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GRAPH THEORETICAL APPROACH TO LOCAL AND OVERALL AROMATICITY OF BENZENENOID HYDROCARBONS

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Abstract—Structural indices which characterize individual benzene rings in benzenoid hydrocarbons have been suggested. For each ring separately we count the number of classical valence structures in which the ring is formally represented by a Kekulé benzene formula. The ratio of this number and the total number of classical valence structures for the molecule is suggested as a measure of benzenoid-like character of the ring considered. Rings with local indices approaching one, the value belonging to benzene, correspond to more isolated pi-electron sextets, those with an intermediate values indicate more delocalized environment. Rings with very small indices, approaching zero or being zero, are typical for rings not contributing to conjugation significantly. Limited experimental evidence is consistent with the concept of local ring character as illustrated by a correlation between Me doublet separation in NMR spectra of selected dimethyl substituted polycondensed benzenoid hydrocarbons. The sum of the contributions of all rings constitute a molecular index of benzenoidity which can serve as a topological measure of molecular aromaticity.

INTRODUCTION

The concept of aromaticity has been one of the most important notions in organic chemistry, yet its precise definition remains elusive.[1] Here we are concerned with the topological properties of benzenoid hydrocarbons, some of which are to be associated with their aromatic nature. In particular we try to recognize the essential structural features responsible for their characteristic properties. We consider an index which describes a local benzenoid character of individual rings, and also when summed over all rings indicate the degree of benzenoidity of a molecule as a whole. The new parameter can be considered as a measure of local and overall aromaticity of a molecule. A brief discussion of other indices characterizing local and overall aromaticity is presented and compared, without a pretence to completeness. A use of the proposed index is illustrated in a correlation with experimental data attributed to a local molecular character.

Topological indices for characterization of local molecular properties

We would like to characterize a molecular fragment, in particular an individual ring in a polycondensed benzenoid hydrocarbon, from a purely structural information on the system. Benzene and benzenoid hydrocarbons are unique in requiring two or several classical valence formula for their representation. The information we have at a disposal is contained in the set of valence structures, such as the five structures of phenanthrene shown in Fig. 1. A closer examination of individual classical valence structures reveals differencies in representation of the two nonequivalent rings. We can count for each ring separately in how many structures it is formally represented by a Kekulé benzene structural formula. As an index of local benzenoid character of a particular ring we take the ratio of the number of structures in which the ring is given by classical Kekulé formula and the number of classical structures for the molecule as a whole. This seems a plausible suggestion, as those structures in which the particular ring has no classical Kekulé structure of benzene do not contribute to the benzene-like character of the ring. For instance in the first of the five structures of phenanthrene (Fig. 1) the terminal rings are benzene-like, i.e. are formally represented by alternating single and double bonds, while the central ring has four single bonds and does not contribute to benzene character. Thus the amount of benzene-like character of individual rings follow from the count of structures. The calculated parameter signify a semblance of individual rings with benzene. It can be expected therefore to be a measure of local aromaticity, although in view of no clear definition of aromaticity it is better referred to as benzene-like character of benzenoidity (benzeneoidicity).[2]

Let's illustrate the procedure and the concept by considering phenanthrene. The five valence bond structures are shown in Fig. 1. We observe that in four out of five structures the terminal rings appear formally benzene-like. We attribute therefore the value 4/5 to these rings to indicate the relative magnitude of their local resemblance to benzene. The central ring in phenanthrene by contrast appears only in two structures as a classical benzene valence formula, hence the corresponding index of local aromaticity is only 2/5.

The index of local aromaticity, or more precisely benzene-like character, here introduced may be considered an extension of the famous Pauling bond order concept. The extension is made by applying essentially the same approach to larger molecular fragments, here rings. Instead of counting single and double bond character of a bond one makes a corresponding count for individual rings. The approach quantitatively discriminates between nonequivalent rings in general, although as will be seen later in some instances nonequivalent rings result in an identical index.

