

Aromaticity of Polycyclic Conjugated Hydrocarbons

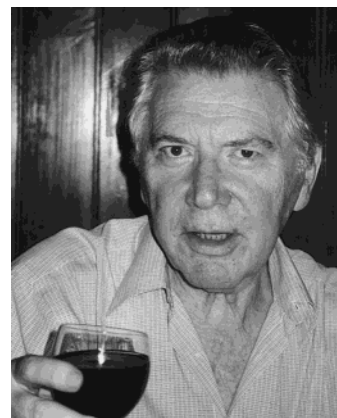
Milan Randić*

National Institute of Chemistry, Ljubljana, Slovenia

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Milan Randić is a native of Croatia, born in 1930, and is a citizen of the United States and Croatia. He studied theoretical physics at the University of Zagreb (1954) under Professor Ivan Supek (a student of Werner Heisenberg). Supek introduced him to the book by Linus Pauling, *The Nature of the Chemical Bond*, with a request to get involved in quantum chemistry. He got his Ph.D. degree in Cambridge in 1958, studying high-resolution infrared molecular spectra with Dr. Norman Sheppard. At the Rudjer Bosković Institute in Zagreb, Croatia, in 1960, he founded the theoretical chemistry group. Since 1971, he has visited several U.S. universities. From 1980 to 2000, he was in the Department of Mathematics and Computer Science at Drake University, Des Moines, Iowa. Among the awards he has received are the City of Zagreb Science Award, the Boris Kidrič Science Award (of Republic of Slovenia), The Governor's Science Award (Iowa), and the Skolnik Award (American Chemical Society). He is a member of the Croatian Academy of Sciences and Arts. His continuing interest is to advance a better understanding of chemical graph theory. Since January 1, 2000, he is Professor Emeritus at Drake University, while continuing a three-months-a-year visitation at the National Institute of Chemistry in Ljubljana, Slovenia. His other interests include development of a universal language, NOBEL.

PHOTOGRAPH CAPTION: The author is in full agreement with Plutarch (46–119 A.D.), who characterized wine as, "Of drinks — the most useful; Among medication — the most tasteful; Among food — the most enjoyable."

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* Professor Emeritus, Department of Mathematics and Computer Science, Drake University, Des Moines, IA 50311. Permanent address: 3225 Kingman Rd., Ames, IA 50311. Fax: (515) 292-8629.

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PRACTICAL POINTS: Molecular structures are numbered according to the figure in which they are shown by a fraction x/X , where x is the number of the molecule and X is the number of the figure showing its skeleton. In the list of references, in the case of review articles we have given the title of each article as this offers some information on the particular content of the review. In addition, we may have indicated the length of the review by listing the full page range of such articles.

If a man can preach a better sermon, write a better book, or make a better mouse-trap than his neighbor, though he build his house in the woods, the world will make a beaten path to his door.

R. W. Emerson (1803–1882),
American essayist and poet,
a leading figure in
American literary history.

a molecule. That the presence of $4n$ conjugated circuits is detrimental to molecular stability has been witnessed already for aromatic compounds in which $4n + 2$ conjugated circuits dominate and enforce the planar geometry for the systems in which $4n$ conjugated circuits are also present. Hafner and Schneider⁵⁵³ considered alkyl derivatives of aceheptylene and observed that these compounds depart somewhat in their properties from the “standard” non-benzenoid conjugated systems. Clearly this “departure” is due to the presence of anti-aromatic $4n$ contributing conjugated circuits.

