Correlation of Delocalization Indices and Current-Density Maps in Polycyclic Aromatic Hydrocarbons

Stijn Fias,[a] Patrick W. Fowler,[b] Juan Luis Delgado,[b, c] Uwe Hahn,[b, d] and Patrick Bultinck*[a]

Abstract: Using multicentre delocalization indices, the ring current maps of a large set of polycyclic aromatic hydrocarbons (PAH) are reconstructed and compared with ab initio computations of the same maps in the pseudo-π version of the ipsocentric approach to magnetic response. The quality of the comparison indicates that both delocalization and ring current approaches capture the same information about the aromatic nature of the PAH. Aromaticity as a global property, requires knowledge of more than single circuits, but the present results suggest no need to introduce a "multidimensional character" for aromaticity.

Keywords: aromaticity · delocalization · NICS · ring currents

Introduction

The concept of aromaticity is fundamental and widespread in chemistry,[1–4] but aromaticity is not itself a directly measurable quantity. This absence of an immediate observable has resulted in a proliferation of approaches which have been suggested to describe and quantify the aromaticity of a molecule, typically based on energetic,[5] geometric,[6] quantum chemical[7] or magnetic considerations.[8–12] Lack of correlation between different measures has provoked suggestions that aromaticity should be considered a multidimensional phenomenon.[5, 13–16] Multidimensionality has been much debated, but as all molecular properties, including aromaticity indices, are ultimately derived from the same molecular wave function, it is hard to envisage a physical justification for different well founded approaches to aromaticity yielding contradictory results.

A related concept is that of electron delocalisation. There has been an upsurge of interest in ways of quantifying the extent of delocalization. Among the more popular are the Para Delocalization Index (PDI)[7,17] and the Fluctuation (FLU)[7,18] Index. Recently, one of the present authors introduced Multi Centre Bond Indices (MCBI) to quantify electron delocalization in aromatic systems.[19–22] In fact, all three quantities were originally introduced as aromaticity indices, but there is an important distinction that should be kept in mind when using a delocalization index to quantify aromaticity.

The distinction emerges when we examine the magnetic properties of an aromatic system. It has long been known that aromatic and antiaromatic systems sustain ring currents in the presence of a magnetic field. This forms the basis of the use of ring current (RC) maps[11,12] as an indicator of aromaticity and antiaromaticity. Both aromaticity and antiaromaticity imply a delocalized electronic structure, but a molecule could have a delocalized system, and still not show a ring current when exposed to a magnetic field. In a perturbation theory approach, distribution and intensity of ring currents depends on the availability of virtual orbitals of appropriate symmetry.[11,23,24] In this sense, significant delocalization is a necessary but not a sufficient condition for ring current. Moreover, if a ring current does appear, the delocalization index does not reveal information on its sense: dia-

[a] S. Fias, Prof. Dr. P. Bultinck
Department of Inorganic and Physical Chemistry
Ghent University, Krijgslaan 281 (S3), 9000 Ghent (Belgium)
Fax:(+32) 926-44-983
E-mail: Stijn.Fias@UGent.be
Patrick.Bultinck@UGent.be

[b] PRof. Dr. P. W. Fowler, Dr. J. L. Delgado, Dr. U. Hahn
Department of Chemistry, University of Sheffield
Sheffield, S3 7HF (UK)

[c] Dr. J. L. Delgado
Present address: Departamento de Química Orgánica
Facultad de Química, Universidad Complutense
28040 Madrid (Spain)

[d] Dr. U. Hahn
Present address: Departamento de Química Orgánica
Facultad de Ciencias, Universidad Autónoma de Madrid
28049 Cantoblanco (Spain)

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tropic aromatic and paratropic antiaromatic currents are both associated with delocalization.

