent Clar's valence structures. They have somewhat different indices and the structures represented with an isolated sextet at the central ring has a larger

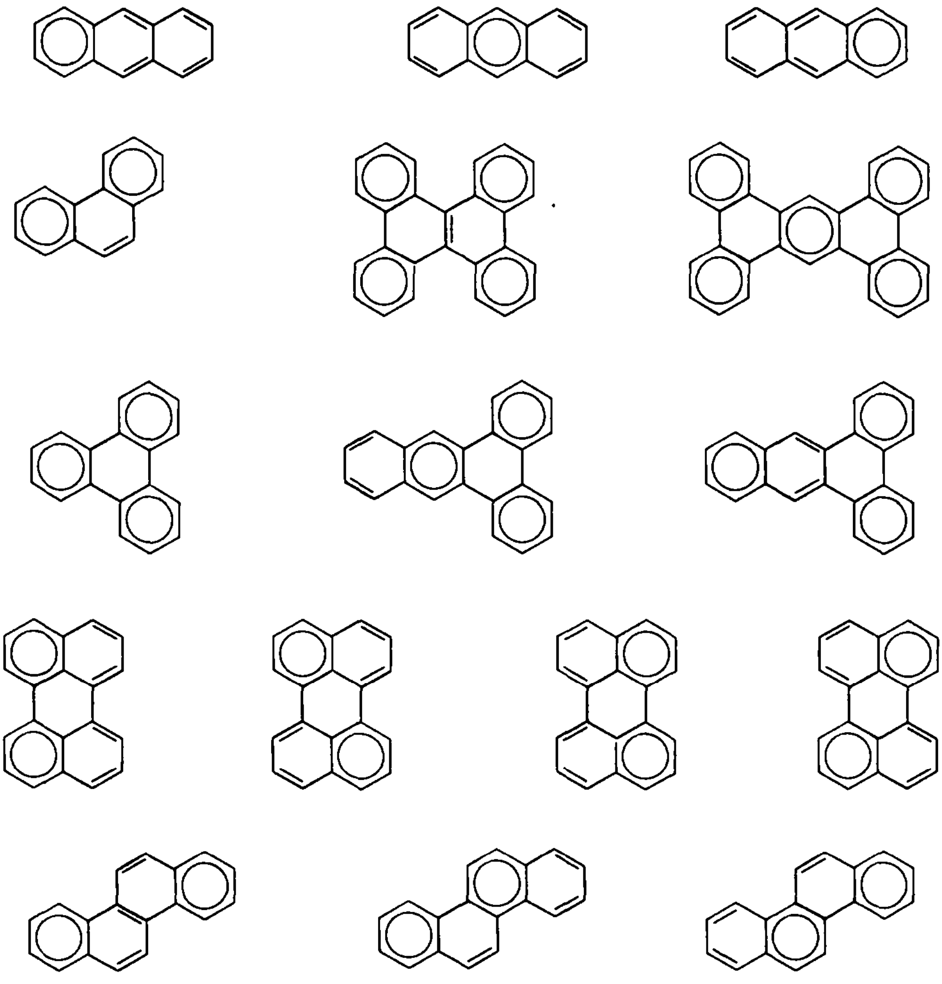

Fig 1. Examples of Clar's symbols for several benzenoid hydrocarbons

Table 1. Aromaticity indices for various Clar's valence structural formulas for a selection of benzenoid hydrocarbons


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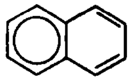
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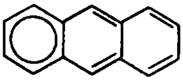
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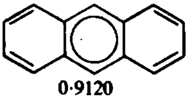
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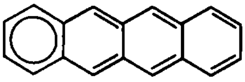
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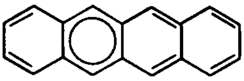
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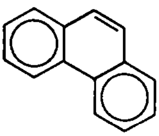
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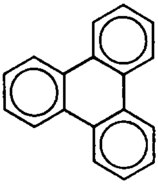
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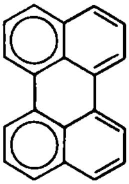
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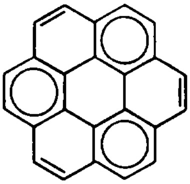