For a compound to qualify as anti-aromatic, however, we must have a dominant anti-aromatic contribution. Hafner and co-workers⁶⁵⁵ designed a clever way to arrive at anti-aromatic compounds by “forcing” a molecule that has undergone the Jahn–Teller distortion back into a more symmetrical geometric form. This was accomplished by introducing bulky *tert*-butyl substituents on the *s*-indacene skeletal frame. Calculations done by Gellini et al.⁶⁵⁶ show that CC bonds in *s*-indacene alternate in length, assuming typical CC double (around 1.32–1.33 Å) and CC single (1.47–1.49 Å) bond lengths, respectively, and results in a structure having C_{2h} symmetry. This structure represents a more stable system than the hypothetical structure without bond alternation (having symmetry D_{2h}). In contrast, calculations on 1,3,5,7-tetra-*tert*-butyl-*s*-indacene (TTBI) show that the more stable system is the one with more equalized peripheral CC bond lengths (around 1.40–1.41 Å), in agreement with the available X-ray data. Hafner and co-workers, after careful analysis of infrared and Raman spectra of 1,3,5,7-tetra-*tert*-butyl-*s*-indacene, concluded that “*The tert-butyl effect on the TTBI structure results in a larger delocalization of the π -electron density over the indacene plane, giving rise to a molecular structure close to D_{2h} symmetry.*”⁶⁵⁶

Hence, because *tert*-butyl groups do not constitute conjugated fragments and are ignored in the conjugated circuits model, we may conclude that “modified” *s*-indacene, that is, 1,3,5,7-tetra-*tert*-butyl-*s*-indacene, represents an anti-aromatic species. More recently, Baldrige and Siegel⁶⁵⁷ have theorized that cyclooctatetraene (COT) can similarly be forced to adopt a planar rather than a tub conformation. A flat form for COT would make contributions from $4n$ conjugated circuit be “felt” and thus would approach an anti-aromatic structure. According to calculations, the two annealed bicyclo[2.2.1]hexene fragments would result in a planar structure that would have localized π -electrons. Matsuura and Komatsu^{658,659} synthesized the compound, and indeed the X-ray confirmed the calculations indicating the presence of CC double bonds in the endo conformation with respect to annealed bicyclo[2.2.1]hexeno fragments. Adding four annealed fragments resulted in a planar structure with exocyclic CC double bonds with respect to the fragments. Finally, by placing annealed bicyclo[2.2.1]hexeno fragments two bonds apart, one prevents CC double bond “fixation”, and as a result one obtains a fully anti-aromatic “modified” cyclooctatetraene. These recent achievements show that

Table 39. ABC's of Aromaticity

$A = \frac{RE(4n + 2) - RE(4n)}{RE(4n + 2) + RE(4n)}$	aromaticity
$B = \frac{RE(R_1) - RE(R_{n \neq 1})}{RE(R_1) + RE(R_{n \neq 1})}$	benzene character
$C = \frac{RRE(R_1) - RRE(R_{n \neq 1})}{RRE(R_1) + RRE(R_{n \neq 1})}$	Clar index

anti-aromaticity that was for the most part “fictitious” is becoming “factual”.

An indirect “proof” that anti-aromatic compounds are elusive comes from data on inter-stellar compounds.^{660–662} In view of the low density of matter and extremely low temperatures in outer space, structures that would be difficult to observe in the laboratory may have long enough life in the inter-stellar space to be detected. Thus, for instance, among others, the smallest aromatic compound, cyclic $C_3H_3^+$, has been identified in the inter-stellar space. The search for anti-aromatic compounds in the inter-stellar space thus appears to be an interesting project. However, as of today, no anti-aromatic compounds have been detected in outer space,⁶⁶³ although, as is well known, the inter-stellar space is rich in hydrocarbons.

In discussing aromaticity/anti-aromaticity, the problem that needs better understanding is why some aromatic compounds (having $4n$ conjugated circuits) have modified properties, as was the case with Hafner's hydrocarbons, and in other compounds, like biphenylene, $4n$ conjugated circuits apparently do not show a visible manifestation of the presence of $4n$ conjugated circuits. We will address this problem in section XXXII (Biphenylenes Revisited).

