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A Simple Approach for the Evaluation of Local Aromaticities

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In the present work, an extensive study of the π-localized molecular orbitals of a set of 80 polycyclic hydrocarbons has been undertaken in order to clarify the relationship between resonance energies, local aromaticity, and electronic delocalization. A simple way of obtaining local resonance energies corresponding to bonds or rings is given; addition of these local resonance energies reproduces the global resonance energy of the system. According to the present analysis, aromaticity in alternant systems is consistently related to local electronic delocalization. In nonalternant systems, however, local electronic delocalization is affected by charge separation and cannot be systematically related to aromaticities.

Introduction

Notwithstanding some recent criticisms, which have undoubtedly helped to clarify its precise meaning, aromaticity still remains one of the central concepts of organic chemistry.[1] Therefore, and despite the difficulty of giving a definition of aromaticity that can be directly related to experimental quantities,[2] the numerical evaluation of resonance energies (REs) continues being a subject of unabated interest. Without doubt the most important contribution in this field was made by Dewar several years ago,[3] when he defined the (π) RE of a conjugated system as the difference in the total (π) energy of the system and the (π) reference energy of a suitable localized system (an acyclic conjugated polyene, in the case of cyclic conjugated hydrocarbons). Since for a (π) localized system the total (π) energy can be expressed, to a good degree of approximation, as a sum of (π) bond energies,[4] the (π) RE of a conjugated system is given by eq 1 where B is the number

$$\mathrm{RE} = E_\pi(\text{conjugated molecule}) - \sum_{i=1}^{B} n_i E_i \qquad (1)$$

of different bond types of acyclic polyenes, n_i is the number of bonds of each type present in the system under investigation, and E_i is the mean π-energy of the corresponding bond type. REs were calculated originally within the framework of Pariser–Parr–Pople theory,[3,4] but qualitatively similar results have been obtained either with ab initio,[1e,5] Hückel,[6] or graph–theoretical methods.[7] Somewhat conceptually different approaches based in valence-bond formalisms[8] or in the absolute hardness concept[9] also produce essentially equivalent sets of REs. In any case, it is empirically true that for conjugated systems, the molecular RE is a parameter which gives a generally useful measure of the kinetic and thermodynamic stability.[10] Moreover, it has been shown[11] that there is a direct theoretical relationship between REs and magnetically induced molecular ring currents.

Although according to the definition of RE (eq 1) aromaticity is a *global* molecular property, both experimental evidence and chemical intuition (based on Hückel aromaticity rule for monocyclic systems) tend to indicate that individual rings in a polycyclic compound may have different degrees of aromatic character. This idea, in connection with the so-called Fries rule[12] on the relative importance of individual Kekulé structures, was first introduced by Clar,[13] who proposed a symbolic representation of polycyclic benzenoid systems in which the individual rings presented different degrees of "benzene-like" character, according to the presence or absence of "aromatic sextets". More recently, several ways of putting these ideas on a more quantitative (and theoretically more sound) basis have been developed, mainly in the framework of graph theory. Of special significance appear to be the conjugated circuit method introduced by Randić,[8d,14] the

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partial structure count procedure of Herndon,[8a,b,15] and the reduced acyclic reference polynomial concept forwarded by Aihara.[16] Significantly, ring aromaticities obtained by either method agree reasonably well with each other and have been correlated to experimental local magnetic properties.[14b,c] A problem associated with these procedures is, however, that since some rings can be expressed as the envelope of smaller ones, the individual ring aromaticities do not add up to the total RE of the molecule. There have also been some attempts to derive REs associated with individual bonds,[17] but their application has been very limited because of computational difficulties.[17a]

On the other hand, the energetic stabilization associated with the aromaticity of a cyclic conjugated system has usually been related to electronic delocalization, which in turn can be associated with experimentally observable "aromatic" properties, such as bond-length equalization.[18] In the framework of π-electron MO theory, the delocalization of canonical molecular orbitals (CMOs)[19] has been (erroneously) regarded as a proof of electronic delocalization in conjugated π-systems. Several years ago, England and Ruedenberg[20] pointed out that electronic delocalization should in fact be evaluated by means of the delocalization degree of localized molecular orbitals (LMOs), and they ascribed the positive RE of aromatic conjugated systems to the fact that even the maximally localized π-molecular orbitals were more delocalized than the ethylene π-orbital, so that the electronic energies were accordingly lower. In a similar way, Lipscomb[21] has proposed that there is a close relationship between the near-indeterminacy of LMOs in π-orbital localizations and the concept of local aromaticity.

It should be noted however that since ethylene cannot be considered as an adequate reference structure for the evaluation of REs,[3] the above results do not constitute a completely valid proof of the relationship between aromaticity (positive RE) and electronic delocalization. More recently, Haddon[22] has analyzed the degree of localization of the π-LMOs of cyclobutadiene, benzene, and cyclooctatetraene relative to that of the central π-bond of 1,3,5-hexatriene, and has found that it can be correlated with the REs of these compounds. Since hexatriene is more similar to Dewar's acyclic reference structure than ethene, this result suggests that in general any conjugated system with a positive RE should exhibit a stronger degree of electronic delocalization than its acyclic reference structure. Proceeding along these lines, we have undertaken an extensive study of the π-LMOs of conjugated polycyclic hydrocarbons, in order to clarify the relationship between RE, local aromaticity and electron delocalization in these systems.

