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MULTICENTER BOND INDICES AS A MEASURE OF AROMATICITY

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Abstract

A MO multicenter bond index involving the $\sigma+\pi$ electron population is proposed as a measure of aromaticity. It is related both to the energetical and to the magnetic criteria. The index is applied to linear and angular polycyclic hydrocarbons with benzenoid rings, to hydrocarbons including non-benzenoid rings, to monocyclic azines, benzoazines and other heterocyclic compounds with 5m-rings. The index gives satisfactory values for monocyclic molecules and is shown to be quite suitable in discriminating the relative aromaticity of the different rings in polycyclic ones.

Key-words: Aromaticity; Multicenter bond index; Aromaticity for individual rings.

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Introduction

The statement that aromaticity is an elusive concept has been repeated again and again, so as to become a commonplace. It happens, however, that there is no magnitude defining it unambiguously; it is not an observable property.[1a] Heilbronner is extremely critical about the term, regarding both "the understanding of the chemistry and the physics of the molecules so classified" and the usefulness of explaining it to the students.[1a] Labarre goes further, suggesting the elimination of the term "aromaticity" from scientific vocabulary and proposing to replace it by several different words, each of them referring to one of the multiple aspects comprehended by the word "aromaticity".[1b]

Yet, the term has survived, and even today it is used in the literature, amidst hot discussions. Other authors are in favour of preserving the notion of aromaticity as a general qualitative structural feature, [2a] underlining its important role in teaching and in organic chemistry research,[2b] but defining strictly which particular aspect of aromaticity is meant.[2a] As a consequence of the large number of properties associated when the concept of aromaticity is invoked, several criteria have been proposed, grouping together different kinds of properties. [3a] The main criteria are: i) energetic, taking into account increased stability; ii) structural, reflecting the averaging of bond lengths; iii) magnetic, stemming from different magnetic properties,[3b,4,5] this last criterion having been stoutly contested.[6] It has been proposed to treat quantitatively characteristics related to the three criteria, through principal component analysis (PCA) [7] , or also asserting that aromaticity is multidimensional.[8] Again, the eventual orthogonality of the different criteria is a polemical topic. It has been claimed that classical and magnetic concepts may not be orthogonal, linear relationships existing among the three criteria which may be even extended to antiaromatic systems.[9] We shall not deal here with the possibility of a quantitative interrelation between the different aromaticity indices with which we compare our index.

Even now, organic chemistry textbooks may be found, where a compound is said aromatic meaning *only* "that its π electrons are *delocalized* over the entire ring and that it is *stabilized* by the π-electron delocalization".[10] This is striking, taking into account that more than forty years have elapsed since the contribution of σ electrons to the stabilization of long polyenes and benzene was suggested.[11] The π electrons would have a lower energy in a ring of "cyclohexatriene"-like shapes and σ electrons would be responsible for the regular hexagon structure.[12]

Labarre et al. clearly underlined the role of σ electrons in molecular aromaticity. Based on Faraday effect, they stated two conditions for a molecule to be considered aromatic:
i) high bond orders, i.e. high π delocalization *together with* ii) the absence of an important gradient of localized (σ+π) charges on the ring atoms, so as to give rise to a Pauling-Pople current.[1b,13] Shaik et al.[14] conclude, from the study of benzene and other systems, that the driving force for a uniform structure originates in the σ frame, π electronic delocalization being a byproduct of the σ-imposed geometric constraint. In line with this viewpoint, an elegant work of Jug and Köster[15] shows that the σ energy tends towards structure delocalization, whereas the π energy tends to bond localization, the total structure depending on the relative dominance of σ versus π trends. Gobbi et al.[16] also assert, from an analysis of the first and second derivatives of the SCF canonical orbital

energies with respect to normal coordinates, that the D_{6h} form of benzene is due to the σ frame.

Nevertheless, the σ–π controversy is not closed. Glendening et al.[17] find misleading to analyze delocalization through a σ–π partition, though π delocalization is a driving force for equal bond lengths. Larsson et al.[18] say that the contradiction between the viewpoints of refs 16 and 17 is apparent and may be resolved. The use of Bader's topological approach[19] leads to conclude that both σ and π electrons contribute to aromaticity.[4]

In the present work, we propose to use as a measure of aromaticity a multicenter bond index introduced by us.[20] About twenty-five years ago, we defined a bond index I_{AB},[21a] generalizing the Wiberg bond index[22] to non-orthogonal bases. This index, an invariant in the tensor sense,[21b] gives the electronic population along the AB bond and gives values agreeing with chemical expectation. The multicenter bond index,[20] an extension of I_{AB} to multicenter bonds, involves the total electron population (despite admitting σ–π separation); hence, testing its performance as an aromaticity index appears to us an appealing challenge.

Other aromaticity indices relate bond indices and ring currents;[15,23] the advantage of this kind of aromaticity indices over the pioneer ones proposed by Julg[1a,24] has been mentioned.[7] It has been remarked[4] the desirability of indices which can measure the aromaticity of individual rings instead of an overall index for the whole system. Several indices of this kind have been proposed.[4, 25-27] In this work we exploit this feature of our I_{ring}, for the suitability in discriminating the relative aromaticity of the different rings in polycyclic compounds. We apply our index to cyclic conjugated hydrocarbons, both benzenoid and including non-benzenic rings; to azines and benzoazines, where it is not so easy to distinguish the relative aromaticity of the benzene and azine rings; and, finally, to heterocycles with 5-m rings. In all cases, we compare with other individual or overall indices from the literature.

Multicenter bond indices

When using non-orthogonal bases in closed-shell systems, the first-order density matrix is written as 2**Π** and **Π** is an idempotent matrix. This property leads to the definition of a bond index I_{AB} for the bond involving atoms A and B:[21]

$$I_{AB} = 4 \sum_{a \in A, b \in B} \Pi_a^b \Pi_b^a \quad (1)$$

I_{AB} is the generalization of the Wiberg bond index[22] to non-orthogonal bases.

The idempotency of **Π** holding for any power, it may be further exploited, allowing us to define a multicenter bond index[20]

$$I_{ABC\ldots L} = 2^L \sum_{a \in A, b \in B, \ldots, \lambda \in L} \Pi_a^b \Pi_b^c \Pi_\lambda^a \quad (2)$$

This definition has proved very successful in the three-center case. I_{ABC} is most adequate for hydrogen bonds; it also predicts that the peptidic bond should be of the same order of magnitude than strong hydrogen bonds.[20]

In ref 28 we have advanced the hypothesis, relying on results for a few systems involving six-center rings, that the index of the ring could be related to aromaticity.

The I_{AB} index of eq. (10) may be also written as[29]

$$\left\langle \left(\hat{q}_A - < \hat{q}_A >\right)\left(\hat{q}_B - < \hat{q}_B >\right)\right\rangle = -I_{AB} / 2 \tag{3}$$

where $\hat{q}_A$ is the A atom charge operator. I_{AB} represents hence the correlation between the fluctuations of $\hat{q}_A$ and $\hat{q}_B$ from their average values. As we are working within the Hartree-Fock approximation, it must be due to the exchange energy, which is the only correlation recognized at this stage. Similarly, the multicenter generalization of I_{AB}, eq. (2),[20] when linked to aromaticity, may be considered an energetic aromaticity index.