A very popular aromaticity index also based on ring currents is the Nucleus Independent Chemical Shift (NICS).[8,9,25,26] The basic idea of NICS is that one concentrates all RC information in a single point at which the chemical shift is computed. Typically, this means that the negative of the mean magnetic shielding is computed at the centre of the ring for which the degree of aromaticity is to be assessed. Over time, schemes for the calculation of NICS have been refined to cope with different criticisms, but clearly reduction of the rich information of a RC map to a single number remains questionable, as completely different RC maps could give rise to nearly indistinguishable NICS values. Although criticised on several occasions,[19,27–29] the method remains widely used among computational chemists. In many cases, NICS and RC maps lead to similar conclusions, but for many polycyclic aromatic hydrocarbons (PAH) NICS can give unexpected results. One well known class of problematic cases is when bifurcated circuits arise.[29–31]

Before accepting claims of multidimensionality, one needs to examine in detail the grounds for poor correlation between indices of aromaticity. In a recent contribution, some of the present authors have shown that multicentre indices and NICS can be reconciled, the main conclusion being that the NICS value for a particular ring has significant contributions from delocalisation in longer circuits that contain the ring, as well as from delocalisation within the ring itself.[32] Thus, the NICS computed at the centre of a specific benzenoid ring of a PAH does not reflect solely the aromaticity or ring current of that ring. By taking into account larger circuits, it was shown that NICS and multicentre indices do in fact correlate quite well.

It should be noted that the idea that NICS and ring current maps do not always reflect the local aromaticity of individual circuits was previously discussed also in detail by Aihara et al. using graph theoretical and Hückel calculations.[33–36] In terms of the present paper, the main issue is that one cannot derive from global ring currents and NICS values the degree of aromaticity of a specific circuit. This agrees very well with the conclusions of Aihara et al.[33–36]

In order to establish whether RC maps and multicentre indices can also be reconciled, in the present work we develop a method for extracting approximate maps from the multicentre indices and compare them to the ab initio maps for a very large set of PAH. The main aim of the present study is thus to assess whether RC maps and multicentre indices lead to the same chemical conclusions, thereby reducing the scope for a "multidimensional character" of aromaticity.

Method

In a recent contribution, some of the authors have shown that there is a significant influence of different higher-order circuits on NICS, in addition to the local (benzenoid) aromaticity.[32] It was confirmed statistically that the total NICS

at the centre of a given six-membered ring X can be expressed as a linear combination of the six-centre index (SCI), ten-centre indices (TCI) and fourteen-centre indices (FCI-a and FCI-b) for the circuits that include X. The notion of inclusion is the intuitive one: for example, in the infinite graphite sheet, a ring X defines one six-centre-circuit and is included in six ten-centre-circuits, 9 fourteen-centre-circuits of type a and 18 of type b. Figure 1 illustrates the circuits for anthracene and phenanthrene. The correlation is expressed in terms of four fitting parameters a to d:

$$\text{NICS}(r_X) = a\text{SCI} + b\sum_j \text{TCI}_j + c\sum_k (\text{FIC}-a_k+\text{FCI}-b_k) + d$$

(1)

In this expression, j and k run over all circuits of length ten and fourteen that include X, and FCI-a and FCI-b are the fourteen-centre indices in the linear and angular circuits of length fourteen, respectively.
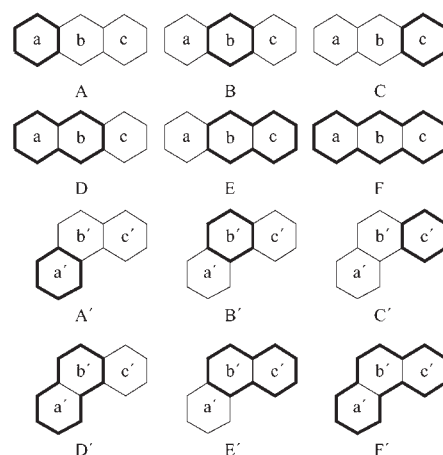

Figure 1. Different circuits in anthracene and phenanthrene.

For 109 polycyclic aromatic hydrocarbons, leading to a total of 493 symmetry-unique rings, all six-, ten-, and fourteen-centre indices (SCI, TCI, and FCI) were calculated and the above regression was derived. It was found that the SCI contribution is the largest, at about 50 % of the total sum of SCI, TCI and FCI contributions to the NICS value, followed by a TCI contribution of about 32 % and the FCI contribution of about 18 % of the total. The constants a to d for reconstructing different members of the NICS family using Equation (1) were calculated in a previous study using multiple linear regression[32] and the explicit values are given in the Supporting Information.