Table I. π-Bond Energy Parameters and Mean π-LMO Energies of Acyclic Conjugated Polyenes

bond type	$E_i/2$[a]	$\langle e_i^L \rangle$[b]
$H_2C{=}CHCH{=}$	1.1117	1.1270
$H_2C{=}CHCR{=}$	1.1168	1.1181
$H_2C{=}CR{-}$	1.2160	1.2219
$={CRCH}{=}CHCR{=}$	1.2499	1.2329
$={CHCH}{=}CHCR{=}$	1.2622	1.2459
$={CHCH}{=}CHCH{=}$	1.2697	1.2637
$-HC{=}CR-$	1.3762	1.3570
$-RC{=}CR-$	1.4985	1.4737

[a] Half-values of parametrized energies, in β units. [b] Mean energies of LMOs, in β units.

Procedure

In fact, the well-known eq 1 offers a very direct way for a partition of the global RE of a conjugated system into quantities ascribable to individual bonds, provided that one can find a suitable partition of the total π-electronic energy of the system. For the sake of simplicity, we will restrict ourselves to the framework of Hückel molecular orbital (HMO) method, but the ideas we shall develop are valid for higher levels of theory.[23]

Within the HMO model, the total π-energy of a conjugated system is simply given by twice the sum of orbital energies, so that the most coherent way to effect a partition of the π-energy would be to assign to each bond twice the energy of the LMO centered upon it. If the total π-electron energy of the acyclic polyene reference structure is then partitioned among the same set of bond types defined by the LMOs of the system under study, the global RE can be decomposed in quantities corresponding to the *local* resonance energies (LREs) of the individual π-bonds. In this way, eq 1 can be reformulated as

$$\mathrm{RE} = 2\sum_i (e_i^{\mathrm{L}} - E_i/2) \qquad (2)$$

where the summation runs over the π-bonds of the system, e_i^{L} is the orbital energy of the π-LMO centered upon bond i, and E_i has the same meaning as in eq 1. Each individual term can be regarded as the local resonance energy per electron (LREPE) or bond i:

$$(\mathrm{LREPE})_i = e_i^{\mathrm{L}} - E_i/2 \qquad (3)$$

Since these quantities are additive, one can now define *ring* resonance energies (RREs) which are also additive with respect to the global RE, simply by adding the weighted LREPE values of the bonds contained in the ring:

$$(\mathrm{RRE})_k = \sum_{i \epsilon R_k} w_i (\mathrm{LREPE})_i \qquad (4)$$

where the summation runs over the bonds i contained in the ring k, and w_i equals one or two, depending on whether the bond i is shared by another ring or not.

The most widely used set of acyclic reference structure parameters E_i is that derived by Schaad and Hess.[6] These parameters are however not useful for the purpose of calculating LREs because of several reasons. Firstly, the arbitrary π-bond type classification of Schaad and Hess includes "single" and "double" π-bonds, and they cannot

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(23) In fact, a sufficient condition is that the system can be described by a monodeterminantal wave function, since in this case the global electronic energy can always be decomposed in terms ascribable to individual MOs (either CMOs or LMOs).

be directly compared with π-LMOs, which are centered upon "double" π-bonds only. Secondly, because of inherent redundancy relations between the bond types, the E_i values can only be obtained after the assignment of arbitrary values to two of them, so that the individual "bond" energies do not have unique values.

On the other hand, we have shown[24] that the arbitrary bond-type classification of Schaad and Hess can be replaced by a natural classification obtained from a systematic study of π-LMOs of acyclic conjugated polyenes. After a least-squares fit to the total π-energies of acyclic polyenes, a set of eight bond-energy parameters E_i can be derived. Since no arbitrary value has to be assigned to any of them, the individual bond energies have well-defined values, which are moreover very close to twice the mean LMO energies of the corresponding bond types, $\langle e_i^L \rangle$ (see Table I).

The global REs obtained with the parameters E_i of Table I are very close to those of Hess and Schaad,[6a] so they can be used as global aromaticity indices with similar reliability to that of other methods.[3-6] In the present work, we have undertaken a systematic study of the π-LMOs of 80 mono- and polycyclic conjugated systems (including buckminsterfullerene, 80); the orbital energies thus obtained, in conjunction with the E_i parameters of Table I, have allowed for the first time an extensive evaluation of "local" or "bond" aromaticities (LREs) which upon addition reproduce the global RE of the molecule.

The localization has been effected on π-CMOs obtained at the Hückel level,[24] (so that the results can be easily compared with the most extensive sets of global REs[6,7]) by means of a localization method which relies only on molecular topology.[25] The essentials of the method are the following:

For a conjugated hydrocarbon of N carbon atoms, any minimal-basis π-MO ϕ_i can be expressed as a linear combination of a set of N p_π AOs, χ_r:

$$\phi_i = \sum_{r=1}^{N} \chi_r C_{ri} = \mathbf{X}\mathbf{C}_i \; (i = 1, ..., N) \tag{5}$$

In the HMO approximation the M occupied π-CMOs of a closed-shell $2M$-electron system in its ground electronic state are the M eigenvectors of the adjacency matrix $\mathbf{T}$ with lowest eigenvalues, obtained according the matrix equation

$$\mathbf{TC} = \mathbf{CE} \tag{6}$$

where $\mathbf{C}$ is an $N\times M$ matrix whose columns are the $\mathbf{C}_i$ vectors (which will be supposed to be real) and $\mathbf{E}$ is a diagonal $M\times M$ matrix whose elements are the energies of the occupied CMOs (in β units and taking $\alpha = 0$ as the origin). If a suitable additional condition is now imposed, one can select the set of MOs which present the maximum degree of localization (LMOs). We have shown that a straightforward way of obtaining π-LMOs[24,25] is by maximization of the functional S (called localization sum)