On the other hand, I_{AB} is also the electronic charge along the AB bond;[21] eq. (2) arises from higher order terms in the decomposition of N, the system's number of electrons. Thus, a magnetic side may be ascribed to it, as this electronic charge is liable to conjugation; [30] if a magnetic field is applied, it gives rise to an electric current. Both aspects are entangled in such a way that we do not feel able to separate the influence of each one of them.

Multicenter bonds have been mentioned in the literature for many years, both in MO and VB frameworks.[31]

In a recent paper towards a better understanding of chemical reactivity, Yamasaki and Goddard[32] consider how pairs of bonds interact with each others and devise an index measuring the degree of coupling between bond pairs. The expression for their index involves the calculation of our equation (2) for 2, 3 and 4 centers. Aromaticity is undoubtedly related to the mutual simultaneous interaction of all the bonds of an aromatic ring. If the concept of the Yamasaki-Goddard index could be enlarged so as to take into account more general couplings, it would open an exciting new way towards extracting interpretations from the wave functions. This is a more ambitious goal. Meanwhile, we propose in this work to study the adequation of I in eq. (2) as a measure of aromaticity for different types of rings.

Our calculations have been carried out within the framework of the MOPAC package.[33] PM3 multicenter indices were obtained, previously optimizing geometry using the AM1 Hamiltonian of HYPERCHEM[34] with a standard gradient of 0.01.

Cyclic conjugated hydrocarbons

A. Polycyclic benzenoid aromatic hydrocarbons

We have reported in Table 1 the I_{ring} of eq. (2) for polycyclic benzenoid aromatic hydrocarbons with linearly fused rings and in Table 2 the comparison with other ring indices appearing in the literature.[4,27,35] The I_{ring} values decrease both for external and internal rings as the number of fused rings increases. On the other hand, I_{ring} *increases* going from the external towards the internal ring of a certain molecule, indicating thus that internal rings are more aromatic than external ones. These behaviours, the vertical one and the horizontal one in the Table, are seen to be in close agreement (leaving out benzene) with the ring current calculations, relying on experimental proton chemical shifts, of ref. 26.

We have plotted in Figure 1 the highest I_{ring} value in each molecule of Table 1, as a function of the number of fused rings. The decrease, rather than being linear, is an exponential one, tending towards a limit of ≅0.032. This value corresponds to ≅37% that of benzene. Linear annelation is known to yield decreasing stability with increasing number of rings.[36, 37] Ref 27 has a similar saturation limit of 66% for the external rings; for these, our limit is ≅0.020, i. e. ≅23% that of benzene.

The ability to sustain a diatropic ring current is a characteristic of aromatic systems; it has been recently proposed to use the absolute magnetic shieldings, computed at *ring centers* with available quantum mechanics programs, as an aromaticity/antiaromaticity criterion[35], for the sake of comparison with quantitative measurements of aromaticity. The correspondent quantity is named “nucleus-independent chemical shift” (NICS). We have reproduced in Table 2 values for it and for the geometrical index HOMA (harmonic oscillator model of aromaticity)[4] for the linear polyacenes concerning us. Both indices show the same (let us say horizontal) trend than our I_{ring} external rings for a certain molecule, having indices which increase when going towards the central ring; see also ref 38. The opposite behaviour is obtained in ref 27, although there is an agreement with ours in the vertical sense of Table 1. In this ref, ring currents are calculated within a π PPP electron model including explicitly accurately treated electron correlations.

The correlation between our index and the HOMA one has $R^2 = 0.7269$ taking into account all the hydrocarbons of Table 2; leaving out the internal ring of coronene, it goes to 0.7966 and ignoring completely coronene it gives 0.8216.

Table 3 shows the I_{ring} values for phenanthrene and angular four-ring polyacenes. Rings denoted as external are intended to have less points of ring fusion than those denoted as internal. Between parentheses, we have added theoretical ring current intensities (relative to benzene’s), obtained through London-type MO calculations, in satisfactory agreement with experimental proton shifts.[25] It is seen that our indices are in qualitative agreement for the molecules considered there. The trend here is the opposite of that of linear polyacenes, the external rings having now higher I_{ring} values than the internal ones, with the only exception of ring 2 in 1,2-benzo anthracene. Let us remark that HOMA and NICS show the same behaviour (Table 2), as does phenanthrene in ref 27. It is not clear for us if the middle ring of phenanthrene can be viewed as an ethylenic ring connecting two rings of a biphenyl molecule[27] (Figure 2): although $I_{4a,4b}$ is 1.10, i.e. a nearly single bond, $I_{9,10}$ is 1.73, not enough close to a double bond as ethylene's.

Let us propose to take the phenanthrene molecule as a paradigm for our discussion of this series of compounds as well as the next one of Table 4. In 1,2 benzo-anthracene ring 2 may be seen as anthracenic when looking at it from the left and as a phenanthrenic one from the right. From either side, its aromatic character is hence reinforced.

This approach may be also applied to the angular pentacyclic benzenoid hydrocarbons of Table 4, where several rings may be considered either anthracenic, phenanthrenic or both. In Table 3 the highest I_{ring} corresponds to ring 1 of triphenylene (twice type-1 phenanthrenic) and the lowest to ring 2 of the same molecule (thrice type 2-phenanthrenic). In Tables 3 and 4, whichever the compound, the highest I_{ring} values for external rings are always higher than the highest I_{ring} values of internal rings of a molecule in Table 1 with the same number of rings. That is, the most aromatic ring of an angular hydrocarbon is more aromatic than the most aromatic one of a linear hydrocarbon having equal number of cycles[36] (see further on). We find the same feature for coronene (Table 2) compared to heptacene (Table 1); in the former molecule, I(1)=0.0348 and I(2)=0.0113, agreeing with HOMA and with NICS values. The central ring of coronene has been predicted to have a substantially diminished aromatic character, having even been found a very unusual NICS value of +0.8, which would point it as antiaromatic.[39]

In a classical paper which uses a modification of London's MO theory of π-electron ring currents,[40] the relation between individual ring currents and that of benzene is given for the series of benzenoid pentacyclic hydrocarbons (see Table 4). To our knowledge, it is the only reference to individual ring currents for this series of compounds. It may be seen that there is a general good agreement with our results for the ring aromaticity in each molecule. We predict that the most aromatic ring is always an external phenanthrenic one; so does ref 40 in most cases. Even closer is the agreement between both methods as to the less aromatic ring, which is an internal phenanthrenic ring.

The angular compounds are known to be more stable than their linear analogs; they are less reactive and hence more aromatic, as we have mentioned above.[36] Our indices agree well with this behaviour, as several energetical indices do. We have assembled in Table 5 some of these: REPE (resonance energy per π electron) is defined as the difference between the total π energy of the molecule and the total π energy of a fictitious localized structure which uses empirical π bond energies, divided by the number of π electrons,[36,41] TREPE is the topological REPE[41] and the absolute hardness is the HOMO-LUMO gap, having been proposed as an alternative aromaticity measure.[41] We find that there appears to be a link between the relative aromaticity of two systems having the same number of rings and their highest I_{ring} value. For instance, the energetical magnitudes of the Table indicate that 1,2 benzopyrene (22) is more aromatic - therefore more stable- than 3,4 benzopyrene (17), in agreement with our highest I_{ring} for each of these key systems.[3c]

We have no reasons to expect a good linear correlation between our I_{ring} and indices regarding the complete molecule rather than the individual rings. Despite this fact, it appears to exist between our I_{ring} value for the *external* ring of each molecule in Table 5 and the other indices. For TREPE, REPE and hardness we have respectively $R^2 = 0.7416$, 0.7386 and 0.6826. If we leave out coronene, as we have done with HOMA, R^2 goes respectively to 0.8320, 0.8170 and 0.7299. These values may be considered quite satisfactory.