In the present work, using the constants a, b and c of Equation (1), approximate RC maps have been derived from the multicentre delocalization indices. Such approximate maps will be denoted as MCBI-RC maps in what follows. To obtain the maps, the values of the SCI were projected as vectors on the bonds of the benzenoid ring in a diatropic manner. In this method, the SCI vectors of two ad-

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joint benzenoid rings partially cancel (or strengthen) each other on their common bond. The same was done for the ten-, and fourteen-centre indices (TCI, FCI). For the fourteen-centre indices, anthracene- and phenanthrene-like circuits (F and F′ in Figure 1, respectively) were calculated and used with equal weight to construct one fourteen-centre vector set. The parameters obtained from the regression in equation 1[32] were used as weighting factors to scale and then sum the SCI-, TCI- and FCI-vector maps to construct the final MCBI-RC map.

As many of the PAH are quite large molecules, an efficient scheme for the evaluation of MCI and RC maps is most desirable. Paradoxically, results of modern high level calculations for the present class of molecules have revived the pseudo-π technique, based on a 1937 idea of London.[37] In this technique, extensive use is made of the analogy between the π system in a planar molecule and the σ system of an array of hydrogen atoms using only s-type orbitals. This method has been shown to give pseudo-π RC maps which are nearly indistinguishable from RC maps computed for the full molecule.[38] It has also been shown that MCBI obtained using this pseudo-π method exhibit a very tight correlation with MCBI obtained at higher levels of theory.[39] Moreover, it was recently shown that pseudo-π NICS values exhibit a good correlation with the recommended π-density based NICS indices.[32] Using this method it is possible to reduce the computer time drastically, allowing the calculation of the properties of increasingly larger systems.[40] For consistency, both the MCBI and the ab initio RC maps used for comparison were obtained using the pseudo-π method. Within the pseudo-π model, σ current in the molecular plane is a near-quantitative model for the current at a height of 1 Bohr in the actual molecule, which is the height at which the current is usually displayed in a RC map.

In the present work, both the MCBI-current maps and full ring current maps were calculated and compared for 394 PAH, constructed from one to seven benzenoid rings. The molecules were taken to be in ideal geometries, with a uniform C−C bond length of 1.4 Å. Previous studies have shown that optimization of the molecular structure has only a minor influence on calculated values of ring current and MCBI. Calculation of RC maps used the SYSMO program;[41] calculations of HF wavefunctions for the delocalization indices were performed using Gaussian 03,[42] using the STO-3G basis prescribed in the pseudo-π model; MCBI were calculated using the Ghent Kekulé program, based on Global Population Analysis[43–45] in the Mulliken approach.[46–51]

Results and Discussion

Using the methods described above, RC and MCBI-RC maps were computed for the entire range of PAH. In order to study the relation between both types of RC maps and to document the good agreement between them, this section presents a detailed discussion of several specific cases, including some known to be difficult in terms of correlation between aromaticity indices.

Linear polyacenes: Local aromaticity within linear polyacenes is a major point of interest in recent literature.[19,27,33,52–55] According to some indices, such as NICS, the central rings of linear polyacenes are the most aromatic, whereas other indices, such as SCI, predict the reverse.[19,20] From chemical reactivity, one would also conclude that the central ring is the least aromatic. As there is divergence in views already for a simple molecule like anthracene, reconciliation of NICS and MCBI data might seem a hopeless task. Nevertheless, in a recent contribution it was shown by some of the authors that the main reason for this apparent disagreement between indices arises from different views of local aromaticity.[32] A NICS value computed for a single point does not reflect solely the current in the six-centre ring encircling this point, but contains significant contributions from other encircling circuits. The MCBI for a specific circuit is by definition related to that circuit alone, and influenced only indirectly by other circuits via the charge and bond order matrix.

Figure 2 shows how the MCBI-RC map for a linear polyacene can be constructed in a step-wise fashion for anthracene. Figure 2a shows the MCBI-RC map obtained from only the SCI of all three rings. As the SCI is slightly smaller for the central ring than for the outer rings, the MCBI-RC is slightly stronger in the outer rings, but already correctly shows the concentration of ring current on the perimeter. Introduction of TCI and then FCI, gives maps 2b–2c, which show significant changes with respect to 2a. Finally, Figure 2d shows the ab initio computed RC map. Clearly, this directly computed map is in very good agreement with that constructed from 6, 10 and 14-centre indices (2c). Concerning quantitative agreement between the ab initio RC and MCBI-RC maps, the correlation between ab initio computed ring current intensities along the C−C bonds and the intensities from the MCBI-RC for benzene, naphthalene, anthracene and phenanthrene exhibits a linear regression correlation coefficient of 0.97. This shows that the agreement is excellent, even in the quantitative sense.