$$S = \mathrm{Tr}(\mathbf{Q}^t\mathbf{Q}) \tag{7}$$

where $\mathbf{Q}$ is a $N\times M$ matrix whose elements are

$$\mathbf{Q}_{ri} = (\mathbf{C}_i\mathbf{C}_i^t)_{rr} = (C_{ri})^2 \tag{8}$$

It is well known[20a,21,26] that in the case of aromatic molecules the π-LMOs arising from intrinsic localization methods appear often in the form of three-centered MOs which cannot be directly related to any of the bond-types of acyclic polyenes, whose LMOs are always essentially bicentric.[24] In order to overcome this difficulty, we have used when necessary an external localization variant of the above procedure.[25,26] Given a Kekulé structure, we can obtain the LMOs adapted to it simply by maximizing the modified localization sum

$$S = \mathrm{Tr}(\mathbf{Q}^t\mathbf{KQ}) \tag{9}$$

where $\mathbf{K}$ is a $N\times N$ matrix whose elements are $\mathbf{K}_{rt} = 1$ if AOs r and t are joined by a π-bond in the Kekulé structure, and 0 otherwise. With this choice the localization sum reduces to

$$S = 2\sum_{i=1}^{M} \sum_{r,t}^{\pi\text{-bonds}} \mathbf{Q}_{ri}\mathbf{Q}_{ti} \tag{10}$$

where the second summation runs only over the AO pairs π-joined in the Kekulé structure. In this way, one obtains π-LMOs centered preferentially upon the double bonds of the chosen Kekulé structure.[26] When, as it often happens in the case of polycyclic compounds, more than one (not symmetry equivalent) Kekulé structure can be written, we have selected the one with largest Kekulé index,[27] i.e. the covalent resonance structure which would probably have the most important weight in a valence-bond calculation.[28] In any case, the resulting global REs have been shown to be very insensitive to the choice of Kekulé structure.[6a]

After having obtained the set of coefficients ($\mathbf{C}_i$), $i = 1, ..., M$ which give a maximum value of the localization sum of eqs 7 or 10, the energies e_i^L of the π-LMOs are given (in β units and taking $\alpha = 0$ as the origin) by

$$e_i^L = (\mathbf{C}^t\mathbf{TC})_{ii} = \sum_{r,t}^{N} C_{ri}T_{rt}C_{ti} \tag{11}$$

so that it can be readily seen that the energy of a π-LMO of a conjugated hydrocarbon increases (in absolute value, since β is a negative magnitude) with increasing delocalization degree of the orbital.[20] The LREs that we have defined by eq 3 should therefore increase (in absolute value) with the local electronic delocalization of the bond. A positive value of RE per electron in β units (REPE) for a cyclic conjugated system implies then that *on the average*, its π-electrons are more delocalized than those of the corresponding acyclic reference structure.

In summary, global aromaticity (as measured by RE) is directly related to global electronic delocalization (relative to that of the acyclic reference structure). This does not imply however that all of the bonds or rings in an aromatic compound are delocalized, since relatively localized substructures can coexist with others which are much more delocalized. In the next sections we present the results of our analysis of REs in terms of local quantities (LREPEs or RREs) in an extensive set of conjugated hydrocarbons which spans many different structural types.

Results and Discussion

1. Polycyclic Benzenoid Hydrocarbons. The LREPE and global REPE values of a set of benzenoid hydrocarbons, together with the Kekulé structure chosen for the calculation, are shown in Table II. "Aromatic" double bonds (i.e., with LREPE/β > 0.010) appear in boldface, "antiaromatic" double bonds (LREPE/β < −0.010) appear as broken lines, and those with intermediate

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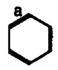
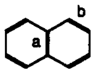
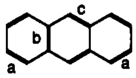
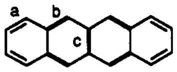
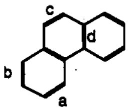
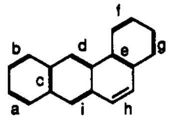
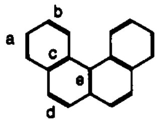
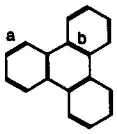
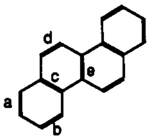
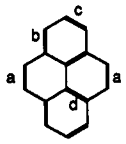
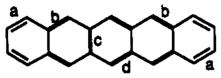
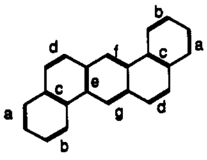
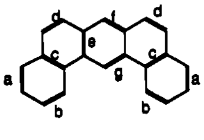
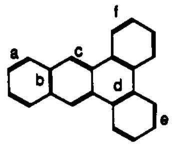
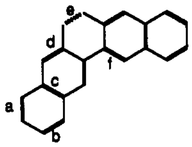
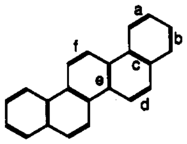
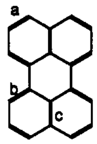
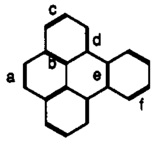
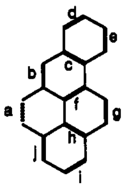
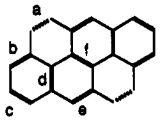
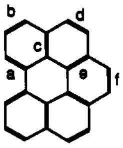
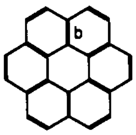
Table II. Global Resonance Energies (REPE) and Local Resonance Energies (LREPE) of Polycyclic Benzenoid Hydrocarbons