B. Hydrocarbons including non-benzenic rings

We give in Table 6 our I_{ring} value for other cyclic hydrocarbons which include non-benzenic rings, together with the indices obtained through other methods. Benzene and cyclobutadiene are usually taken as archetypes for aromatic and antiaromatic systems respectively.[3d] We have been considering only systems with benzenic rings. Let us now see a few systems including the other extreme reference, as well as some ones with pentagonal rings.

Cyclobutadiene has been isolated in an argon matrix not so long ago; [42] the TREPE and REPE values reflect its high instability. Accordingly, our I_{ring} is negligible.

Notwithstanding the sign of our index may as well be positive as negative,[29] the values obtained in this work happen to be all positive. From the values of Table 6, we propose to take $I_{ring} \cong 0.017$ as the boundary for aromaticity. The competition between aromaticity and antiaromaticity has been recently analyzed for phenylenes.[43] In the case of annulenoannulenes, the aromatic character was found to be determined by the aromaticity of the fused rings rather than by that of the molecular periphery.[44]

Benzocyclobutadiene has an accentuated antiaromatic character, having been generated only under extreme conditions.[3e] The antiaromaticity of cyclobutadiene prevails hence over benzene's aromaticity; TREPE and REPE values clearly agree on this point and are in qualitative agreement with our I_{ring} values. It has been also proposed to consider this molecule as a 6 π-electron 6-m (six-membered) ring and an isolated π bond in the other cycle.[3e,45] Our I_{AB} values support this model, showing an alternation between 1.66 and 1.15 in the C-C benzene bonds and the vertical bond to the right of the cyclobutadiene moiety having I_{AB}=1.90; that is, a clear alternation on one hand, and a quite-close-to-double bond on the other hand.

Pentalene, isomer of benzocyclobutadiene, is a typical antiaromatic compound; the values in the table correspond to the expectation.

In biphenylene, the aromaticity of the benzene rings and the antiaromaticity of the 4-m ring is further confirmed by a calculation of the ring current with the McWeeny method, which gives respectively 0.563 and -1.028.[46] Our bond indices, of 0.99 for the bridge bond and 1.18 for the fused bond in the 4-m ring, indicate absence of conjugation through it, although HF/6-31G* Löwdin π bond orders predict a more accentuated difference.[43] The cyclopendienyl and cycloheptatrienyl ions are discussed further on.

Azulene, isomer of bicyclo [6,2,0]-decapentaene and naphthalene, is less aromatic than naphthalene, as is seen comparing with the energetic indices of Table 5. In Table 6, the I_{ring} for the 5-m cycle is close to the one for the anthracene external ring but less than naphthalene's (see Table 1). In contrast to the 5-m cycle, I_{ring} for the 7-m cycle is below the limit which we have proposed for a cycle to be regarded aromatic. It is closer to that of the central 6-m ring of triphenylene (0.0094) and the also central one of coronene (0.0113), which we have discussed in the preceding section.

A theoretical MNDOC calculation assigns to bicyclo[6.2.0] decapentaene a weakly aromatic character, due to a low resonance energy.[47] A previous elegant study about a unified theory of aromaticity and London diamagnetism[48] concludes that the compound, although diatropic, is antiaromatic. Our I_{ring} values incline clearly towards antiaromaticity.

For pyracylene, an intriguing viewpoint has been proposed, namely to consider it as a naphthalene core plus two vinyl bridges.[49] Actually, we could apply it also to acenaphthylene. In both molecules, the 6-m I_{ring} is quite near to naphthalene's; as to the "vinyl" bond, it would have I_{AB}=1.858 for pyracylene and 1.840 for acenaphthylene.This in turn is consistent with antiaromaticity for the 5-m ring in both molecules, which has a quite lower index than azulene's.

Fluoranthene and corannulene, as well as pyracylene, are the leitmotifs of the fullerene molecule C_{60}, whose existence was suggested having in mind the very notion of aromaticity.[3f, 50] However, its aromaticity is far from being a settled subject.[51] Its striking stability could be rather owed to the lack of hydrogens and of peripheral reactive carbons on its surface.[52]

Fluoranthene is a stable aromatic hydrocarbon. Having sixteen π electrons, at first sight it does not fulfill the requirement of the Hückel 4*n*+2 rule. However, it may be considered as formed by the connection of two systems of 6 and 10 electrons respectively,[27] each one of them obeying it. In fact, the I_{ring} values picture two 6-m rings with naphthalene characteristics (0.046), the other one being much closer to benzene's (0.074). The 5-m ring is decidedly antiaromatic.

The values for corannulene do not correspond to a very aromatic molecule. Its 6-m ring resembles to pentacene's highest value (0.0363), while its 5-m ring, although not so antiaromatic as fluoranthene's, has a value below the aromaticity boundary.

The trend for this series is similar for our values and NICS; there is a good qualitative agreement, as there was in Table 2. Quantitatively, the correlation is poor because our I_{ring} values cover a small range (0 – 0.1), while the NICS range is very large (-20 – 20).

The agreement between our values and the ring currents of ref 27 is reasonable except for azulene where the predicted behaviour is the opposite. Taking into account both Tables 2 and 6, if 5-m rings are left aside, the correlation with ring currents is good (R^2 = 0.8733); their inclusion makes R^2 fall to 0.5661. This is due to the negative values which, as we have said, do not appear in our results.

Heterocyclic compounds

The aromaticity of heterocyclic compounds, particularly that of N-containing ones, has been subject of many quantum chemical studies.[3g] We restrict ourselves here to the 6-m rings of monocyclic azines, benzoazines and some other heterocycles with 5-m rings.

A . Azines with 6-m rings

Table 7 shows our I_{ring} values for the 6-m monocyclic azines, together with other aromaticity indices reported in the literature: three of them (RCI, RC_v, I_A) may be considered as associated with geometric criteria, one (relative diamagnetic anisotropy γ) with magnetic criteria and two (ΔE and RE) with energetic criteria.

Homogeneity appears to be the outstanding feature of the I_{ring} values. Actually, six or seven of the twelve molecules exhibit a value of 0.088, which is the same as benzene's, as if the replacement of the =CH− fragment by the −N= atom had little importance. George et al. predicted essentially the same value for the aromatic stabilization of benzene and pyridine derived from empirical resonance energies.[53] Our results agree with the conclusion of ref 54: their values for the π-delocalization energies ΔE in Table 7 are essentially unaffected under the mentioned replacement. Hexazine has the highest I_{ring} value and 1,3,5 triazine the lowest one.

The minimal bond order in a ring system is adopted as an aromaticity index definition based on ring current (RCI).[23] An alternative to it is RC_v, based on what the authors call bond valence,[15] actually our $I_{AB;}$[21] this index of aromaticity is the minimum bond valence of all ring bonds in a monocyclic ring. The percentage of variation between the highest and lowest value, both for RCI and RC_v, are the least ones in Table 7; even so, both agree with us in assigning the highest to hexazine and the lowest to 1,3,5 triazine.