0·8975

index value. The same situation is found in other linear polyacenes (naphthacene, pentacene). The larger Kekulé index has been interpreted as indicating the greater importance of the particular valence bond structure. The empirical Fries rule[10] and its theoretical justification support such an interpretation.[11] The Fries rule implies that the valence bond structure having the largest number of formal Kekulé benzene valence structures also has the greatest stability. Since the stability can be associated with the aromaticity we may attempt to formulate an analogous rule relating to Clar's valence formulas. The more general rule thus implies a combination of a pair of Kekulé-type formulas, which are no longer considered separately. It can be formulated as: Valence bond structures with maximal number of formally isolated pi-electron sextets (i.e., minimal number of isolated CC double bonds) will have the greatest aromatic stability. This is in fact Clar's postulate, and by making the above formulation we only wished to bring to the attention the close similarity of the two empirical rules, that of Fries and the more recent one of Clar. There is a substantial difference, however, between the content of the two postulates. The Fries rule refers to a *single* canonical VB structure, while Clar's concept of maximal number of isolated sextets refers to a 2n complementary VB structures. Nevertheless the close formal similarity between the two empicical postulates is very interesting as it indicates a definite underlying principles concerning valence bond representations. Thus when one refers to properties of aromatic systems which require interpretation via a single valence structure, Fries rule appears important. On the other hand, if the properties require a couple of valence structures Clar's postulate emerges to govern the selection of the structures.

In discussing the calculated indices of Clar's structures (briefly C-index or C-value) it would be safer to confine the discussion to comparisons between molecules with similar structural features, since the relative accuracy of approximate wavefunctions from which the bond orders are extracted may vary considerably with the size and type of a system. We will consider a few such structurally related systems. For instance, along the series benzene, naphthalene, anthracene and naphthacene, a monotonic decrease of the average C-value results. The origin of this trend can be traced to the decrease of the mean bond orders 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 magnitudes of Clar indices of these molecules. Although it is dangerous to speculate on the origin of the trend, nevertheless one might associate with it the dilution of benzene-like character due to sextet migrations among rings, the number of which increases along the series.

Characterization of local aromatic properties

In order to characterize local molecular properties one has to consider molecular fragments and derive appropriate indices for them. Kekulé indices can be easily obtained for molecules fragments by restricting the summation of overlap contributions to respective regions in a molecule. Such considerations are of importance when examining aromatic systems for which local (aromatic) properties have been postulated. For the explicit expressions of the indices corresponding to molecular fragments we formally replace the summation over *all* pairs (μ, ν) of atoms forming double bonds by *selective* pairs (μ, ν) which constitute the valence bond representation of the fragment (or a ring) considered (*cf*, Eq (11) in Ref 8):