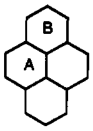
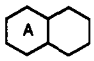
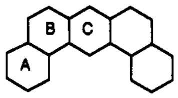
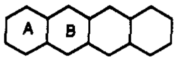
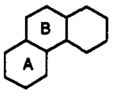
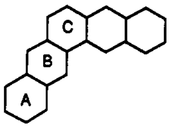
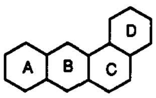
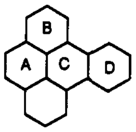
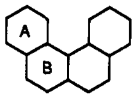
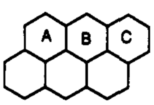
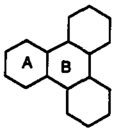
compd	Kekulé structure	LREPE[a]	REPE[a]
1		a: +0.0636	+0.064
2		a: +0.0921 b: +0.0506	+0.051 +0.051
3		a: +0.0225 b: +0.1124 c: +0.0774	+0.051
4		a: +0.0004 b: +0.0702 c: +0.1309	+0.046
5		a: +0.0566 b: +0.0565 c: +0.0393 d: +0.0815	+0.061
6		a: +0.0456 b: +0.0459 c: +0.1091 d: +0.0614 e: +0.0436 f: +0.0650 g: +0.0633 h: +0.0005 i: +0.0682	+0.056
7		a: +0.0549 b: +0.0548 c: +0.0844 d: +0.0455 e: +0.0706	+0.061
8		a: +0.0606 b: +0.0684	+0.063
9		a: +0.0548 b: +0.0549 c: +0.0846 d: +0.0461 e: +0.0711	+0.061
10		a: +0.0129 b: +0.0640 c: +0.0711 d: +0.0915	+0.053
11		a: −0.0021 b: +0.0438 c: +0.1337 d: +0.0836	+0.043
12		a: +0.0600 b: +0.0609 c: +0.0620 d: +0.0186 e: +0.1002 f: +0.0678 g: +0.0740	+0.059
13		a: +0.0601 b: +0.0608 c: +0.0617 d: +0.0174 e: +0.1001 f: +0.0739 g: +0.0680	+0.058
14		a: +0.0474 b: +0.1062 c: +0.0538 d: +0.0378 e: +0.0659 f: +0.0669	+0.059
15		a: +0.0475 b: +0.0479 c: +0.1033 d: +0.0548 e: −0.0158 f: +0.0449	+0.053
16		a: +0.0554 b: +0.0553 c: +0.0838 d: +0.0442 e: +0.0744 f: +0.0530	+0.062
17		a: +0.0559 b: +0.0408 c: +0.0927	+0.057
18		a: +0.0382 b: +0.0885 c: +0.0675 d: +0.0540 e: +0.0283 f: +0.0674	+0.062
19		a: −0.0120 b: +0.0458 c: +0.0931 d: +0.0507 e: +0.0527 f: +0.0807 g: +0.0450 h: +0.0926 i: +0.0674 j: +0.0605	+0.058
20		a: −0.0120 b: +0.0587 c: +0.0634 d: +0.1011 e: +0.0448 f: +0.0899	+0.055
21		a: +0.0468 b: +0.0637 c: +0.0871 d: +0.0431 e: +0.0776 f: +0.0554	+0.063
22		a: +0.0516 b: +0.0810	+0.066

[a] In β units.

LREPE values ("nonaromatic") are denoted by a pair of continuous lines.

As it can be seen, the individual bonds have generally positive LREs. Some exceptions are found, however: (i) The terminal rings of the linear polyacenes beyond anthracene (3) have essentially nonaromatic bonds (cf. 4 and 11). (ii) The peripheral bonds of some hydrocarbons are either nonaromatic (cf. bond h of benzanthracene 6) or even slightly antiaromatic (cf. bond e of pentaphene 15 or bond a of anthanthrene 20). It is interesting to observe

Table III. Ring Resonance Energies (RRE) of Benzenoid Hydrocarbons

compd	rings	RRE[a]	compd	rings	RRE[a]
1		+0.382	10		A: +0.118 B: +0.362
2		A: +0.295			
3		A: +0.202 B: +0.422	13		A: +0.304 B: +0.144 C: +0.384
4		A: +0.016 B: +0.412			
5		A: +0.308 B: +0.242	15		A: +0.294 B: +0.303 C: −0.032
6		A: +0.292 B: +0.368 C: +0.045 D: +0.300	18		A: +0.253 B: +0.332 C: +0.028 D: +0.298
7		A: +0.304 B: +0.246	20		A: −0.024 B: +0.281 C: +0.345
8		A: +0.205 B: +0.311			

[a] In β units.

that the more localized bonds always correspond to the regions of lowest 1,2-bislocalization energy.[21,29]

By means of eq 4, RREs can be easily calculated from the LREs given in Table II. Some selected examples are given in Table III. In the case of symmetry equivalent bonds (or rings) which have different LREPE (or RRE) values for a given Kekulé structure (this happens when several symmetry equivalent Kekulé structures can be written for the molecule), we have quoted the average value; note that this does not affect to the correct additivity of local REs.

In this case, some discrepancies are found with Dewar's ring aromatic energies,[29] or with the graph–theoretical partial REs obtained by Aihara,[16] since in general we find that electronic localization is greater in peripheral rings than in central ones. The origin of this discrepancy lies in the fact that Dewar's and Aihara's energies refer to the RE which is lost by the system when a particular ring is removed (and in fact, are closely related to 1,4-bislocalization energies[29]), while our RREs are a measure of the intrinsic "aromaticity" of a given ring.

On the other hand, it is interesting to observe that in every case the location of the more aromatic benzenoid rings obeys Clar's rule of maximal number of isolated sextets.[13b,14b] We can therefore conclude that for polycyclic benzenoid systems the presently derived LREs constitute both a verification and a quantification of Clar's "aromatic sextet" formalism.