The underlying idea of RCI is related to the graphical method devised in ref 30 in order to obtain γ, the diamagnetic anisotropy relative to that of benzene. The conjugation volume required in the corresponding calculation is delimited by the π charge density contour line of *maximum conjugation*. It is thus not unexpected for us that both methods show quite similar trends. If the contour lines of maximum conjugation were the only factors determining γ, monocyclic azines would show more uniform values than they do; the other factors taken into account lead to increased discrimination.[30] Ring currents RC of ref 27 and our I_{ring} behave similarly, with more differentiation for RC, particularly for pyrimidine and 1,3,5 triazine.

Bird’s unified aromaticity index I_A, an improvement of his own index based upon a statistical evaluation of the variations in peripheral bond orders,[55] exhibits an equivalent differentiation. The resonance energies RE are founded upon the Harmonic Oscillator Stabilization Energy (HOSE), using experimentally determined molecular dimensions;[56] it is the index showing the utmost discrimination in the Table.

Whether or not aromaticity changes under substitution of the =CH– fragments by =N– atoms, is far from being a settled question. For example, in an experimental and theoretical study of molecular and electronic states of 1,2,4,5 tetrazine it is suggested that the increase in the number of N atoms would be accompanied by a decrease in aromaticity in line with increasing stability.[57] According to the authors of ref 58, the NICS (π) values for 1,3,5 triazine and benzene (-15.3 and -16.8 respectively) indicate similar aromaticity. A quite different picture arises from an analysis of the magnetic anisotropies of 1,3,5 triazine and a derivative of it.[59] The conclusion is drawn that a replacement of three =CH– groups in benzene by –N= atoms with such a symmetry localizes electronic charge on the nitrogen atoms, reducing then appreciably the delocalization. As we have mentioned above, although less pronounced, our results as well as other ones in Table 7, point in the same direction. We have picked up this admittedly faint effect in Figure 3, going from benzene, which has no N atoms, to hexazine, which has no C atoms. For the intermediate cases, with more than one molecule having the same number of N (or C) atoms, we have chosen the molecule having the lowest I_{ring} value. The 1,3,5 triazine plays thus the role of a mirror image between the molecules at both sides of it, which are mutually “complementary”; the molecules with 1, 2, 4 and 5 nitrogen atoms have C_{2v} symmetry. Two almost symmetric straight lines are obtained.

Hexazine shows a striking I_{ring} value ($I_{AB} \approx I_{AB}$ for benzene), despite being consistent with other authors’.[3h] Let us remind that there is no evidence of even its transitory existence, as happens also for 1,2,4,6 tetrazine and pentazine.[56] Hexazine (even in hypothetically more probable structures than, for example, the D_{6h} one) would be highly unstable towards the dissociation in three N_2 molecules[60]. It has been mentioned[61] that AM1 predicts that the NN bonds in hexazine alternate in length. We have actually obtained through AM1 optimization in HYPERCHEM and the gradient of 0.01, with full delocalization as starting geometry, r(NN) = 1.316 Å (I_{NN} = 1.421); the PM3 I_{ring} is 0.0898, as reported in the Table. If the HYPERCHEM AM1 optimization is run with a gradient of 0.001, starting or not from full delocalization, alternant bond lengths of 1.418 Å and 1.244 Å are obtained, being I_{NN} respectively 1.020 and 1.864, and I_{ring} = 0.0353, obviously lower than before. If, with this last input for MOPAC, we allow for further optimization, we are led to dissociation in three N_2 molecules, with the corresponding I_{NN} = 3 (r_{NN} = 1.01 Å) and I_{ring} = 0. While, if we start from the D_{6h} symmetry in MOPAC and further optimization is permitted, nothing changes.

B. Benzoazines

Table 8 shows I_{ring} values for benzoazines together with other aromaticity indices. Here too I_{ring} values are similar, but now to naphthalene. The compounds resemble naphthalene, in the same way in which pyridine resembles benzene.[62] Our I_{ring} values split into two groups: one for the benzene ring, above naphthalene's, the other one for the azine ring, below naphthalene's. Cinnoline shows the wider gap in the table for $I_{ring}(1)$ - $I_{ring}(2)$. Along this series, our results indicate more aromaticity for the benzene ring. It is known that electrophilic substitution takes place in the benzenic ring of quinoline, isoquinoline and benzodiazines.[63]

To our knowledge, the RC values reported in the Table[27] are the only individual ring results for this type of molecules; the relative aromaticity of benzenic and azine rings is different from ours.

While the greatest I_{ring} values difference reaches a maximum of 24%, for I_A and RE the range keeps respectively within 10% and 12%. RE, as other energetical indices, are quite close for naphthalene, quinoline and isoquinoline.[41] The same thing happens with the magnetic susceptibility exaltation Λ of these three compounds, which is 27.4, 26.85 and $24.75\text{-}10^{-6}$ cm^3 mol^{-1} respectively.[62]

C. Heterocycles with 5m-rings

We report in Table 9 I_{ring} values for heterocycles with 5m-rings containing one or two heteroatoms, as well as other authors' aromaticity indices. Our values show clearly three groups, pyrrole's being the one with highest values and furan's the one with lowest values. It has been suggested that the lower aromaticity of furan compared with pyrrole's is due to the contraction of oxygen's p_z orbital, while the p_z of nitrogen would have the optimal size for the delocalization in the π system.[63, 64] In each group, the second heteroatom (a pyridinic nitrogen) does not seem to play an equally relevant role. That is, the molecular behaviour concerning aromaticity would be determined by the atom furnishing the π

system with two electrons.[65] Other results in the Table (I_A and RE) agree in assigning the lowest aromaticity to the furan group. Instead, the Bird index η, based on absolute hardness reformulated in terms of molar refractivity, ascribes the highest values to this group and the lowest to the thiophene group.[66] As to $\Delta\varepsilon_\pi$, which is the difference between the lowest natural MO's eigenvalues and the corresponding lowest π delocalized MO's eigenvalues, it ascribes the highest values (i.e. highest aromaticity) to the thiophene group.[67] The geometrical criteria RCI[23] and RC_v[15], as the magnetic quantity Λ,[62] do not lead to a separation conforming to the three families.

The relative aromaticity of pyrrole and thiophene has been a controversial subject for at least thirty years.[1d] According to some authors, pyrrole is more aromatic,[9, 68] while other ones assert that it is thiophene.[67] Even within the same criterion discrepancies arise between different indices; for example, in opposition to the RE values of Table 9, aromatic stabilization energy (ASE) assigns the highest value to pyrrole (see Table 10).[8] Even more, the same magnitude gives different ordering when comparing the results obtained by different authors; this happens, for instance, with Λ in Tables 9 and 10. If the uniformity of delocalization through the ring has something to do with aromaticity, pyrrole is the most and furan the less aromatic.[63a] We have reported in Table 11 the I_{AB} values and their mean variation for the three systems and the result agrees with the above assertion.

The appealing topological charge stabilization rule[69] applies when heteroatoms are inserted in conjugated hydrocarbons with nonuniform charge density (typically, nonalternant hydrocarbons and dications or dianions of alternant hydrocarbons). It states that, in terms of stabilization, molecules in which the electronegativity of heteroatoms match the pattern of charge densities in the isolelectronic hydrocarbon are favoured.[3i,69] The rule is intended for π charges; let us see if it works when using total carbon charges and comparing with our I_{ring} values, in the case of diazapentalenes of Table 12. For pentalene, the reference hydrocarbon, the PM3 charges are:

$q_1 = q_4 = -0.001$; $q_2 = q_5 = -0.157$; $q_3 = q_6 = -0.040$

According to these charges, the most stable molecule in Table 12 should be 2,5-diazapentalene, followed by 3,5-diazapentalene. Our I_{ring} values agree with this ordering, as the other indices in the table.