We will examine the results for several benzoid hydrocarbons in more detail in order to see how different environment of an incorporated ring is reflected on the benzenoid character of the ring. Consider the series: benzene, naphthalene, anthracene. (Table 1). The ring index for all rings of a given member of linear polyacene is same. Each successive member has a decreased ring index. As the number of rings increases the ring index

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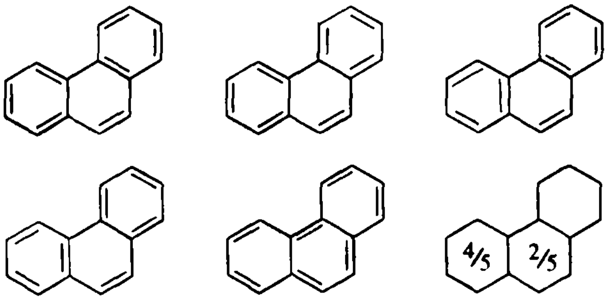


Fig. 1. Classical (Kekulé-type) structures for phenanthrene and the count of benzene-like character of individual rings.

monotonically decreases from the maximal value of 1·000 found in benzene (i.e. an isolated pi-electron sextet) to 2/3, 2/4, 2/5, 2/6, etc. for naphthalene, anthracene, tetracene, pentacene etc., respectively. The benzene-like character is evidently diluted with an increase of the size of these linear polycondensed benzenoid systems. The stability and other aromatic characteristics of benzene are well known, so an increase of the size of these linear polyacenes may even produce unstable systems. The topological ring index introduced provides the basis for a quantitative measure of "dilution" of the benzenoid character. The excessive degeneracy of ring indices can be traced to an excessive degeneracy of Pauling bond orders in such linear polyacenes. One can observe that the non-equivalent rings having the same ring index are attached to nonequivalent CC bonds which have a same Pauling bond order.

The overall molecular index is obtained by summing individual ring contributions. The aromaticy index of benzene is 1·000, and thus presents the unity on the scale of our measurement of aromaticity. None of the individual rings attain an index of local (ring) aromaticity larger than 1·000. At the same time none of the molecules considered has an overall index smaller than that of benzene. Table 1 lists individual ring indices and the total aromaticity index for some 20 selected condensed benzene hydrocarbons. Along homologous series it is possible to derive simple explicit expressions for the magnitudes of ring indices as a function of the number of constituting benzene rings. For instance if we designate with N the number of fused rings in a linear polyacene, the ring index is given by: 2/(N + 1). The overall index of aromaticity is simply N times larger in this case. As N increases we approach the limiting value of 2·000, a value characterizing linear polyacene of infinite length.

Several different molecules have the same overall index. In some cases this is a coincidence as the contributions in phenanthrene and pyrene show. In other cases it is a result of some structural relationship or identical Pauling bond orders for nonequivalent bonds. Also the overall indices of different magnitude are sometimes related. Thus perylene has twice the value of naphthalene and tetrabenzopyrene twice the value found for anthracene. This shows that pericondensation does not produce interference between the linked fragments, which may be considered as effectively joined by single CC bonds. Thus one may expect perylene to be considered as composed of two almost isolated naphthalene parts and tetrabenzopyrene as consisting of two isolated anthracene moieties. Experimental evidence seems to support such features of the proposed model. Perylene and zethrene have the same overall indices which follow from the nature of the coupling of the napthalene fragments. The index of the central rings in these examples is equal zero signifying their non participation in conjugative accumulation of the aromatic character. Clar,[3] in his intuitive characterization of aromatic systems refers to such rings as "empty". On comparing these and other structures with the qualitative description of Clar one occasionally observes that some rings have small non zero magnitude of the index, rather than zero, and are thus "almost empty" rather than fully isolating the molecular rings.

For larger molecules enumeration of structures in which a particular ring is formally benzene-like is not simple because of vast number of structures. This number is however simply related to corrected structure count (CSC) for benzene residual considered by Herndon.[4] The quantity signifies the number of exchanges that permute three pairs of electrons in a single ring and is proportional to the number of structures in which a benzene ring is formally represented by a Kekulé structure. A procedure for obtaining CSC values is quite simple even for moderately large systems. If SC represent a structure count,[4] i.e. the total number of classical Kekulé-type structures for a considered system an expression portraying a benzene-like nature of a ring in a larger molecular system is given by:

(Ring CSC) (Ring SC)/(Molecular SC).

The expression is written in a form which is ready for generalization to other than ring components. One only need to replace ring CSC and ring SC by the corresponding fragment CSC and fragment SC. Thus in the case of benzene and naphthalene fragments the proportionality factors (fragment SC) are 2 and 3 respectively.

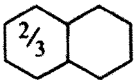
The index of local aromaticity appears of some interest in analysing theoretical contributions to the resonance energy of a system. It, of course, represents a partitioning of the resonance energy of the system assuming that only Kekulé structures contribute as basic functions, and that only benzene-type resonance occurs between the structures. It corresponds thus to the resonance energy per ring as calculated by Herndon[4] neglecting higher "exchange" integrals. Obviously there will be some correlation with resonance energies since in adequate units the summation of ring indices represents a sizable fraction of the total resonance energy.