2. Cyclobutadiene-Containing Alternant Hydrocarbons. The LREPE and RRE values of some cyclobutadiene-containing alternant polycyclic systems are shown in Tables IV and V, respectively. These compounds are very interesting, particularly when they contain "aromatic" $4n + 2$ and "antiaromatic" $4n$ rings. In this case, the global REs appear to be determined by a subtle interplay between the relative number and topology of both kinds of rings.[30] It is also interesting to observe that while the vast majority of the parent hydrocarbons shown are not known, in some cases the substitution of a bond (intuitively identified as the most "antiaromatic") has allowed the isolation of the compound (cf. naphtho[*b*]cyclobutadiene **25**[31]). In this context, the LREPE values can be very useful for future synthetic studies on these compounds, helping to identify the regions which will need to be substituted.

Some general rules, regarding ring aromaticities, can be formulated for these systems according to the present results: (a) When fused to six-membered rings, four-membered ones are always antiaromatic or nonaromatic. (b) In systems with a linearly fused cyclobutadiene ring (cf. compounds **27**, **31**, **33**, and **37**), terminal benzenoid rings are always aromatic. (c) In systems with an angularly fused cyclobutadiene ring (cf. compounds **26** and **32**), terminal six-membered rings are always nonaromatic or even slightly antiaromatic. (d) When fused to other $4n$-membered rings, cyclobutadiene rings can either be aromatic or antiaromatic.

In connection with the above rule d, which may seem at first glance somewhat surprising, it is interesting to consider in some detail the case of bicyclo[6.2.0]decapentaene, **43**. This compound has been synthesized[32] and experimentally characterized as being weakly aromatic.[33] Although the global REPE value of -0.024β would classify

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(29) Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum Press: New York, 1975.

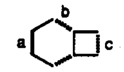
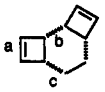
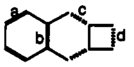
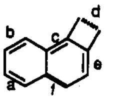
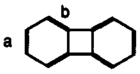
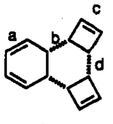
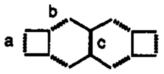
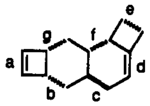
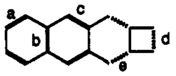
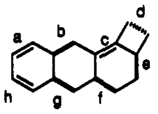
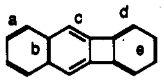
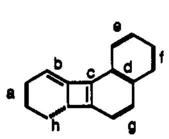
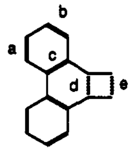
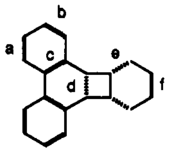
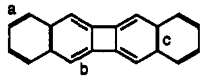
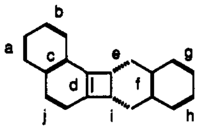
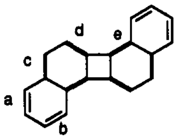
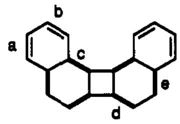
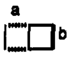
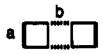
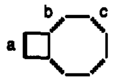
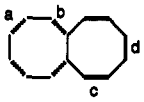
(30) (a) Cava, M. P.; Mitchell, M. J. *Cyclobutadiene and Related Compounds*; Academic Press: New York, 1976. (b) Vollhardt, K. P. C. *Top. Curr. Chem.* **1975**, *59*, 113. (c) Baker, W.; Mc Omie, J. F. W. In *Non-Benzenoid Aromatic Compounds*; Ginsburg, D., Ed.; Interscience: New York, 1959. (d) Lloyd, D. *Carbocyclic Non-Benzenoid Aromatic Compounds*; Elsevier: New York, 1966. (e) Snyder, J. P. *Nonbenzenoid Aromatics*, 2 Vols.; Academic Press: New York, 1969–1971.

(31) (a) Cava, M. P.; Hwang, B.; Van Meter, J. P. *J. Am. Chem. Soc.* **1963**, *85*, 4032. (b) Toda, F.; Dan, N. *J. Chem. Soc., Chem. Commun.* **1976**, 30.

(32) (a) Oda, M.; Oikawa, H. *Tetrahedron Lett.* **1980**, *21*, 107. (b) Kawka, D.; Mues, P.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1003.

(33) Kabuto, C.; Oda, M. *Tetrahedron Lett.* **1980**, *21*, 103.

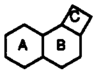
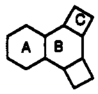
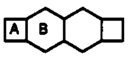
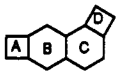
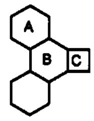
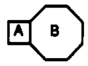
Table IV. Global Resonance Energies (REPE) and Local Resonance Energies (LREPE) of Cyclobutadiene-Containing Alternant Hydrocarbons

compd	Kekulé structure	LREPE[a]	REPE[a]
23		a: +0.0301 b: −0.0172 c: −0.0772	−0.020
24		a: −0.0084 b: −0.1113 c: −0.0431	−0.043
25		a: +0.0659 b: +0.0740 c: −0.0228 d: −0.0339	+0.021
26		a: −0.0002 b: +0.0000 c: −0.0027 d: −0.0772 e: +0.0068 f: +0.0629	−0.002
27		a: +0.0567 b: +0.0238	+0.035
28		a: −0.0036 b: −0.0321 c: −0.0027 d: −0.1054	−0.026
29		a: −0.0610 b: −0.0271 c: +0.0559	−0.025
30		a: −0.0065 b: −0.0633 c: +0.0405 d: −0.0077 e: −0.0644 f: −0.0248 g: −0.0631	−0.027
31		a: +0.0494 b: +0.1052 c: +0.0565 d: −0.0225 e: −0.0658	+0.020
32		a: −0.0048 b: +0.0184 c: +0.0091 d: −0.1001 e: +0.0121 f: +0.0763 g: +0.0195 h: −0.0043	+0.003
33		a: +0.0573 b: +0.0901 c: −0.0010 d: +0.0322 e: +0.0613	+0.041
34		a: +0.0391 b: −0.0093 c: −0.0090 d: +0.1047 e: +0.0461 f: +0.0477 g: +0.0815 h: −0.0112	+0.036
35		a: +0.0509 b: +0.0464 c: +0.1165 d: −0.1478 e: −0.2277	+0.007
36		a: +0.0548 b: +0.0527 c: +0.0931 d: −0.0269 e: −0.0118 f: +0.0370	+0.039
37		a: +0.0557 b: +0.0079 c: +0.0924	+0.044
38		a: +0.0490 b: +0.0476 c: +0.1026 d: +0.0034 e: −0.0296 f: +0.0777 g: +0.0608 h: +0.0609 i: −0.0314 j: +0.0768	+0.042
39		a: +0.0041 b: +0.0053 c: +0.0856 d: +0.0500 e: +0.0338	+0.036
40		a: +0.0041 b: +0.0064 c: +0.0413 d: +0.0429 e: +0.0850	+0.036
41		a: −0.1625 b: +0.1511	−0.058
42		a: +0.0591 b: −0.1895	−0.065
43		a: +0.0673 b: −0.0796 c: −0.0144	−0.024
44		a: −0.0167 b: −0.0528 c: +0.0419 d: +0.0207	−0.005