Holistic comments

At this point, we would like to express some considerations about our I_{ring}. It may be seen from eq. (2) that, as the number of atoms involved increases, so does the number of factors less than 1; it is hence expected that the index decreases accordingly. The low index for the 8-m ring in compound **38** of Table 6 is thus not surprising. Nevertheless it is doubtless, from the values of this table, that the index of the benzenoid ring (except for the examples underlined through the text) uses to have an index decidedly higher than that for 5-m and 4-m rings. It is thus a fair measure of cycle aromaticity. As for 5-m and 4-m rings, the boundary adopted for aromaticity would lead to say that for hydrocarbons 5m-rings use to be slightly antiaromatic (or non aromatic) and 4m-rings much more.

The value for the cycloheptatrienyl cation (tropilium cation) **36**, which is an ion of unusually high stability, is similar to those of benzenoid rings. That for the cyclopentadienyl ion is even too high. Both ions share the common feature of an aromatic electronic sextet and our I_{ring} behaves as if it in some way seizes the aromatic character.

In short, through the tables, I_{ring} has shown to be satisfactory regarding several aspects, in qualitative agreement with relative aromaticity along the different series of molecules considered.

Nevertheless, the values of Table 9 for the pyrrole family are higher than expected, above benzene's. As benzene is the established paradigm for aromaticity, this is not satisfactory. Other indices suffer from the same drawback. For instance, Bird's molecular hardness η reported in Table 9[66] ascribes higher aromaticity to the 5m- heterocycles than to benzene (η=6.60); the same thing happens with NICS in Table 10. Diamagnetic susceptibility exaltation Λ, which has been recognized particularly appropriate as aromaticity measure,[70] assigns in Table 10 much more aromatic character to the cyclopentadienyl anion than to benzene and predicts for pyrrole a value near to benzene's. The objection applies also to some energetical indices, as ASE (Table 10), Parr's hardness[41] and TREPE.[41]

Although electrophilic substitution may not be a general characteristic property of aromatic molecules,[70] chemical reactivity is undoubtedly a valid criterion of aromaticity. From this viewpoint, it is well known that 5m-heterocycles undergo typical electrophilic reactions, such as nitration, halogenation or sulphonation. They are much more reactive than benzene, their reactivity being similar to that of the most reactive benzene derivatives.[71]

Taking into account the above considerations for the families of 5m-rings, perhaps a simple correction factor would do. In order to improve the quantitative correlation when going from benzene to the fused rings, the same prescription comes to mind. This shall be done elsewhere, together with a systematic application to other series of compounds.

We feel that an unambiguous definition of aromaticity is lacking; otherwise it is difficult to resist the temptation of Labarre's pessimistic hypothesis.[1b] One of the most fascinating quantum chemical theories of the last twenty years, Molecular Similarity,[72] is intimately linked to molecular reactivity[73]. Electrophilic reactivity being one of the oldest properties ascribed to the aromaticity concept, we feel that molecular similarity may open new different insights into the aromaticity concept, with solid chemical and mathematical foundations.

Conclusions

- For polycyclic benzenoid aromatic hydrocarbons with linearly fused rings, I_{ring} increases going from the external ring towards the internal ones.
- Phenanthrene, whose external I_{ring} is higher than the internal one, may be adopted as a paradigm for the interpretation of rings relative aromaticity in angular polycyclic aromatic hydrocarbons.
- In hydrocarbons including non-benzenoid rings, I_{ring} describes correctly the compounds' aromatic (antiaromatic) character; also, within a certain system, the aromaticity (antiaromaticity) of each ring, in qualitative agreement with other energetic, magnetic and structural indices.
- Monocyclic azines have an I_{ring} close to that of benzene.
- For benzoazines, I_{ring} indicates that the benzene ring is more aromatic than than the azine ring.
- For I_{ring}, pyrrole is more aromatic than thiophene.

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Figure captions

Figure 1. Highest I_{ring} value for each molecule, in linear polycyclic benzenoid aromatic hydrocarbons as a function of the number of fused rings.

Figure 2. Atom labelling for phenanthrene.

Figure 3. I_{ring} for benzene and monocyclic azines as a function of the number of N atoms (see text). The value for 1,3,5 triazine has been taken into account in tracing both straight lines.