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

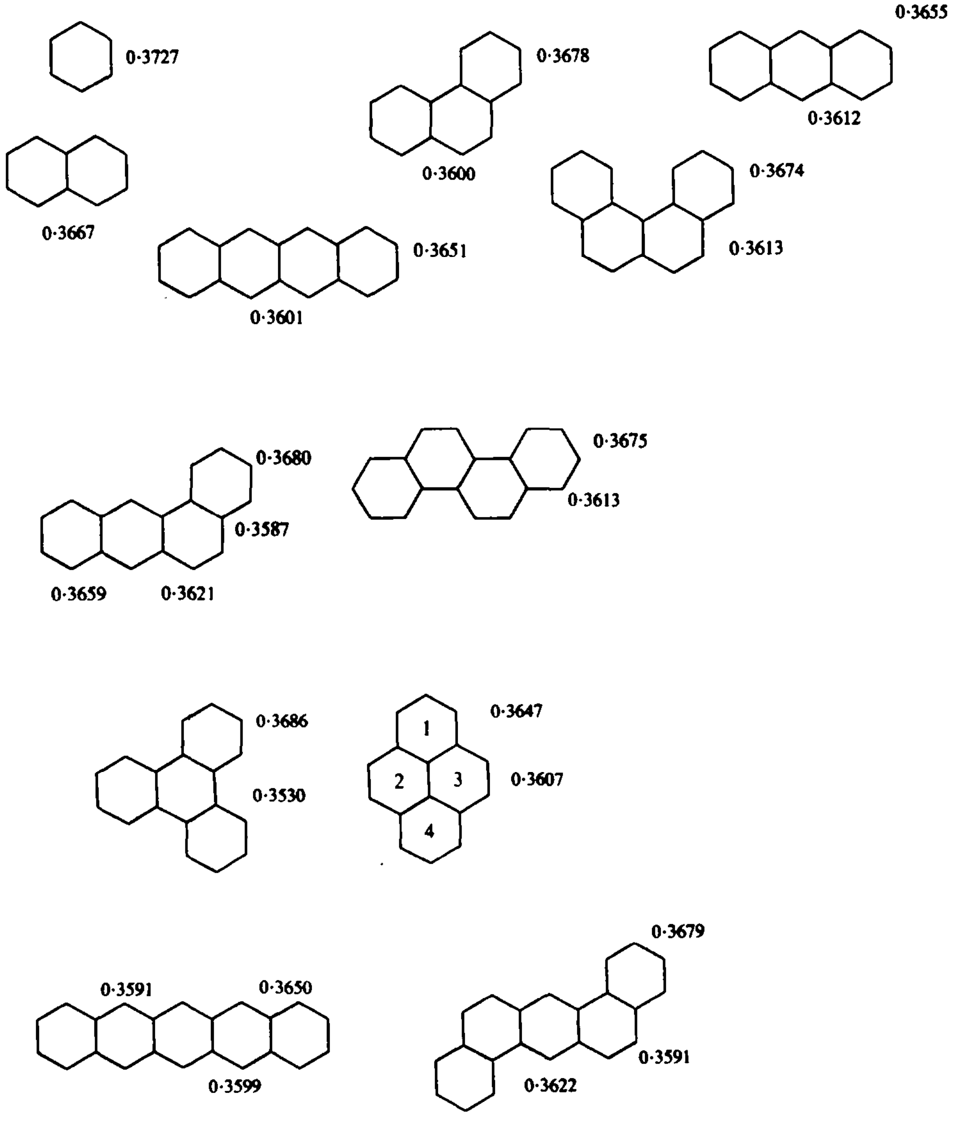
When benzenoid systems are considered within HMO all q are 1 and we have

$$K = \left(\frac{\sqrt{2}}{6}\right)\sum_{(\mu,\nu)} (1 + p_{\mu\nu})^{1/2}$$

The proposed index for a benzene ring fragment is a function of average bond orders of the ring. A characterization of the local aromaticity by such an index resembles the scheme of Kemula and Krygowski, who argue that a compound is more aromatic if the mean bond order is greater[12]—except that now these ideas apply to individual rings, rather then to a molecule as a whole. The approach is empirical in nature and therefore its validity ultimately rest upon the success or failure of the theoretical index to correlate well with relevant experimental data.

