

Interpreting Aromaticity and Antiaromaticity through Bifurcation Analysis of the Induced Magnetic Field

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In all molecules, a current density is induced when the molecule is subjected to an external magnetic field. In turn, this current density creates a particular magnetic field. In this work, the bifurcation value of the induced magnetic field is analyzed in a representative set of aromatic, non-aromatic and antiaromatic monocycles, as well as a set of polycyclic hydrocarbons. The results show that the bifurcation value of the ring-shaped domain adequately classifies the studied molecules according to their aromatic character. For aromatic and nonaromatic molecules, it is possible to analyze two ring-shaped domains, one diatropic (inside the molecular ring) and one paratropic

(outside the molecular ring). Meanwhile, for antiaromatic rings, only a diatropic ring-shaped domain (outside the molecular ring) is possible to analyze, since the paratropic domain (inside the molecular ring) is irreducible with the maximum value (attractor) at the center of the molecular ring. In some of the studied cases, i.e., in heteroatomic species, bifurcation values do not follow aromaticity trends and present some inconsistencies in comparison to ring currents strengths, showing that this approximation provides only a qualitative estimation about (anti)aromaticity.

Introduction

Different concepts of chemistry, such as reactivity,^[1] chemical bond^[2] and aromaticity^[3] are theoretically rationalized through the analysis of three-dimensional mathematical functions. The calculation and analysis of three-dimensional functions are very well known; however, their global graphical representation and visualization is not as easy as for one- or two-dimensional functions. Thus, one resorts to contour maps or isosurface plots to represent them, with a consequent loss of information. In order to have a more unambiguous way to analyze a three-dimensional (or higher dimension) function, one could use the framework of the topological analysis. In theoretical chemistry, this has already been done in the pioneer works of Bader, which originated the Quantum Theory of Atoms in Molecules^[4] (QTAIM). Later, this topological analysis has been applied to interpret the Electron Localization Function,^[2,5] and more

recently to the Fukui function.^[1,6] Regarding this current work, we are particularly interested in the bifurcation analysis applied to one magnetic property, the induced magnetic field (B^{ind}). This analysis is applied to a series of molecular rings, and consists in identifying the (3, -1) critical points of the scalar function $B^{\text{ind}}(r)$ that connect a number of irreducible domains forming a global reducible ring-shaped domain.

Aromaticity is one of the most commonly cited concepts in chemical literature due to its broad application to rationalize the stability of a great variety of molecules nowadays.^[7] Although aromaticity is not an experimentally measurable quantity, many indices from different criteria have been proposed to characterize and quantify it^[3-9] (see references above for further details). The magnetic criteria is based on the fact that aromatic compounds sustain an induced ring current density in the presence of both a normal -to the molecular plane- and a uniform external magnetic field^[8] (B^0). In turn, this current induces a characteristic magnetic field^[9] (B^{ind}), which is different to the external magnetic field (B^0). Aromatic/antiaromatic compounds show a diatropic/paratropic ring current^[10] and a consequent magnetic field (inside the molecular ring) with opposite/same direction regarding^[11] the external magnetic field (B^0). This theoretical background led to the proposal of the nucleus independent chemical shift (NICS) by Schleyer et al.^[11] in 1996, defined as "the negative of the absolute magnetic shielding". This index is by far, the most popular tool for the assessment of aromaticity in molecules. However, its indiscriminate use has been criticized.^[10b,12] On the other hand, the out-of-plane component (NICS_{zz})^[8a,13] which is equivalent to the z-component of the induced magnetic field (B_z^{ind}) proposed by Merino et al.^[8b,9] have been found to be particularly sensitive to π -aromaticity. The B_z^{ind} has been analyzed using different strategies. For instance, two-dimensional maps have been used by several authors to describe the electronic delocalization^[8b-f,12e,14] and, more recently, the chemical bond^[15]

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in different compounds. These maps provide more detail regarding the delocalization of various systems and have been applied qualitatively to describe aromaticity. Additionally, Kleinpeter et al.^[16] built three-dimensional grids of magnetic shielding and called them isochemical shielding surfaces (ICSS). These isosurfaces offer qualitative pictorial information regarding the long-range effects of mono and polycyclic aromatic systems. The use of these grids was initially proposed to quantify the influence of both the presence of functional groups (with multiple bonds) and the ring current effect of arenes, on the anisotropy of the chemical shielding.