Figure 1

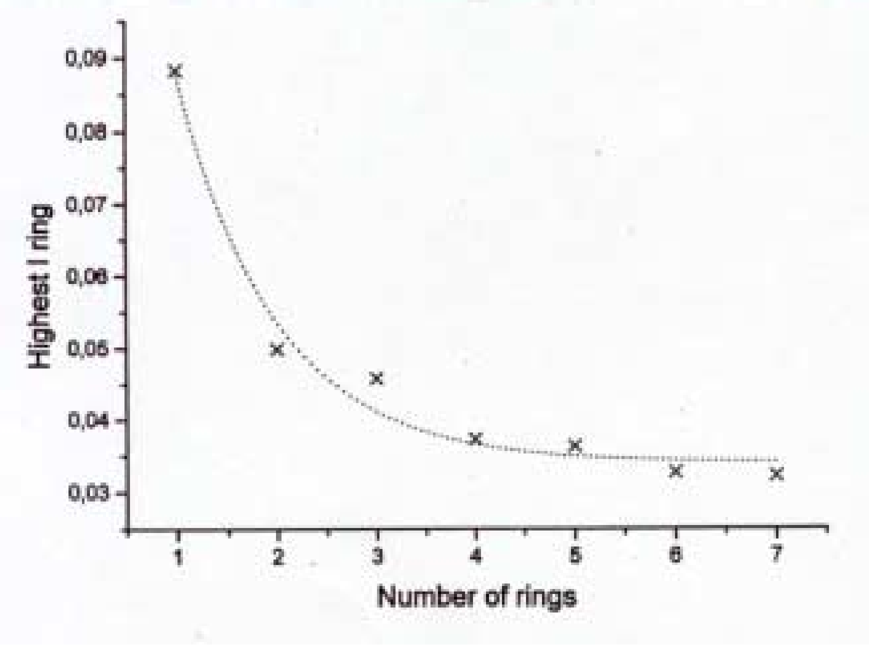

0,09
0,08
0,07
0,06
0,05
0,04
0,03
Highest I ring
1
2
3
4
5
6
7
Number of rings

Figure 2

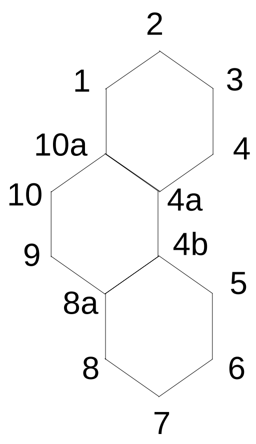


Figure 3

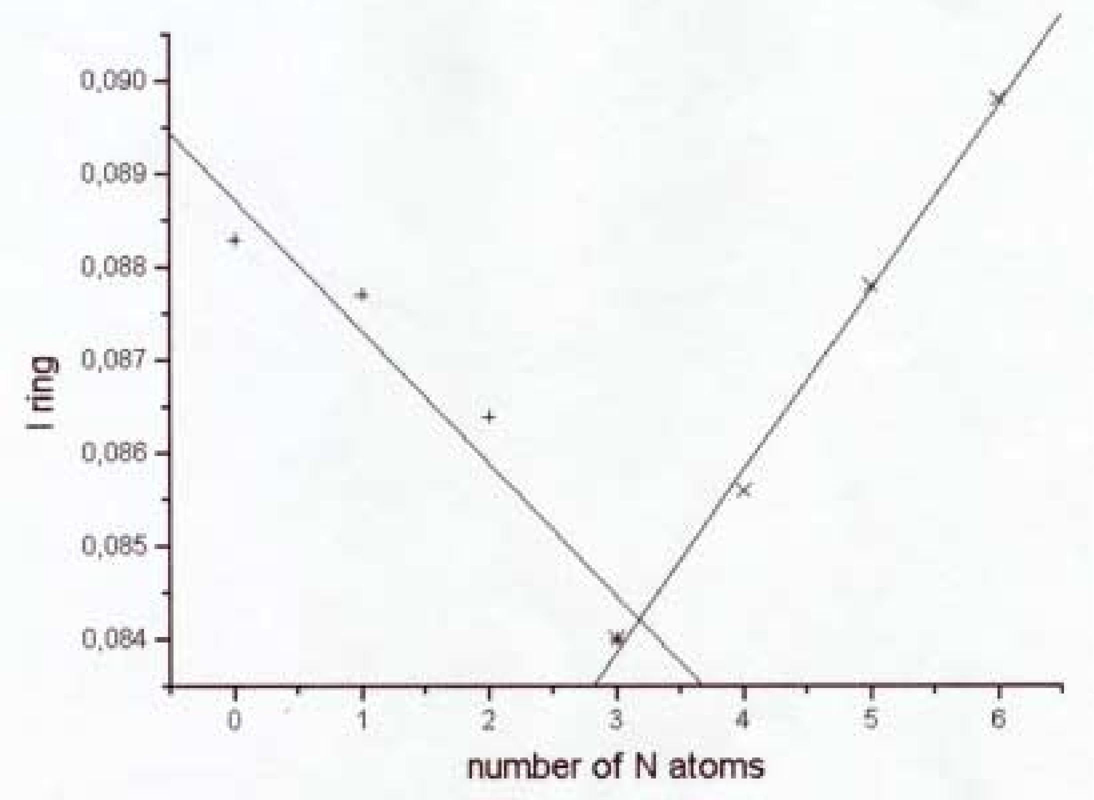

0,090
0,089
0,088
0,087
0,086
0,085
0,084
I ring
0
1
2
3
4
5
6
number of N atoms

Table 1. Ring indices for linear polyacenes. The values between parentheses are the relative ring-current intensities taken from Table I of ref 26.

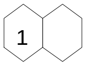
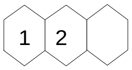
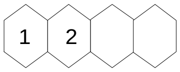
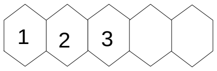
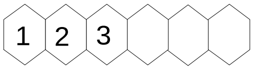
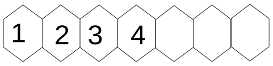
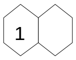
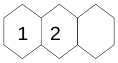
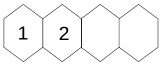
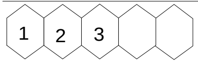
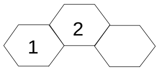
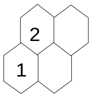
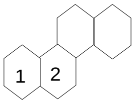
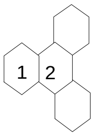
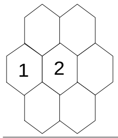
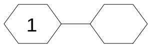
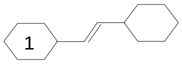
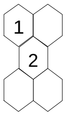
Molecule	I_{ring}			
	1	2	3	4
 1 benzene	0.0883 (1.000)			
 2 naphthalene	0.0449 (1.093)			
 3 anthracene	0.0327 (1.085)	0.0458 (1.280)		
 4 tetracene	0.0246 (1.068)	0.0373 (1.305)		
 5 pentacene	0.0204 (1.06)	0.0301 (1.30)	0.0363 (1.35)	
 6 hexacene	0.0181 (1.048)	0.0253 (1.291)	0.0327 (1.352)	
 7 heptacene	0.0166 (1.045)	0.0220 (1.285)	0.0288 (1.348)	0.0322 (1.361)

Table 2. Aromaticity index in this work (I_{ring}) and in other works, for benzenoid hydrocarbons.

Molecule	Ring	Indices			
		I_{ring}	NICS [a]	HOMA [b]	RC [c]
 1 benzene	1	0.0883	-11.5	0.990	+1.0
 2 naphthalene	1	0.0499	-11.4	0.777	+0.79
 3 anthracene	1	0.0327	-9.6	0.516	+0.71
	2	0.0458	-14.3	0.882	+0.70
 4 tetracene	1	0.0246	-6.7	0.321	+0.7
	2	0.0373	-13.1	0.770	+0.64
 5 pentacene	1	0.0204			+0.70
	2	0.0301			+0.63
	3	0.0363			+0.60
 8 phenanthrene	1	0.0640	-11.7	0.901	+0.86
	2	0.0208	-7.4	0.414	+0.53
 9 pyrene	1	0.0577	-14.5	0.952	
	2	0.0185	-5.6	0.475	
 10 chrysene	1	0.0585	-11.5	0.858	
	2	0.0300	-8.7	0.557	
 11 triphenylene	1	0.0708	-10.8	0.929	
	2	0.0094	-3.0	0.069	
 14 coronene	1	0.0348	-12.1	0.765	
	2	0.0113	-5.4	0.628	
 15 biphenyl	1	0.0826			+0.975
 16 stilbene	1	0.0815			+0.983
 30 perylene	1	0.0473	-9.4	0.790	
	2	0.0051	+6.8	-0.111	

[a] NICS, nucleus independent chemical shifts, ref 35. [b] HOMA, harmonic oscillator model of aromaticity, ref 4. [c] RC, ring current, ref 27.

Table 3. Ring indices for phenanthrene and angular four-ring polycenes. The values between parentheses are the ring current intensities (relative to benzene's) taken from ref 25.

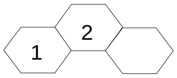
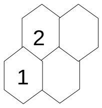
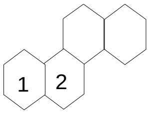
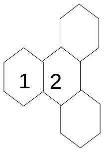
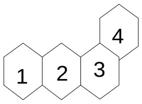
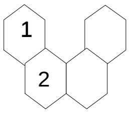
Molecule	I_{ring}			
	1	2	3	4
 8 phenanthrene	0.0640 (1.133)	0.0208 (0.975)		
 9 pyrene	0.0577 (1.329)	0.0185 (0.964)		
 10 chrysene	0.0585	0.0300		
 11 triphenylene	0.0708 (1.111)	0.0094 (0.747)		
 12 1,2 benz-anthracene	0.0401	0.0471	0.0133	0.0687
 13 1,2,7,8 dibenzonaphthalene	0.0595	0.0293		

Table 4

I_{ring} for pentacyclic benzenoid hydrocarbons. Under each value, we report between parentheses the ring currents of ref 40.