[a] In β units.

this molecule as being slightly antiaromatic, the analysis of LREPEs shows that the antiaromaticity is due to the cyclooctatetraene π-bonds, the cyclobutadiene π-bond being essentially aromatic. This fact is easily rationalized if one assumes that, in the same way that antiaromaticity decreases with ring size in monocyclic compounds, the π-electron distribution of a polycyclic system tends to locate the antiaromaticity in the largest ring, in order to reduce its value. Moreover, the location of antiaromaticity in the eight-membered ring is even more favorable in the real molecule, which can diminish its value simply by folding of this ring (mechanism which would not be operative if the antiaromaticity was located in the much more rigid four-membered ring). This explains the relative stability of the compound, whose cyclooctatetraene moiety slightly deviates from planarity.[34] It is also interesting

Table V. Ring Resonance Energies (RRE) of Some Cyclobutadiene-Containing Alternant Hydrocarbons

compd	Rings	RRE[a]
23		A: −0.009 B: −0.154
24		A: −0.395 B: −0.017
25		A: +0.338 B: −0.017 C: −0.068
26		A: 0.000 B: +0.134 C: −0.154
27		A: +0.209 B: 0.000
28		A: −0.014 B: −0.339 C: −0.005
29		A: −0.122 B: −0.053
30		A: −0.013 B: −0.253 C: +0.016 D: −0.129
35		A: +0.311 B: +0.085 C: −0.603
43		A: +0.135 B: −0.376

[a] In β units.

to observe that the localization degree of the π-bonds of bicyclo[6.2.0]decapentaene, as measured by the bond ellipticities calculated with both the HF/STO-3G and MNDOC methods, increases in the order a < c < b, in complete agreement with the present simple results.[34]

3. Nonalternant Hydrocarbons. The LREPEs of several nonalternant mono- and polycyclic hydrocarbons are shown in Table VI. In the same set we include also some alternant fulvenes and radialenes, for comparison purposes.

The aromatic character of nonalternant conjugated hydrocarbons has always been the subject of some controversy. In his pioneering study of REs, Dewar[3] claimed that the HMO method was not adequate for the estimation of the aromaticities of nonalternant hydrocarbons, because the α and β parameters for those systems were substantially different from those of alternant hydrocarbons, and their π-energies could not be directly compared to those of the acyclic reference structures, which are always alternant. On the other hand, Hess and Schaad[6a] argued that a judicious choice of the bond-type classification in the reference structures could overcome this basic deficiency. Their opinion was substantiated by the fact that the REs of nonalternant systems showed a remarkable agreement with experimental stabilities, as well as with REs calculated by more involved procedures.

The global REPE values obtained by us[24] essentially reproduce the earlier results of Hess and Schaad[6a] and therefore show a satisfactory correlation with the available experimental data on those systems. In this connection, our REPE value of +0.027β for buckminsterfullerene (**80**) is in complete agreement with the most recent aromaticity evaluations on this compound.[35] Moreover, some interesting results emerge when the RE is analyzed in terms of its local contributions.

In the first place, inspection of Table VI shows that the bonds contained in three- or seven-membered rings are generally aromatic, while those contained in five-membered rings are generally antiaromatic, irrespectively of the global aromaticity of the system. In fact, the only exceptions are found in the case that the odd-membered ring is fused to a benzenoid moiety (cf. dipleiadiene, **78**).

In the second place, it is readily seen that the bonds which are exocyclic only to five-membered rings are always aromatic, while those exocyclic exclusively to three- or seven-membered rings are antiaromatic. When a bond is exocyclic to both kinds of rings at the same time, it is always aromatic.

This leads to the quite unexpected result that even in globally aromatic nonalternant systems such as calicene (**59**), sesquifulvalene (**61**), or azulene (**68**) one finds bonds with a large negative LREPE value. In fact, this reflects the known tendency of five-membered rings to acquire a partial negative charge and the opposite behavior of three- or seven-membered rings, which stabilize by acquiring a net positive charge. In terms of LMOs, this implies that a three-membered ring tends to be described by *one* LMO (in order to attain the "aromatic" number of two π-electrons), while both five- and seven-membered rings tend to be described by *three* LMOs (in order to attain the equally "aromatic" number of six π-electrons). As an illustrative example of the above considerations, we will take the case of a simple fulvene such as methylenecyclopropene, **49**. While the REPE value of 0.008β correctly reproduces its global nonaromatic character,[36] the strong contribution of dipolar π-resonance structures in which the three-membered ring appears as a cyclopropenium ion causes a strong π-electron delocalization in the ring (and a corresponding electron localization on the exocyclic π-bond). The two opposite effects however very nearly cancel out, and the π-delocalization energy of **49** has been estimated to be similar to that of 1,3-butadiene.[36]

In summary, the LMOs of three- and seven-membered rings tend to be more delocalized than the corresponding acyclic reference structure LMOs, while the LMOs of five-membered rings tend to be more localized due to the fact that they tend to accommodate six electrons on only five atomic centers, irrespectively of the presence or absence of cyclic conjugation. The LREPEs are then systematically either overestimated (in three- and seven-membered rings) or underestimated (in five-membered rings) relative to those of alternant systems. In most cases however the two opposite effects mentioned above cancel each other, so that the global REPE values still give a reasonable estimation of the global aromaticity of the system.