This indicates that SCI results and RC maps do not contradict, but rather reflect two different factors. When RC maps are inspected or NICS data examined, one is inclined to attach a degree of local aromaticity to a specific ring by applying a 3D condensation scheme to "cut" the entire map into pieces. This decomposition is spatially, rather than graph-theoretically based, and the connection is with rings rather than circuits. MCBI, on the other
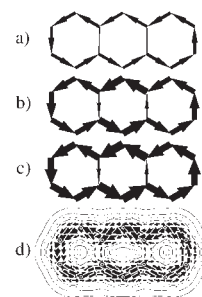

Figure 2. Step-wise build-up of the MCBI-RC map for anthracene.

hand, directly reflect individual graph circuits. It is gratifying that both approaches can be reconciled. It is not so much that local aromaticity has multidimensional character as that it can be viewed in two different ways. The spatial decomposition picture has the advantage of "what you see is what you get" approaches, but the circuit picture is also well defined. Choice between the different pictures is more a matter of taste than an objective question.

The RC and MCBI-RC maps for the linear acenes are shown in Figure 3. In all cases, in both the RC and MCBI-RC maps the current increases towards the central rings, implying a higher NICS value, but not because of an intrinsically larger SCI value for the middle ring, but because of the higher number of circuits.
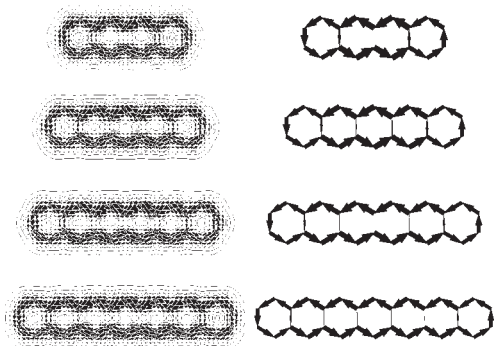

Figure 3. RC and MCBI-RC maps for the linear acenes tetracene to heptacene.

In both RC and MCBI-RC maps the maximum current on the inner rings appears to converge to a limit with system size. This trend is also found in the NICS values of these systems, and gives support to the observations of Randic[56] and some of the authors that the influence of higher-order circuits becomes less important in energetics and properties for increasingly larger circuits.[32] This implies that both NICS and ring currents can be modelled accurately using the MCBI with circuits of sizes up to fourteen.

Kinked polyacenes: Figure 4 shows maps for phenanthrene and triphenylene as typical examples of nonlinear PAH. In these molecules there is a larger difference in SCI between inner and outer rings, but TCI and FCI are smaller than in anthracene, which causes a change in the balance of currents. Although the dominant current is on the central ring in anthracene, it is on the outer rings of phenanthrene and triphenylene. This change leads to a distinct pattern of current on the inner ring, with an alternation of para- and diatropic senses. These cases illustrate that reduction of RC map information to a single number can lose the subtleties of the physical phenomenon. NICS would characterize the middle rings of these polyacenes as aromatic, whereas the full current pattern will only be revealed by the full RC map or in the MCBI-RC map.
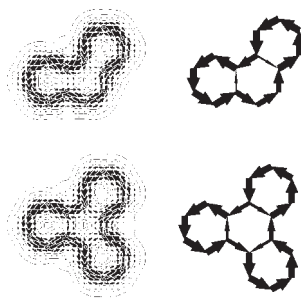

Figure 4. RC and MCBI-RC maps for the kinked acenes phenanthrene and triphenylene.

Pyrene: Figure 5 shows maps for pyrene. The main current runs on the periphery and only two outer rings have closed circulations. The RC map shows how to interpret the NICS values for the four rings: NISC(0) is −11.65 ppm for the outer and −4.65 ppm for the inner rings. The "aromatic" value for the outer ring and non-aromatic value for the inner ring reflect the respective closed and open nature of the currents. Most of the current in pyrene is running along the periphery, and NICS exaggerates the difference between the two rings. It is not clear that the inner rings can be termed aromatic in any significant sense.
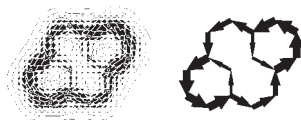

Figure 5. RC maps and MCBI-RCM for pyrene.