Some years ago, some of us,^[5] proposed an aromaticity scale based on the topology of the electron localization function (ELF). This scale uses the bifurcation values of the ring-shaped domain (present in molecular rings). These values are interpreted as a measure of the interaction among the different basins and, chemically, as a measure of electron delocalization. This methodology has been successfully applied to a series of organic hetero- mono- and polycyclic compounds, and all-metal clusters. Later, Solá and coworkers^[17] pointed out that this bifurcation value corresponds to the (3, -1) critical points of this scalar function. In this work, we extend this strategy to analyze a magnetic response property, specifically the bifurcation values of the ring-shaped domains of the z-component of the induced magnetic field (B_z^{ind}). This methodology has been applied to different organic compounds that include monocycles, a series of heterocycles analogues of benzene and polycyclic aromatic hydrocarbons (Clar structures). The results clearly evidence a flawless classification of aromatic, antiaromatic and nonaromatic systems according to these bifurcation values.

Computational Methods

All calculations reported in this work were performed using Gaussian 09 computational package at the PBE0/6-311g**^[18] and PBE0/def2-TZVP^[19] level. The latter basis set uses quasi-relativistic effective core potentials for the heavier atoms (As, Sb, Bi) and was used for the calculations involving the heterocycles analogues of benzene. For the fully optimized molecules, vibrational frequency calculations were performed at the same level to ensure that we obtained a true minimum on the potential energy surface, with the exception of the model molecules cyclooctatetraene (C_8H_8), benzene dication ($C_6H_6^{2+}$), and planar cyclobutene (C_4H_6), which have an imaginary frequency. Their magnitudes are 132.6i, 520.9i and 148.5i cm^{-1} , respectively. The B_z^{ind} values were computed employing the gauge-including atomic orbital^[20] (GIAO) in gas phase at the above-mentioned level. The three-dimensional B_z^{ind} isosurfaces were constructed using the Multiwfn software.^[21] Visualization of these isosurfaces and bifurcation values have been obtained using Chemcraft.^[22]

Results and Discussion

Monocyclic Hydrocarbons. Twelve cyclic hydrocarbons have been selected to apply the bifurcation analysis of the B_z^{ind} (four aromatic, four non-aromatic and four antiaromatic). First, it is important to summarize what the standard analysis of the

three-dimensional isosurfaces of the B_z^{ind} consists of. Aromatic/antiaromatic molecules exhibit a long-range shielding/deshielding (diatropic/paratropic) region inside the molecular rings. This means that shielding/deshielding regions slowly decay and persist at distances far above and far below the molecular rings. For non-aromatic compounds, this long-range behaviour is absent. Consequently, the distance along the main axis at which an isosurface of a small value (e.g. $+/-5$ ppm) is projected has been used as a quantitative descriptor of aromaticity.^[16a] In Figure 1 the isosurfaces of the B_z^{ind} for the studied monocycles, using the isovalues of $+/-20$ ppm, are depicted. The shapes and space distribution of these surfaces are consistent with the above-mentioned features of aromatic, non-aromatic and antiaromatic molecules.

The bifurcation isosurfaces and the corresponding bifurcation values for benzene (aromatic), cyclohexane (nonaromatic) and benzene dication (antiaromatic), as representative cases, are shown in Figure 2. The aromatic and nonaromatic molecules exhibit two concentric ring-shaped domains: the inner (diatropic) is placed around the molecular ring and the outer (paratropic) is placed surrounding outside the global molecule. In the case of the antiaromatic molecule, only the outer ring-shaped domain is present, which is diatropic in this case. The inner ring is replaced by an irreducible domain with an ellipsoidal shape (paratropic). These bifurcation values are rationalized as follows: higher bifurcation values (considering absolute values) means that additional contributions to the induced magnetic field (coming from the ring current) are manifested between local domains (coming from the local bonds and core electrons). For the case of the external ring-shaped domain, the rule is the same, higher bifurcation values correspond to aromatic or antiaromatic molecules. However, the sign of these domains is opposite to the inner ones. This is in total agreement with a classical Biot-Savart representation of the ring current phenomena and its consequent induced magnetic field, which for aromatic molecules is expected to be intense and shielding (in opposite direction to the external magnetic field) inside the molecular ring and, moderately intense and deshielding (in the same direction to the external magnetic field) outside the molecular ring.