Nevertheless, the present findings clearly reinforce the original criticisms of Dewar[3] about the adequacy of an alternant acyclic reference structure (without appreciable bond polarization) for the evaluation of REs in nonalternant systems (which in most cases exhibit strong bond polarization). It appears therefore that while in alternant systems a close relationship exists between positive REs

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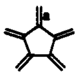
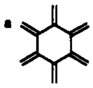
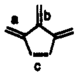
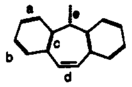
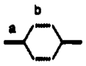
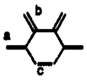
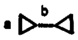
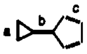
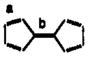
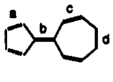
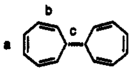
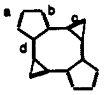
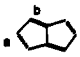
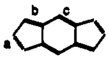
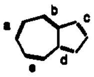
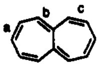
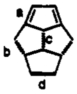
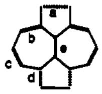
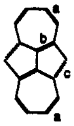
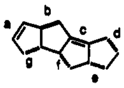
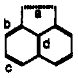
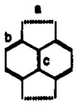
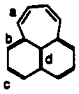
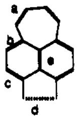
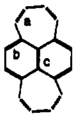
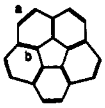
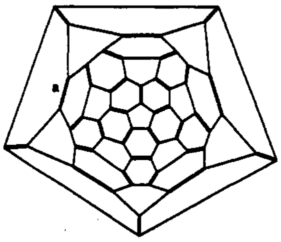
[34] For theoretical studies on **43**, see: Cremer, D.; Schmidt, Th.; Bock, Ch. W. *J. Org. Chem.* **1985**, *50*, 2684 and references cited therein.

[35] (a) Haymet, A. D. J. *J. Am. Chem. Soc.* **1986**, *108*, 319. (b) Klein, D. J.; Hite, G. E.; Schmalz, T. G.; Hite, G. E.; Seitz, W. A. *J. Am. Chem. Soc.* **1986**, *108*, 1031. (c) Hess, B. A., Jr.; Schaad, L. J. *J. Org. Chem.* **1986**, *51*, 3902. For a simple HMO solution of buckminsterfullerene, see: (d) Dias, J. R. *J. Chem. Ed.* **1989**, *66*, 1012.

[36] Norden, T. D.; Staley, S. W.; Taylor, W. H.; Harmony, M. D. *J. Am. Chem. Soc.* **1986**, *108*, 7912.

Table VI. Global Resonance Energies (REPE) and Local Resonance Energies (LREPE) of Nonalternant Hydrocarbons. Some Alternant Hydrocarbons Are Included

compd	Kekulé structure	LREPE[a]	REPE[a]
45		a: +0.0008	+0.001
46		a: −0.0089	−0.009
47		a: 0.0000	0.000
48		a: +0.0008	0.000
49		a: −0.1190 b: +0.1343	+0.008
50		a: +0.1190 b: −0.0632	−0.002
51		a: +0.0085 b: +0.0080 c: −0.0236	0.000
52		a: −0.0298 b: +0.0042 c: +0.0085	−0.003
53		a: +0.0735 b: +0.0727 c: +0.0479 d: −0.0037 e: −0.0319	+0.050
54		a: −0.0392 b: +0.0003	−0.026
55		a: +0.0282 b: −0.0180	+0.005
56		a: +0.0265 b: −0.0112	+0.008
57		a: +0.0107 b: +0.0028 c: −0.0159	+0.001
58		a: +0.1161 b: −0.4985	−0.089
59		a: +0.2338 b: +0.0762 c: −0.0567	+0.049
60		a: −0.0582 b: +0.0853	−0.030
61		a: −0.0578 b: +0.0712 c: +0.0705 d: +0.0518	+0.025
62		a: −0.0046 b: +0.0026 c: −0.0854	−0.012
63		a: −0.0389 b: −0.0465 c: +0.1073 d: +0.0977	+0.046
64		a: +0.2695 b: +0.0149 c: −0.1041	+0.060
65		a: −0.0897 b: +0.0652	−0.012
66		a: −0.0485 b: +0.0120 c: +0.0798	+0.014
67		a: −0.0203 b: −0.0288 c: +0.0528 d: −0.0541	−0.013
68		a: +0.0628 b: +0.1132 c: −0.0195 d: −0.0796 e: +0.0584	+0.027
69		a: +0.0080 b: −0.0087 c: −0.0029	−0.001
70		a: +0.0006 b: −0.0556 c: −0.1182 d: +0.0719	−0.026
71		a: −0.0164 b: +0.0600 c: +0.0543 d: −0.0343 e: +0.1045	+0.031
72		a: +0.0599 b: +0.0625 c: −0.0739	+0.027
73		a: −0.0052 b: +0.0958 c: −0.0070 d: −0.0412 e: −0.0563 f: −0.0740	−0.022
74		a: −0.0489 b: +0.0623 c: +0.0618 d: +0.0847	+0.047
75		a: −0.0576 b: +0.0613 c: +0.0746	+0.029
76		a: −0.0048 b: +0.0414 c: +0.0515 d: +0.0963	+0.039
77		a: +0.0130 b: +0.0615 c: +0.0740 d: −0.0358 e: +0.0870	+0.044
78		a: −0.0134 b: +0.0420 c: +0.1001	+0.024
79		a: +0.0527 b: +0.0727	+0.063
80		a: +0.0272	+0.027

[a] In β units.

and π-electronic delocalization, this becomes less clear for nonalternant systems.