Perylene and dibenzo[cd,lm]perylene: The ring current pattern of perylene shows two distinct naphthalene-like circuits and the current on the bonds connecting the two naphthalene substructures is essentially zero (Figure 6). The same pattern is seen in the MCBI-RC map. The NICS of the inner ring is positive (NICS(0) = 8.19 ppm), induced by the naphthalene-like circuits above and below the central ring. The inner ring can hardly be seen as anti-aromatic, as its positive NICS value (8.19 ppm) would indicate, it is essentially an empty ring, flanked by two diatropic naphthalene circuits (NICS(0) = −5.10 ppm).

With two more hexagonal rings fused to the naphthalene-like rings, the structure is that of dibenzo[cd,lm]perylene or peropyrene. This molecule shows a completely different ring current pattern. The two
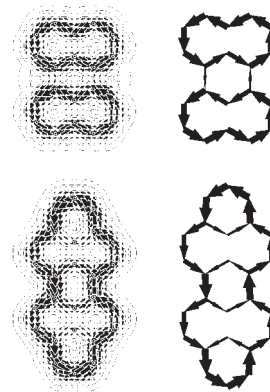

Figure 6. RC and MCBI-RC maps for perylene and dibenzo[cd,lm]perylene.

strong naphthalene circuits are lost, and replaced by a strong current on the periphery, which runs through the outer bonds of the middle hexagon. The three non-naphtalenoid hexagons all support diatropic ring currents, in addition to the strong perimeter current. The MCBI-RCM accurately reproduces this same ring current pattern.

Antanthrene: Typical "hard cases" for which NICS and other aromaticity indices fail are those of molecules which contain bifurcated rings.[29–31] An example of such a molecule is anthanthrene, which has two bifurcated corner-rings, as seen in the maps of Figure 7 (the upper right and lower left corners). These corner rings are neither aromatic nor anti-aromatic, but the NICS(0) value of −1.81 ppm for these rings assign a questionable quantitative measure of aromaticity, whose sign is determined only by the side on which the strongest current happens to run. A correct physical picture is given only by the RC and MCBI-RC map, which shows the bifurcation.
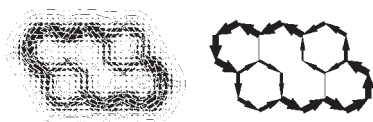

Figure 7. RC and MCBI-RC maps for anthanthrene.

Periphery-only currents: Ring-current maps for some PAH show no current in the centre of the molecules, but an entirely peripheral current. This is the case for the benzo[cd]-pyrene anion and triangulene, shown in Figure 8. It is gratifying to see that, although the SCI values of the benzenoid rings vary (Figure 9), upon addition of the different circuits the MCBI-RC map is able to recover the emptiness of the interior of these molecules. Once again, the NICS reduction of the RC maps to a single value for each ring does not lead to the conclusion of the single peripheral current, exhibited in both RC and MCBI-RC maps.
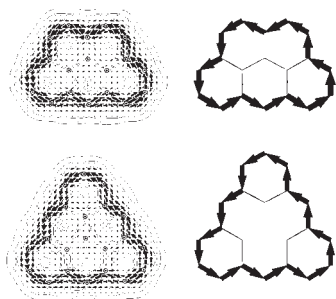

Figure 8. RC and MCBI-RC maps for benzo[cd]pyrene anion and triangulene.

Benzo[ghi]perylene and coronene: Benzo[ghi]perylene (Figure 10) is a molecule that is closely related to coronene, but lacks one hexagonal ring. Because of this gap, the cen-
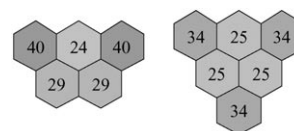

Figure 9. SCI values for benzo[cd]pyrene anion and triangulene, expressed in terms of the percentages of benzene value.

tral ring of the molecule does not have a closed paratropic current as in coronene. Only five of the six bonds have a current in the paratropic sense. The inner ring is not classifiable as purely anti-aromatic, as only the (RC or MCBI-RC) maps show. Only three rings, in *meta* positions on the middle ring, have a full diatropic current. These are the sites of the sextets in the Clar electronic structure of this molecule. This distribution is consistent with the SCI, which has larger values on these positions (Figure 11), favouring a diatropic current. The ring current on the middle ring also alternates in intensity, showing a larger current in the bonds fused to the Clar rings.
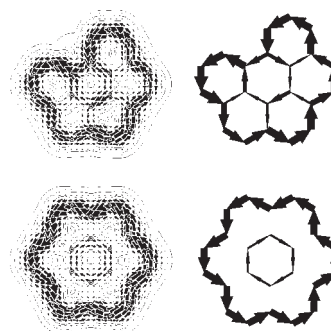

Figure 10. RC and MCBI-RC maps for benzo[ghi]perylene and coronene.