Comparison with other indices of aromaticity

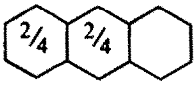
There have been numerous attempts to characterize aromaticity of a molecule. Few selected procedures will be briefly mentioned as they indicate some relationship to

Table 1. Ring indices for selected benzenoid hydrocarbons based on the structural formulas for these compounds. The overall index of aromaticity given under each of the structures is a sum of the contribution from individual rings.

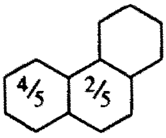
1·0000



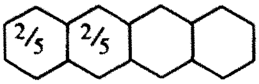
1·3333



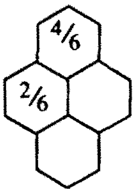
1·5000



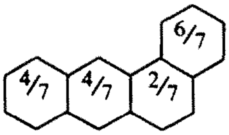
2·0000



1·6000



2·0000



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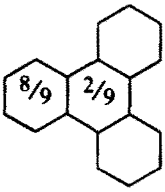

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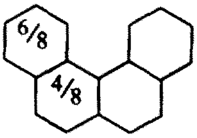
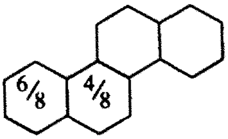
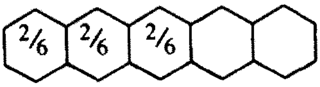


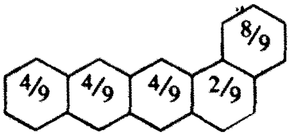
2·5000



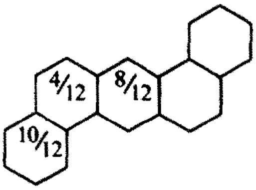
2·5000



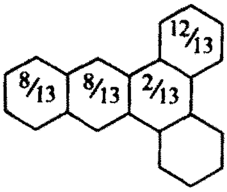
1·6667



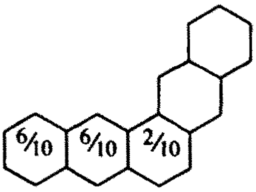
2·4444



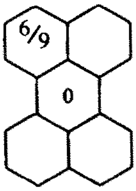
3·0000



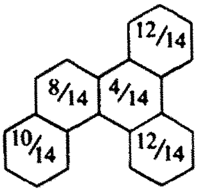
3·2308



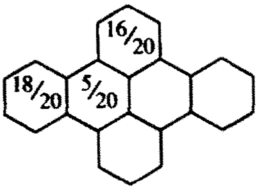
2·6000



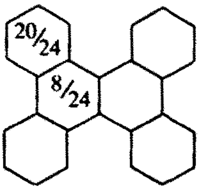
2·6667



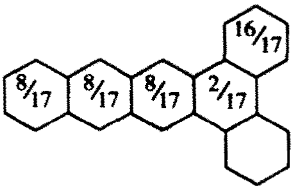
3·2857



3·9000



4·0000



3·4117

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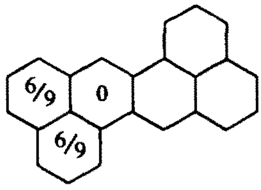
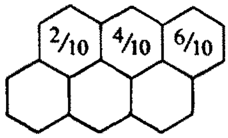
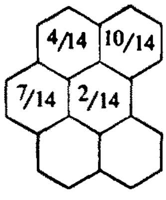


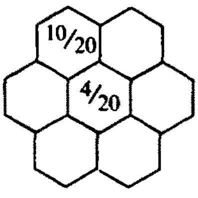
2·6667



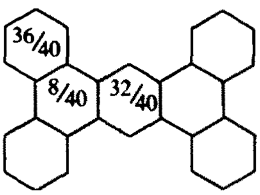
2·4000



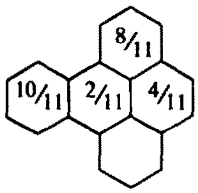
2·6428



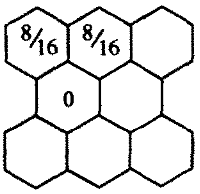
3·2000



4·8000



2·9090



3·0000

the proposed overall index discussed here. These are primarily procedures based on Hückel eigenvalues, which are in fact for considered systems equivalent to topological eigenvalue problem.[5] One such index is based on the difference between HMO energies of a given conjugated molecule and HMO energies of the corresponding classical structure represented by contributions of isolated single and double bonds.[6] Another criterion of aromaticity is based on the difference in pi-electron energies of a cyclic and isoelectronic acylic structures.[7] Both these indices correlate well with the overall topological index derived here.