An interesting particular case is that of the recently synthesized dipleiadiene, **78**.[37] While according to their slightly negative LREPE values the π-electrons in the peri-bridges are appreciably localized, the NMR properties of the compound strongly suggest the existence of a paramagnetic ring current in the periphery of the molecule; on the other hand, both the X-ray structure and the magnitudes of the vicinal H,H coupling constants confirm that considerable bond alternation occurs in these bridges. Another illustrative example is that of pyracylene, **75**, whose X-ray structure has only very recently been determined.[38] In accordance to our simple LREPE values, strong bond fixation appears in the fused cyclopentene moieties. Even more interestingly, bond alternation in **75** is higher than that observed in the closely related system of acenaphthylene, **74**,[39] result which is difficult to rationalize on the basis of simple resonance theory.[38] Notice however that the LREPE value for the peri-bridge bond of pyracylene is more negative than that of acenaphthylene. This is then again a clear example of the fact that for nonalternant hydrocarbons π-electron delocalization, while apparently not directly related to aromaticity, is still a very good indicative of bond equalization (at least in several significant cases).

Conclusions

Although the original derivation of the Hückel ($4n + 2$) rule is strictly valid only for monocyclic conjugated systems, the present results show direct evidence that, when analyzed in terms of LMOs, polycyclic hydrocarbons obey an extended form of this rule, which has been formulated by Glidewell and Lloyd[40] as follows: The total π-electron population in polycyclic systems tends to form the smallest ($4n + 2$) groups and to avoid the formation of the smallest $4n$ groups.

In the case of benzenoid systems (cf. compounds **1–22**) this reduces to the well-known fact that the preferred resonance structures are those which maximize the number of isolated aromatic sextets (Clar's rule).[13]

The same principle is seen to hold in the case of systems containing a mixture of four- and six-membered rings (cf. compounds **23–40**); in fact, a closed loop of four π-electrons can be found only in compound **35**, because in this way two aromatic sextets can be constructed.

We can conclude moreover that for alternant systems there is in general a close relationship between aromaticity and local electronic delocalization, since the maximally delocalized LMOs in these compounds are usually found in the rings with smallest $4n + 2$ groups (i.e., in the rings which present an aromatic sextet). Note that the only exceptions occur when increasing the electron delocalization in a ($4n + 2$) ring would enhance the antiaromaticity of two ($4n$) rings (cf. **24** and **28**).

An interesting result of the present study is that such a relationship does not longer hold in general for nonalternant systems (cf. compounds **49–52**, **58–65**, **66–73**). Since these systems also obey Glidewell and Lloyd's rule, their electronic localization is related not only to global or local aromaticity but to the size of the smallest odd-membered ring in which an aromatic doublet or sextet can be included; namely, three- and seven-membered rings are very often delocalized, while five-membered rings are generally localized.

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Registry No. 1, 71-43-2; **2**, 91-20-3; **3**, 120-12-7; **4**, 92-24-0; **5**, 85-01-8; **6**, 56-55-3; **7**, 195-19-7; **8**, 217-59-4; **9**, 218-01-9; **10**, 129-00-0; **11**, 135-48-8; **12**, 53-70-3; **13**, 224-41-9; **14**, 215-58-7; **15**, 222-93-5; **16**, 213-46-7; **17**, 198-55-0; 18, 192-97-2; **19**, 50-32-8; **20**, 191-26-4; **21**, 191-24-2; **22**, 191-07-1; **23**, 4026-23-7; **24**, 61960-82-5; **25**, 277-98-5; **26**, 249-99-0; **27**, 259-79-0; **28**, 13357-18-1; **29**, 42951-00-8; **30**, 236-34-0; **31**, 259-58-5; **32**, 4026-25-9; **33**, 259-56-3; **34**, 252-47-1; **35**, 250-03-3; **36**, 252-23-3; **37**, 258-47-9; **38**, 4023-71-6; **39**, 252-44-8; **40**, 252-24-4; **41**, 1552-98-3; **42**, 71278-50-7; **43**, 20455-01-0; **44**, 257-55-6; **45**, 3227-90-5; **46**, 3227-91-6; **47**, 3227-92-7; **48**, 3227-93-8; **49**, 4095-06-1; **50**, 497-20-1; **51**, 53477-08-0; **52**, 539-79-7; **53**, 2975-79-3; **54**, 5291-90-7; **55**, 32796-95-5; **56**, 502-86-3; **57**, 82849-63-6; **58**, 1608-08-8; **59**, 6249-23-6; **60**, 91-12-3; **61**, 1961-84-8; **62**, 531-45-3; **63**, 73091-52-8; **64**, 1552-99-4; **65**, 250-25-9; **66**, 267-21-0; **67**, 13969-16-9; **68**, 275-51-4; **69**, 257-24-9; **70**, 569-40-4; **71**, 193-85-1; **72**, 3526-04-3; **73**, 13357-37-4; **74**, 208-96-8; **75**, 187-78-0; **76**, 208-20-8; **77**, 194-32-1; **78**, 193-90-8; **79**, 5821-51-2; 80, 99685-96-8.

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