For coronene, the MCBI-RC map reproduces the well known current map with a large diatropic current on the edge of the molecule and a small paratropic current around the middle ring. The genesis of this current pattern is already seen in the SCI map, where the outer benzenoid rings have larger delocalization than the inner (Figure 11).
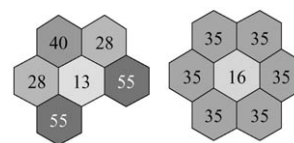

Figure 11. SCI maps for benzo[ghi]perylene and coronene, expressed in terms of the percentages of benzene value.

Applicability of the MCBI-method: As the above examples show, multicentre delocalization indices contain the information necessary for the prediction of current density maps in PAH. Formally, the multicentre delocalization indices quantify the delocalization of the π-electron cloud within a

chosen circuit, whereas the RC map refers to the response of the molecule to a magnetic field. The agreement of MCBI-RC and RC maps suggests that the forces on the electrons for the different circuits are at least approximately proportional to the respective multicentre delocalization indices.

Having established that the RC and MCBI-RC maps give similar results, it is appropriate to comment on the range of applicability of MCBI as an aromaticity index. As noted earlier, the MCBI reflects delocalization. All the circuits in the PAH are aromatic in nature, and the MCBI relates to the aromaticity, but it is possible to imagine cases where such simple reasoning could conceivably fail, for example, rings of other sizes or heterocyclic systems. There are difficulties in applying the pseudo-π model to heterocyclic systems[57] and it would be necessary to make further checks on the agreement between MCBI-RC and RC maps.

The RC model allows quantitative comparison of currents by calculation of the flux of the current through planes cutting bonds, although this is quantity is not immediately evident in the usual pictorial presentation. Relative sizes of the longest arrows in ring current maps can also be used to compare to a standard, for example, the benzene π-current at a height of one Bohr. The MCBI-RC map essentially assigns a numerical value to each bond, which can easily be used for comparison and provides a useful link between RC, NICS and delocalization.

Conclusion

The present results show that MCBI delocalization indices and RC maps can be reconciled in a chemically intuitive way. In previous work, similar reasoning can be used to reconcile NICS and MCBI. As there is a good correlation between the MCBI and other local aromaticity indices such as the Polansky index,[58,59] the same correlations will hold for these indices, and in general it is expected that the above reasoning can be used to reconcile delocalisation based and magnetic indices. The claimed evidence for multidimensionality of aromaticity vanishes in these cases, as it is apparently only a consequence of a choice of description, in terms of rings or graph circuits. By making a suitable combination of the delocalisation indices for different circuits, the RC map picture is recovered.

Acknowledgements

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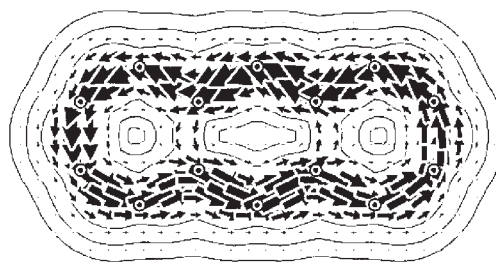
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Aromaticity ───────

S. Fias, P. W. Fowler, J. L. Delgado,
U. Hahn, P. Bultinck *. . . . . ■■■–■■■

Correlation of Delocalization Indices and Current-Density Maps in Polycyclic Aromatic Hydrocarbons

Multicentre delocalization indices have been used to construct approximate ring current maps of a large set of polycyclic aromatic hydrocarbons (PAH), which have been compared to the ab initio maps (see figure). Both methods lead to the same conclusions regarding the aromatic character of individual rings and therefore suggest that there is no need to induce a "multidimensional character" for aromaticity.

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