In Table 2 we list ring indices for a number of benzonoid hydrocarbons. A number of interesting features may be observed. All the ring indices (designed by R) have as their upper limit the R value for benzene. Individual values vary between this limit (0·3726) and the lowest values which approach 0·3500. One can associate in each of the structures

Table 2. Ring indices for a number of benzenoid hydrocarbons



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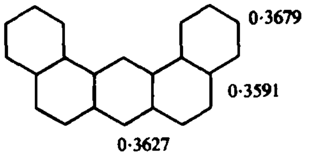

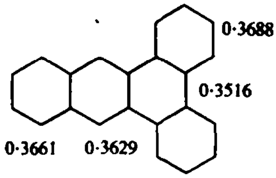

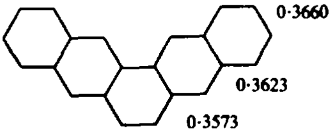

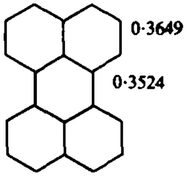

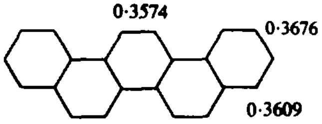

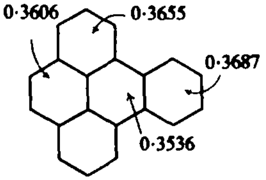

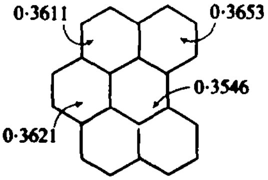

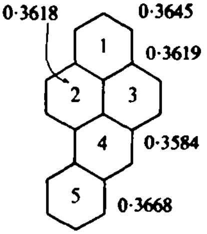

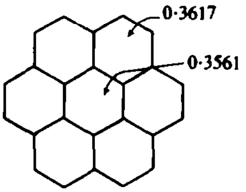

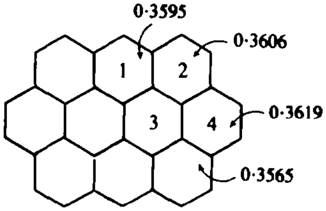

in Table 2, high R value with Clar's isolated sextets and small R values with a ring with fixed CC double bonds or "empty" rings (i.e., having no double bonds at all), while the intermediate R values correspond to rings involved in accommodation of migrating sextets. The absolute magnitudes of the three classes occasionally overlap, but the ring indices close to 0·3680 or higher clearly indicate an isolated Clar's sextet (e.g., phananthrene, benzanthracene, benzpyrene). Intermediate R-values signify a superposition of two Clar's structural formulae (or more) associated with migrating sextets. The superposition may arise from participation of two equivalent components or nonequivalent structures. Examples of the former group are perylene and coronene, while of the latter group contains benzanthracene, dibenzanthracene and benzpyrene.

There are a few interesting cases indicating small departures from the Clar's non numerical representations. In benzpyrene ring no. 5 (Table 2) has a too low R value to allow the interpretation of a migrating sextet. The R values in the region 0·3590–0·3610 seem to characterize a ring with fixed double bond (e.g., phenanthrene, dibenzanthracenes, benzpyrene and benzoperylene). Slightly larger values would indicate a migration of a sextet involving a ring with one double bond. Not only that some rings have larger index than expected from the corresponding Clar's formulas (e.g., pyrene rings 2,3) but some rings have unexpectedly low R values. In ovalene ring no. 1 is expected to have R about 0·3680, which is more characteristic for the situation in which there is a single Clar's formula with a well localized pi-sextet and CC double bonds. The calculated value is even smaller than R index for ring no. 2. This may indicate perhaps that in this case besides the dominant Clar's formula one should consider formulas with less than maximal number of isolated sextets. Alternatively, the reduced magnitude of R for ring 1 can also be accounted by making an allowance for excited covalent structures. It is outside the scope of the present work to further elaborate these particular alternatives. They have been mentioned only to indicate possible further extensions. In particular the importance of excited structures should not be overlooked. There are molecules where an excited structure can lead to a larger number of isolated sextets (e.g., anthracene) which would perhaps compensate for their higher energies. Calculations of K-indices for excited structures of naphthalene indicate, for instance, that contributions of singly and doubly excited structures are appreciable—if judged by the relative magnitudes of the corresponding K-values.[8]

Comparison of R indices with other theoretical indices characterizing local aromaticity