In contrast to plurality of approaches to characterization of aromaticity of a molecule very few attempts have been made to define *local* aromatic character in polycondensed benzenoid systems. Polansky and Derflinger[8] derived a measure of the benzene character of a ring by using benzene MO's as the basis for a representation of MO's of a more complex benzenoid system. In its final analysis their ring index is derived from elements of HMO bond order matrix. An alternative procedure has been recently considered[9] in which the concept of Kekulé indices[10] is applied to individual benzene rings, rather than to a molecule as a whole. The two characterizations of individual rings parallel one another and well correlate with the local ring indices based on the simple procedure of counting formal benzene-like rings in all Kekulé-type structures. Regardless of an occasional difference these conceptually different characterizations have produced generally similar results. This indicates that different theoretical constructions parallel the elusive "aromatic" nature of a molecule. On the other hand the different procedures indicate possible approaches to localization or fixation of molecular features in parts or fragments of a system for structures which have been traditionally considered as fully delocalized. The topological ring index discussed in this paper shows, in addition, that the major manifestation of such a localization can be adequately derived solely from the structural information on the system, such as the totality of classical valence structures.

On a correlation of the local ring indices with experimental data

The local ring indices can be used for establishing a correlation with some NMR data. The Me signals in PMR have been considered by Clar and Mackay[11] as particularly suitable for testing the double bond character of adjacent bonds. We can expect them to provide a measure of the benzenoid character of the rings to which methyls are substituted. In Fig. 2 are plotted for several dimethyl substituted polycyclic benzenoid hydrocarbons Me doublet separations against the local topological ring index of the corresponding ring of substitution. The smooth correlation curve which results provides an evidence for the topological nature of the particular phenomenon. At the same time the results support the concept of localization of conjugation in molecular fragments although the rela-

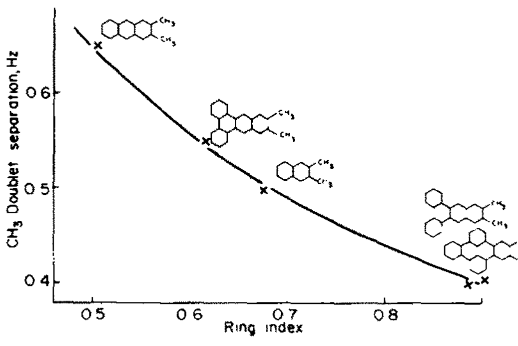


Fig. 2. A plot of the Me doublet separations in NMR spectra of several dimethyl substituted benzenoid hydrocarbons against the local ring index at the substitution site.

tive importance of the two opposing contributions, one due to a complete delocalization, the other due to limited localization can not be simple delineated. The discussed topological indices may supply the basis for a quantitative discussion of Clar's characterization of aromatic benzenoid hydrocarbons. One can look at Clar's and Robinson's representation of benzenoid systems by structural formulas corresponding to isolated sextets of electrons merely as arising from selection of particular covalent (non-excited) structures. In contrast the standard VB approach superimposes all valence structures with an equal weight. The idea of Clar's structures correspond to one extreme situation, that of maximal ring localization, but so does the customary assumption of an equal participation of all structures and subsequent full delocalization represent another extreme. The index of local aromaticity provides some justification for the notion of limited localization of components in some situations and its validity is confirmed by arriving at the result of local characterizations using in fact all, not few selected, classical valence structures.

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REFERENCES

[1] G. Binsch, *Naturwiss.* **60**, 369 (1973).
[2] E. Clar, private communication.
[3] E. Clar, *The Aromatic Sextet.* Wiley London (1972); and numerous refs to the original work of Clar *et al.* given.
[4] W. C. Herndon, *Tetrahedron* **29**, 3 (1973).
[5] K. Ruedenberg, *J. Chem. Phys.* **34**, 1861 (1961).
[6] M. Milun, Ž Sobotka and N. Trinajstić, *J. Org. Chem.* **37**, 139 (1972).
[7] R. Breslow, *Chem. Eng. News* **43**, 90 (1965); *Angew. Chem. Int. Ed.* **7**, 565 (1968).
[8] O. Polansky and G. Derflinger, *Int. J. Quant. Chem.* **1**, 379 (1967).
[9] M. Randić, *Tetrahedron* **30**, 2067 (1974).
[10] A. Graovac, I. Gutman, M. Randić and N. Trinajstić, *J. Am. Chem. Soc.* **95**, 6267 (1973).
[11] E. Clar and C. C. Mackay, *Tetrahedron* **28**, 2943 (1971).