XXIV. ABC of Aromaticity

We can summarize the graph theoretical approach to aromaticity by focusing on the three important aspects pertaining to aromaticity: (A) classification of compounds as fully aromatic or less aromatic; (B) characterization of the degree of aromaticity of fully aromatic compounds; and (C) discrimination of the local aromatic features of larger compounds. We will briefly outline each of these three important steps for clarification of the concept of aromaticity as it applies to polycyclic conjugated hydrocarbons. From Table 39, which summarizes the ABC of aromaticity, one can immediately see that all the three indices are related. In particular, it follows that for aromatic compounds $A > 0$, for azulene and so-called “azulenooid” compounds, built from five- and seven-member rings, $B = 0$, while for rings not participating in conjugated circuits and thus not contributing to molecular RE, like the central rings of perylene and bisanthene, $C = 0$.

A. A of Aromaticity

As we have seen, aromaticity has been defined in terms of the presence and the absence of $4n + 2$ and $4n$ conjugated circuits. The approach has led to a numerical index that estimates the degree of aromaticity for compounds having both $4n + 2$ and the $4n$ conjugated circuits. It appears quite natural to expect

that an index of aromaticity is sensitive to the relative roles of $4n + 2$ and $4n$ conjugated circuits. Construction of such an index is accomplished by partitioning RE into contributions arising from $4n + 2$ conjugated circuits, $RE(4n + 2)$, and destabilizing contributions arising from $4n$ conjugated circuits, $RE(4n)$. By following this reasoning, we arrive at the index A given in Table 39.

The index A assigns the value $A = 1$ to all benzenoid hydrocarbons, which are thus all characterized as “fully aromatic”. However, as we know, there are variations of the degree of aromaticity even among benzenoid hydrocarbons, though they may be relatively small. We have already seen that “fully benzenoid” hydrocarbons, like triphenylene, dibenzopyrene, hexabenzocoronene, and other $6n$ π -electron systems, show unusual stability. Hence, we need a measure of aromaticity that can differentiate aromatic character among “fully aromatic” compounds.

B. B of Aromaticity

In order to characterize these small variations of aromatic features of benzenoid hydrocarbons, we consider another index that will measure the degree of similarity of a given benzenoid hydrocarbon to benzene. Such an index, referred to as the index of benzene character B of benzenoid hydrocarbons, was proposed in 1987 as follows:⁶⁶⁴

$$B = [\text{RE}(R_1) - \text{RE}(R_{1 \neq 1})] / [\text{RE}(R_1) + \text{RE}(R_{1 \neq 1})]$$

Here, $\text{RE}(R_1)$ is the part of the computed resonance energy that comes from the presence of the conjugated circuits R_1 , while $\text{RE}(R_{1 \neq 1})$ is the part of the computed resonance energy that comes from the presence all other conjugated circuits. The denominator, $[\text{RE}(R_1) + \text{RE}(R_{1 \neq 1})]$, is in fact the total molecular RE, which thus makes B a dimensionless number, always less than one, except for benzene, for which by definition $B = 1$.

In Table 40 we have collected B indices for a number of smaller benzenoid hydrocarbons. For comparison, we also show the corresponding aromaticity indices based on bond lengths. According to Julg,^{665–667} one can derive an index of aromatic character from the differences between the actual CC bond lengths in a benzenoid hydrocarbon and the average CC bond distance $\langle d \rangle$ using the expressions

$$J = 1 - 255[\sum \langle d \rangle]^2$$

$$\Sigma = \sum_i [d_i - \langle d \rangle]^2 / N$$

The numerical value of index constructed in this way will depend on the bond lengths used, which could be experimental bond lengths or calculated ones. One of the two Julg's indices shown in Table 40 is based on experimental CC bond lengths, and the other is based on quantum chemical calculations using the AM1 model (which is attributed to Dewar). As we can see from Table 40, the magnitudes of the derived indices based on bond lengths vary somewhat in a relatively small interval, while graph theoretically