In Fig 2, we plot Polansky and Derflinger's ring against the R index introduced in this paper. A very good straight line results with few smaller deviations noticeable in the central portion of the correlation line. The origin of these minor deviations are not quite clear. They might be indicative of some numerical inaccuracies or may even persist as reflecting the differencies of the two approaches. They are not, however, significant for the current comparison and discussion and are neglected. In Fig 2 we also include a correlation of Kruszewsky local aromaticity index (characterizing the accumulation of differences between CC bond lengths of aromatic rings) with the R-values. The respective points in Fig. 2 clearly separate in two correlation lines. R values in the region 0·3680–0·3650 correspond to Kruszewsky's aromaticity index associated with terminal C_6-rings. The correlation is well presented by a linear form. The intermediate rings show somewhat larger scatter of points around an only approximately linear correlation. The existence of these correlations, however, only confirms that the mean bond orders correlate with accumulation of differences of shorter and longer bonds. Thus apparently different molecular properties ultimately are interrelated and can serve as an alternative basis for characterization of the aromaticity of a system (or its fragments).

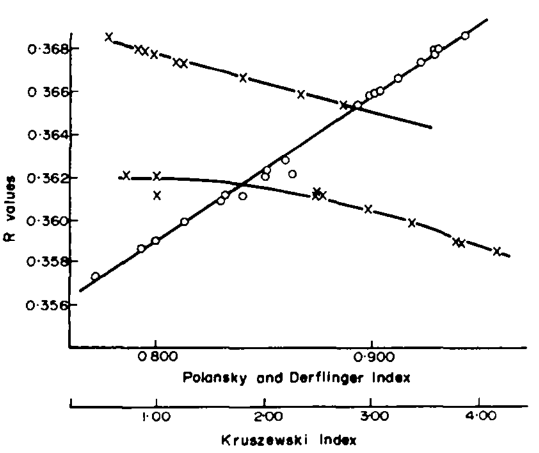

Fig 2. Plot of fractional (ring) indices of Polansky and Derflinger (circles) and of Kruszewski (crosses) against the corresponding ring indices calculated by extending the concept of Kekulé indix to individual rings of benzenoid hydrocarbons.

Each of the three ring indices intercorrelated here have been based on HMO. Therefore they have some of the advantages and disadvantages that are inherent in the Hückel theory. HMO's are related to the topological eigenvalue problem for hydrocarbons in that they are equivalent to the eigenvectors of the adjacency matrix.[13] The ring indices, therefore, indirectly reflect some inherent topological qualities. On the other hand changes in the relative magnitudes of these local aromaticity indices could result when employing different MO wavefunctions. Hopefully more elaborated MO functions may improve correlations with experimental quantities. Significant improvement of a particular correlation would then indicate that the particular property can not be assigned solely or dominantly to topological features of the molecule. In fact HMO bond orders have not been found (not unexpectedly) adequate for prediction of molecular bond lengths. An improved MO description then can bring significant corrections and modifications to the present values for the indices. But such indices, if indeed aromaticity is essentially a topological property, may lead to less satisfactory correlation with local aromaticity properties. If a property is characterized by a single quantity the calculated value will be dependent on the quality of the MO basis. Thus individual bond lengths depend on a single quantity, the corresponding bond order, and will vary with the improvement of the wavefunctions adopted. If a property is characterized by a combination of such single quantities the changes in one may be compensated by changes in another, and that is essentially the reason that mean bond order or accumulation of differencies in bond lengths may serve as an index of a topological properties (which we suspect the aromaticity to belong). Structure of other aromaticity indices based on difference in cyclic and acyclic, or different cyclic structure is in accordance with the suggested reasoning.

Instead of aiming at more and more accurate wavefunctions one can go to another extreme and adopt the experimental bond lengths using them to indirectly arrive at aromaticity indices which characterize local molecular properties. However, to have the full advantage of such a scheme one would require very reliable data which is not always available. But, regardless of possible alternative approaches to evaluating the numerical values of local ring indices, it seems desirable first to test the current scheme. Testing the current scheme requires demonstration of correlation between the theoretical index and relevant experimental data. In the following section we consider that topic.