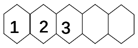
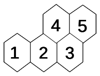
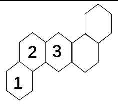
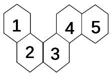
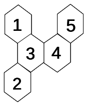
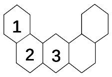
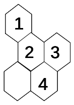
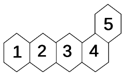
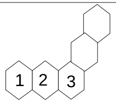
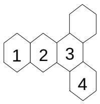
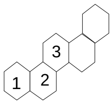
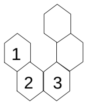
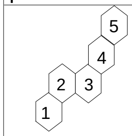
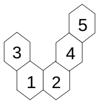
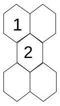
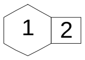
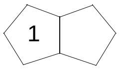
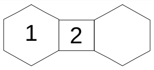
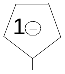
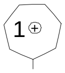
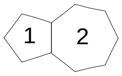
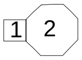
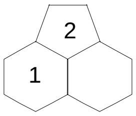
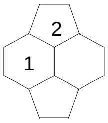
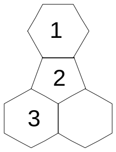
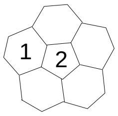
Molecule	I_{ring} (ring current)				
	1	2	3	4	5
 5 pentacene	0.0204 (1.06)	0.0301 (1.30)	0.0363 (1.35)		
 17 3,4 benzo pyrene	0.0513 (1.20)	0.0320 (1.28)	0.0124 (0.839)	0.0277 (1.08)	0.0556 (1.29)
 18 1,2,5,6-dibenz-anthracene	0.0667 (1.14)	0.0164 (0.943)	0.0539 (1.29)		
 19 1,2,5,6-dibenz-phenanthrene	0.0618 (1.15)	0.0255 (1.06)	0.0406 (1.16)	0.0272 (1.05)	0.0597 (1.15)
 20 1,2,3,4-Dibenz-phenanthrene	0.0686 (1.13)	0.0677 (1.14)	0.0128 (0.853)	0.0352 (1.09)	0.0560 (1.10)
 21 1,2,7,8-dibenz-anthracene	0.0666 (1.14)	0.0164 (0.944)	0.0539 (1.29)		
 22 1,2-benzo pyrene	0.0723 (1.10)	0.0088 (0.719)	0.0596 (1.29)	0.0202 (0.987)	
 23 1,2-benznaphtacene	0.0283 (1.09)	0.0417 (1.32)	0.0340 (1.35)	0.0103 (0.847)	0.0706 (1.11)
 24 pentaphene	0.0432 (1.11)	0.0462 (1.23)	0.0086 (1.784)		
 25 1,2,3,4-Dibenz-anthracene	0.0437 (1.12)	0.0466 (1.21)	0.0063 (0.648)	0.0730 (1.08)	
 26 Picene	0.0606 (1.16)	0.0263 (1.06)	0.0409 (1.06)		
 27 3,4,5,6-dibenz-phenanthrene	0.0604 (1.15)	0.0262 (1.06)	0.0401 (1.16)		
 28 2,3,7,8-dibenz-phenanthrene	0.0560 (1.15)	0.0340 (1.08)	0.0191 (0.993)	0.0472 (1.30)	0.0370 (1.12)
 29 2,3,5,6-dibenz-phenanthrene	0.0571 (1.14)	0.0332 (1.08)	0.0184 (1.00)	0.0470 (1.30)	0.0337 (1.12)
 30 perylene	0.0473 (0.970)	0.0051 (0.239)			

Table 5: I_{ring} and energetical aromaticity indices from ref 41.

Molecule		I_{ring}					TREPE[a]	REPE[b]	η[c]
		1	2	3	4	5			
benzene	1	0.0883					0.0454	0.065	1.00
naphthalene	2	0.0449					0.0389	0.055	0.618
anthracene	3	0.0327	0.0458				0.0339	0.047	0.414
tetracene	4	0.0246	0.0373				0.0307	0.042	0.295
pentacene	5	0.0204	0.0301	0.0363			0.0285	0.038	0.220
hexacene	6	0.0181	0.0253	0.0327			0.0270		0.169
phenanthrene	8	0.0640	0.0208				0.0390	0.055	0.605
pyrene	9	0.0577	0.0185				0.0371	0.051	0.445
chrysene	10	0.0585	0.0300				0.0382	0.053	0.520
triphenylene	11	0.0708	0.0094				0.0411	0.056	0.684
1,2 benzo anthracene	12	0.0401	0.0471	0.0133	0.0687		0.0357	0.050	0.452
1,2,7,8 dibenzo naphthalene	13	0.0595	0.0293				0.0381	0.053	0.568
coronene	14	0.0348	0.0113				0.0395	0.053	0.539
biphenyl	15	0.0826					0.0418	0.060	0.704
3,4 benzo pyrene	17	0.0513	0.0320	0.0124	0.0277	0.0556	0.0362	0.049	0.371
1,2,5,6-dibenzo anthracene	18	0.0667	0.0164	0.0539			0.0367	0.051	0.473
1,2,3,4 dibenzo phenanthrene	19	0.0618	0.0255	0.0406	0.0272	0.0597	0.0379	0.052	0.550
1,2,7,8 dibenzo anthracene	21	0.0666	0.0164	0.0539			0.0367	0.051	0.492
1,2 benzo pyrene	22	0.0723	0.0088	0.0596	0.0202		0.0396	0.053	0.497
1,2 benzo naphtacene	23	0.0283	0.0417	0.0340	0.0103	0.0706	0.0330	0.045	0.327
pentaphene	24	0.0432	0.0462	0.0086			0.0339		0.437
1,2,3,4 dibenzo anthracene	25	0.0437	0.0466	0.0063	0.0730		0.0384		0.499
picene	26	0.0606	0.0263	0.0409			0.0379	0.053	0.502
3,4,5,6 dibenzo phenanthrene	27	0.0604	0.0262	0.0401			0.0378	0.052	0.535
2,3,7,8 dibenzo phenanthrene	28	0.0560	0.0340	0.0191	0.0472	0.0370	0.0355	0.049	0.405
perylene	30	0.0473	0.0051				0.0370	0.048	0.347

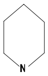
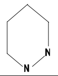
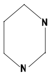
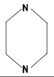
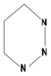
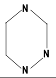
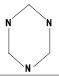
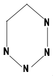
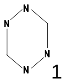
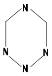
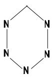
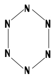
[a] TREPE is topological REPE. [b] REPE, resonance energy per π electron. [c] η, hardness.

Table 6: Indices for systems including non-benzenic cycles.

Molecule	Ring	Indices					
		I_{ring}	NICS [a]	RC [b]	TREPE [c]	REPE [d]	η [e]
 31 cyclobutadiene	1	0.0002			-0.307	-0.268	-0.000
 32 benzo-cylobutadiene	1	0.0552	-4.2		-0.049	-0.027	0.262
	2	0.0073	21.5				
 33 pentalene	1	0.0147	16.9	-1.96		-0.018	0.235
 34 biphenylene	1	0.0636	-6.5		0.010	0.027	0.445
	2	0.0086	18.2				
 35 cyclopentadienyl anion	1	0.1145	-19.4				
 36 cycloheptatrienyl cation	1	0.0450	-8.2				
 37 azulene	1	0.0327	-21.5	-0.07		0.023	0.439
	2	0.0124	-8.3	+0.14			
 38 bicyclo-[6,2,0]-deca-1,3,5,7,9 pentaene	1	0.0087		-0.86			
	2	0.0025		-0.94			
 39 Acenaphthylene	1	0.0461	-9.8			0.039	0.461
	2	0.0168	2.1	+0.02			
 40 pyracylene	1	0.0421	-0.1	+0.71		0.018	0.207
	2	0.0135	12.8	-0.15			
 41 fluoranthene	1	0.0740		+0.89			
	2	0.0094					
	3	0.0464					
 42 corannulene	1	0.0337		+0.69			
	2	0.0157		+0.33			

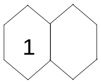
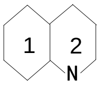
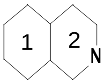
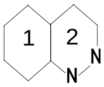
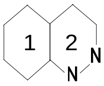
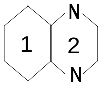
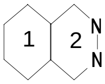
[a] NICS, nucleus independent chemical shifts, ref 35. [b] RC, ring current, ref 27. [c] TREPE, topological REPE, ref 41. [d] REPE, resonance energy per π electron, ref 41. [e] η hardness, ref 41.