Table 40. B Indices for a Number of Smaller Benzenoid Hydrocarbons

benzenoid	B index	Julg's values	
		exptl	calcd (AM1)
benzene	1.000	1.000	1.000
naphthalene	0.751	0.932	0.928
anthracene	0.630	0.889	0.878
phenanthrene	0.778	0.878	0.928
tetracene	0.561	0.870	0.849
triphenylene	0.801	0.906	0.946
chrysene	0.734	0.848	0.922
pyrene	0.630	0.916	0.899
perylene	0.751	0.877	0.890
dibenzo[<i>a,h</i>]anthracene	0.742	0.972	0.906
picene	0.670	0.900	0.921
benzo[<i>e</i>]pyrene	0.712	0.877	0.890
pentacene	0.522	0.880	0.826
dibenzo[<i>a,c</i>]anthracene	0.796	0.891	0.915
dibenzo[<i>fg,op</i>]tetracene	0.800	0.881	0.944
benzo[<i>ghi</i>]perylene	0.649	0.875	0.921
coronene	0.585	0.955	0.933
quaterrylene	0.751	0.889	0.877
hexabenzocoronene	0.741	0.910	0.848
kekulene	0.690	0.877	0.881

derived B indices vary in the interval from about 1/2 to 1, the largest possible value assumed to belong to benzene. A comparison between the B index of aromaticity and indices based on the approach of Julg shows some differences for individual benzenoids. For example, the B indices for naphthalene, perylene, and quaterrylene, which are all formally built by connecting naphthalene units by essentially single CC bonds, are the same. The Julg indices based on AM1 calculations for the same compounds show a decreasing trend, the largest value belonging to naphthalene. Clearly, the decrease of Julg's index can be attributed to the increase in the number of essentially single CC bonds in perylene and quaterrylene, which do not participate in conjugation but nevertheless influence the average bond distance $\langle d \rangle$. For more details on Julg's bond length indices, the reader should consult a recent paper by Kiralj and Ferreira⁶⁶⁸ on predicting CC bond lengths in planar benzenoid polycyclic hydrocarbons, where one can also find a list of over 300 experimental and calculated bond lengths for some 27 smaller benzenoid hydrocarbons.

One can construct other indices for benzene character of benzenoid hydrocarbons, which we will designate as B' in order to differentiate them from the index B . For example, one can consider the Kekulé index,⁵⁹⁵ which assigns to individual Kekulé valence structures an index derived from local properties of molecular orbitals, and take the average over all Kekulé structures. Even though for many Kekulé structures this index is bigger than the Kekulé index of benzene, the average Kekulé index appears smaller for polycyclic benzenoid hydrocarbons than it is for benzene. However, for an index to reflect benzene character, one expects certain trends among structurally related benzenoids to be satisfied, such as

$$B'(\text{naphthalene}) > B'(\text{anthracene}) > B'(\text{tetracene}) > \dots$$

$$B'(\text{fully benzenoid hydrocarbons}) > B'(\text{benzenoid hydrocarbons})$$

While the average Kekulé index satisfies the first condition, it apparently fails to satisfy the second, because B' (naphthalene) $>$ B' (triphenylene), naphthalene having migrating π -sextets and triphenylene being a fully benzenoid hydrocarbon.

Nevertheless, the Kekulé index, which assigns to individual Kekulé valence structures a numerical value, is of some interest, as it reflects the relative importance of individual Kekulé valence structures, a topic which has received some but apparently not sufficient attention in the literature.

C. C of Aromaticity

Some caution is required when considering bigger and bigger molecules, including benzenoid hydrocarbons, in which there could be considerable variations in local properties. Already in smaller benzenoids, such as perylene and bisanthene, in which the central CC bonds are essentially single (that is, they are single CC bonds in all Kekulé valence structures), we have portions of a molecule that are not contributing to RE, and thence to aromaticity. By averaging CC bond lengths, the contributions from various rings, or the contributions from different Kekulé valence structures, we may be diluting the aromatic characteristics of a molecule with spurious contributions. It does appear that useful characterization of benzenoid hydrocarbons may follow if we consider individual benzene rings, rather than taking the average of such contributions from all rings. This leads us to a ring index which we refer to as C of aromaticity, where C stands for Clar, which is defined as⁵³⁹

$$C = [\text{RRE}(R_1) - \text{RRE}(R_{r \neq 1})] / [\text{RRE}(R_1) + \text{RRE}(R_{r \neq 1})]$$