A comparison of local aromaticity index with some experimental data

There is an abundance of data indicating some fixation of pi-electrons in regions such as rings or isolated bonds. However most of the data is indirect or inferential (which should not belittle its importance) and thus not available for a direct correlation with a local aromaticity index. An exception, perhaps, is the data from NMR spectroscopy which provides a probe into local molecular environments. For instance fixation of CC double bonds in phenanthrene type fragments has been proved by the coupling of the Me protons with the neighboring aromatic proton.[1] The Me signals appear to be particularly suitable for testing the double bond character between adjacent atoms because they are well outside other aromatic proton absorption in the NMR spectra. In Fig 3 for 2,3-dimethyl triphenylene (I), 2,3-dimethyl naphthalene (II), 6,7-dimethyl-1,2,3,4-dibenzanthracene (III), and 2,3-dimethyl anthracene (IV) the local aromaticity ring indices R of the rings of the substitution are plotted against Me doublet separations (given in Hz). The number of points is too small to permit one to be overwhelmed by the relatively smooth correlation curve, but it is satisfying to find that a good quantitative correlation is obtained. The influence of the migrating electron pair is reduced in 2,3-dimethyl anthracene by comparison with 2,3-dimethyl napthalene as indicated by the increase in the separation of the Me doublet.[14] This supports the observation of distinct annelation effects in passing from benzene to napthalene and anthracene.[1] This correlation indirectly suggests a possibility for characterizing the annelation effects on somewhat quantitative basis. The indices of local aromaticity may present an adequate basis for such consideration in the future.

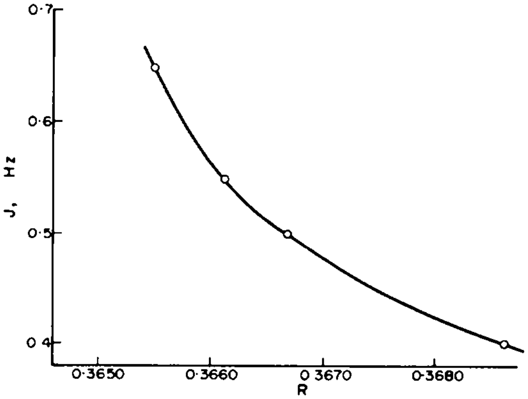

Fig 3. The plot of local aromaticity ring indices for dimethyl substituted: triphenylene (I), naphthalene (II), dibenzanthracene (III), and anthracene (IV) against CH_3 doublet separations (in Hz).

Before concluding the exposition it seems opportune to reiterate that the current index of local ring aromaticity R, as well as the indices introduced by Polansky and Derflinger,[2] and Kruszewski[3] are conceptually *metric* not topological, although they may reflect some topological nature through the fact that HMO may be considered (in hydrocarbons) topological orbitals. The numerical values of the indices depend on the quality of the orbitals selected, or on the approximate nature of the Hamiltonian used in their derivation. They have then some flexibility and can be revised if some significant improvement in MO are reported. However, from their ability to represent local and overall aromatic properties of benzenoid hydrocarbons it remain at present unclear if the latter properties are primarily topological in origin. Some work has been reported considering this issue which assumes topology is the dominant factor and which discusses the consequences for diverse molecular forms.[15] It seems desirable to infer the possible topological origin of aromaticity as directly as possible from molecular topology without manipulating eigenfunctions of the adjacent matrix. In other words one would like to consider a molecular graph which represents molecular topology and to analyse its components in order to derive an indication of the aromatic quality of the system. This seems possible, and indeed a quantitative measure of local and overall aromaticity may be concluded from the topology of conjugated benzenoid hydrocarbons. This particular topic is presented in another publication which primarily is concerned with graph theoretical analysis of Clar's structural valence formulas.[16]

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