Table 7. Aromaticity index in this work (I_{ring}) and in other works, for monocyclic azimes.

Molecule	Indices								
	I_{ring}	RCI[a]	RC_v^b	I_A^c	γ^d		RC[e]	ΔE^f	RE[g]
 1 benzene	0.0883	1.751	1.437	100	1	(1)	1	55	45.8
 43 pyridine	0.0877	1.731	1.422	86	0.926	(0.96)	0.970	55	43.3
 44 pyridazine	0.0878	1.716	1.414	79	0.809	(1.12)	0.983		33.5
 45 pyrimidine	0.0864	1.727	1.411	84	0.852	(0.84)	0.898	58	40.6
 46 pyrazine	0.0878	1.739	1.411	89	0.877	(1.17)	0.976	54	40.9
 47 1,2,6 triazine	0.0875			77					43.1
 48 1,2,4 triazine	0.0871			86					32.9
 49 1,3,5 triazine	0.0840	1.724	1.404	100	0.804	(0.82)	0.791	63	44.9
 50 1,2,3,6 tetrazine	0.0878								29.7
 51 1,2,4,5 tetrazine	0.0877	1.735	1.404	98	0.711			55	21.6
 52 1,2,4,6 tetrazine	0.0856								35.1
 53 pentazine	0.0878	1.746	1.407						16.5
 54 hexazine	0.0898	1.792	1.426						45.8

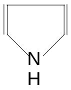
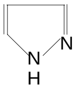
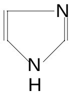
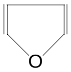
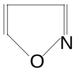
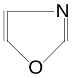
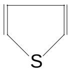
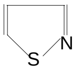
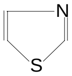
[a] RCI, ring current index, ref 23. [b] RC_v , bond valence criterion, ref 15. [c] I_A, unified aromaticity index, ref 55. [d] γ, relative diamagnetic anisotropy, ref 30, the values between parentheses refer to experimental values reported in the same ref. [e] RC ring current, ref 27. [f] ΔE, π delocalization energy, ref 52. [g] RE, resonance energy, ref 56.

Table 8: Aromaticity indices in this work (I_{ring}) and other works, for naphthalene and benzoazines.

	Indices				
	ring	I_{ring}	RC [a]	I_A [b]	RE [c]
 2 naphthalene	1	0.0499	0.79	142	80.3
 55 quinoline	1	0.0511	0.77	134	81.0
	2	0.0469	0.75		
 56 isoquinoline	1	0.0517	0.77	133	81.0
	2	0.0480	0.94		
 57 cinnoline	1	0.0553	0.74	130	70.3
	2	0.0422	0.78		
 58 quinazoline	1	0.0533	0.77	143	76.5
	2	0.0442	0.70		
 59 quinoxaline	1	0.0528	0.75	132	75.3
	2	0.0435	0.75		
 60 phthalazine	1	0.0538	0.79	136	70.3
	2	0.0466	0.74		

[a] RC, means ring current, ref 27. [b] I_A, unified aromaticity index, ref 55. [c] RE, resonance energy, ref 56.

Table 9. Aromaticity index in this work (I_{ring}) and in other works, for heterocycles with 5-m rings.

Molecule	Indices							
	I_{ring}	RCI[a]	RC_V[b]	I_A[c]	RE[d]	$\Delta\varepsilon_{\pi l}$[e]	η[f]	Λ[g]
61  pyrrole	0.0962	1.464	1.124	85	40.5	0.0860	7.12	10.2
62  pyrazole	0.0964	1.297	1.096	90	40.4	0.1009	7.345	11.4
63  imidazole	0.0960	1.423	1.075	79	40.0	0.0933	7.38	12.3
64  furan	0.0541	1.431	1.081	53	27.2	0.0597	7.42	8.9
65  isoxasole	0.0539	1.361	1.032	52	34.3	0.0747	7.71	13.1
66  oxasole	0.0553	1.393	1.042	47	26.2	0.0688	7.72	10.4
67  thiophene	0.0696	1.450	1.173	81.5	43.0	0.1123	6.74	13.0
68  isothiazole	0.0696			91		0.1071	7.0	
69  thiazole	0.0718	1.389	1.099	79	42.0	0.1005	6.97	11.6

[a] RCI means ring current index, ref 23. [b] RC_V, bond valence criterion, ref 15. [c] I_A, unified aromaticity index, ref 55. [d] RE, resonance energy ref 54. [e] $\Delta\varepsilon_{\pi l}$ steps from natural localized MO's, ref 67. [f] η, hardness, ref 66. [g] Λ, magnetic susceptitility exaltation , ref 63.

Table 10: Aromaticity indices for some 5m-rings and benzene.

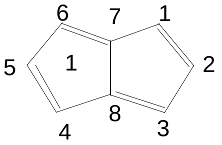
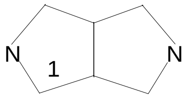
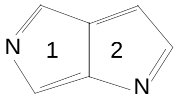
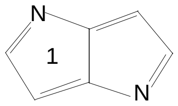
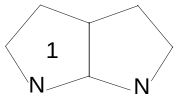
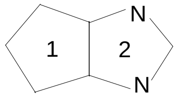
		Index		
		ASE[a]	NICS[b]	Λ[c]
pyrrole	61	25.5	-17.3	-12.1
thiophene	62	22.4	-14.7	-10.0
furan	63	19.8	-13.9	-9.1
cyclopentadienyl anion	35	28.8	-19.4	-17.2
benzene	1	26.6	-11.5	-13.6

[a] ASE, aromatic stabilization energy, ref 8. [b] NICS, nucleus independent chemical shifts, ref 35. [c] Λ, magnetic susceptibility exaltation, ref 8.

Table 11: I_{AB} (eq. 1) and its mean variantion ΔI_{AB} along the cyle for furan, thiophene and pyrrole.

Molecule	I_{12}	I_{23}	I_{34}	ΔI_{AB}
furan 63	1.10	1.69	1.19	0.545
thiophene 62	1.17	1.64	1.24	0.385
pyrrole 61	1.26	1.52	1.33	0.220

Table 12. Indices for diazapentalenes.

		Indices			
Molecule	Ring	I_{ring}	REPE[a]	TREPE[b]	η[c]
 70 pentalene	1	0.0147	-0.018	-0.027	0.235
 71 2,5-diazapentalene	1	0.0188	-0.001	-0.008	0.284
 72 3,5-diazapentalene	1	0.0139	-0,016	-0.022	0.196
	2	0.0159			
 73 3,6-diazapentalene	1	0.0134	-0.033	-0.041	0.117
 74 3,4-diazapentalene	1	0.0092	-0.036	-0.042	0.114
	2	0.0122			
 75 1,3-diazapentalene	1	0.0105	-0.037	-0.047	0.126
	2	0.0146			

[a] REPE, resonance energy per π electron, ref 41. [b] TREPE, topological REPE, ref 41. [c] η, hardness, ref 41.