$\text{RRE}(R_1)$ is the part of the computed ring resonance energy of individual benzene rings that comes from the presence of the conjugated circuits R_1 , while $\text{RRE}(R_{r \neq 1})$ is the part of the computed contribution to the resonance energy for the considered ring that comes from the presence of all other conjugated circuits contributing to RE to the particular benzene ring. The denominator $[\text{RRE}(R_1) + \text{RRE}(R_{r \neq 1})]$ is in fact the total ring resonance energy (RRE), which thus makes C a dimensionless number, always less than one, except for benzene, for which by definition $C = 1$. In the next section we give numerical examples of the RRE.

XXV. Local Aromaticity

It is not only among benzenoids that different molecules show different degrees of aromatic character, but within single polycyclic conjugated hydrocarbons, different rings show different local aromaticities. Dewar explicitly mentioned extending the notion of aromaticity criteria to individual rings in polycyclic systems.⁶⁶⁹ The pioneering work on bridging the gap between calculated MO results and characterization of local aromaticity of benzene rings was attributed to Polansky and Derflinger,⁵⁸² whose work deserves more attention. They found some

justification for Clar's model of localized benzenoid regions in polycyclic conjugated benzenoids, and they derived a ring index characterizing individual benzene rings of a molecule. This ring index is determined from computed MO coefficients when the MO's of the system are expanded in sets of MO's of each ring. The "benzene character" for benzene rings of numerous smaller benzenoid hydrocarbons reported by Polansky and Derflinger was based on using the HMO approach, but conceptually the approach is quite general and can be extended to more sophisticated MO calculations.

A. The Approach of Polansky and Derflinger

In the standard MO approach to conjugated hydrocarbons (e.g., in the HMO calculations), the molecular orbitals are expressed as a linear combination of atomic orbitals. However, it is possible, as Polansky and Derflinger outlined,⁵⁸² to express the same molecular orbitals in terms of molecular orbitals of the benzene ring. As a result, instead of obtaining information on the contributions of molecular orbitals to the bond orders, one obtains the contributions of a set of benzene orbitals to individual benzene rings of polycyclic benzenoid hydrocarbons. In other words, the "benzene character" described by Polansky and Derflinger, "is the projection of occupied π -MO's in a given hexagon L of a polycyclic benzenoid hydrocarbon onto the three occupied MO's of a benzene molecule located on that position."⁵²³

In Figure 92 we illustrate for a collection of smaller benzenoid hydrocarbons the benzene ring indices as reported by Polansky and Derflinger.⁵⁸² The results are quite interesting, if not astounding. As one can see, there are considerable variations among individual rings within a molecule and between rings in different molecules. If we ignore diphenyl and hexaphenyl, in which benzene rings are bridged by a single CC bond rather than fused, and in which higher values for the ring indices were found than in benzene, the ring indices of Polansky and Derflinger are smaller than the value for benzene, varying between about 0.680 to 0.950. Observe also that the variations are more pronounced in some molecules than others. A more careful examination of the results of Polansky and Derflinger shows that the aromatic character of individual rings is far from uniform. Moreover, the variations show some anticipated and some unexpected regularities. As a rule, terminal rings in benzenoid hydrocarbons show greater similarity to benzene, suggesting that the local aromaticity may be influenced to a considerable degree by specifics of molecular periphery patterns. Highly significant are the observed large differences in benzene character among many adjacent rings. This is particularly visible in the cases of triphenylene (**6/92**), tetrabenzanthracene (**15/92**), dibenzopyrene (**13/92**), and hexabenzocoronene (**20/92**). Observe that all the mentioned benzenoids are those that Clar classified as "fully benzenoid". In comparison with rings in other benzenoids shown in Figure 92, they all show a large benzene character for benzene rings which are the sites of aromatic π -sextets. It is significant vindication for Clar's model of

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