Figure 3 (Left) show the bifurcation values for the complete set of studied monocycles. Concerning aromatic systems, the inner diatropic ring-shaped domain bifurcates at around -52.0 ppm for $C_5H_5^-$, C_6H_6 and $C_7H_7^+$, which is consistent with the fact that these three systems possess a similar aromatic character^[23] and have the same number of π -electrons. The cyclopropenyl-cation ($C_3H_3^+$) presents a bifurcation value of -58.0 ppm, higher than that of benzene. A possible explanation is the size of the molecular ring, whose correction is not considered in this work. Non-aromatic and antiaromatic compounds present smaller absolute values around -25.0 and -15.0 ppm, respectively. The same pattern is exhibited when we analyse the outer ring-shaped domain (see Table S1 in the supporting information). In the case of antiaromatic molecules, it was only possible to apply this analysis to the outer and diatropic ring shaped domain. The classification of these molecules, according to their antiaromatic character $C_4H_4 >$

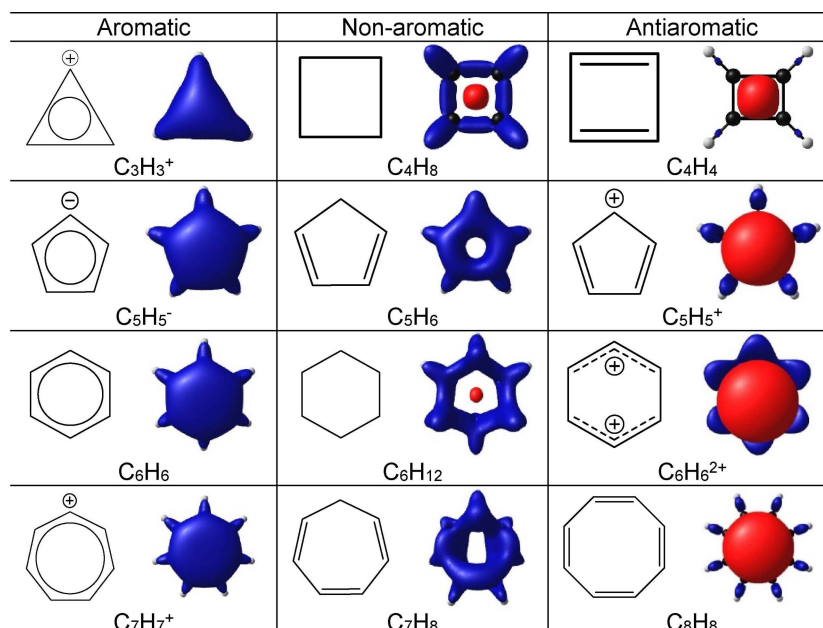


Figure 1. isosurfaces for aromatic, non-aromatic and antiaromatic rings at +/- 20 ppm isovalue. Blue color represents negative (diatropic) values and red color represent positive (paratropic) values.

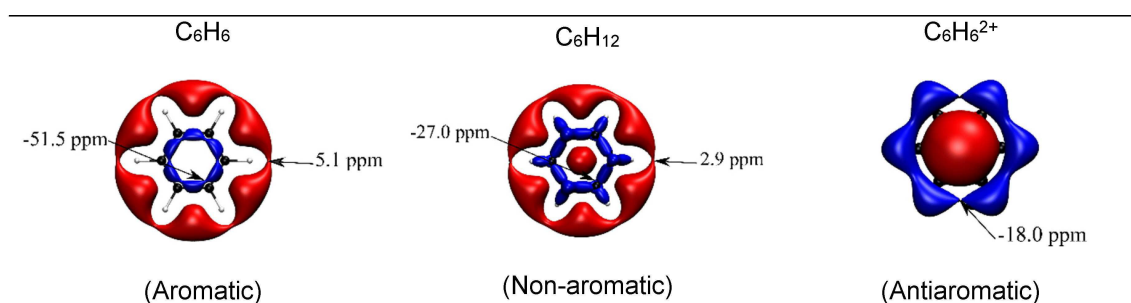


Figure 2. Bifurcation isosurfaces for C₆H₆ (aromatic), C₆H₁₂ (non-aromatic) and C₆H₆²⁺ (antiaromatic). Blue color represents negative (diatropic) values and red color represent positive (paratropic) values.

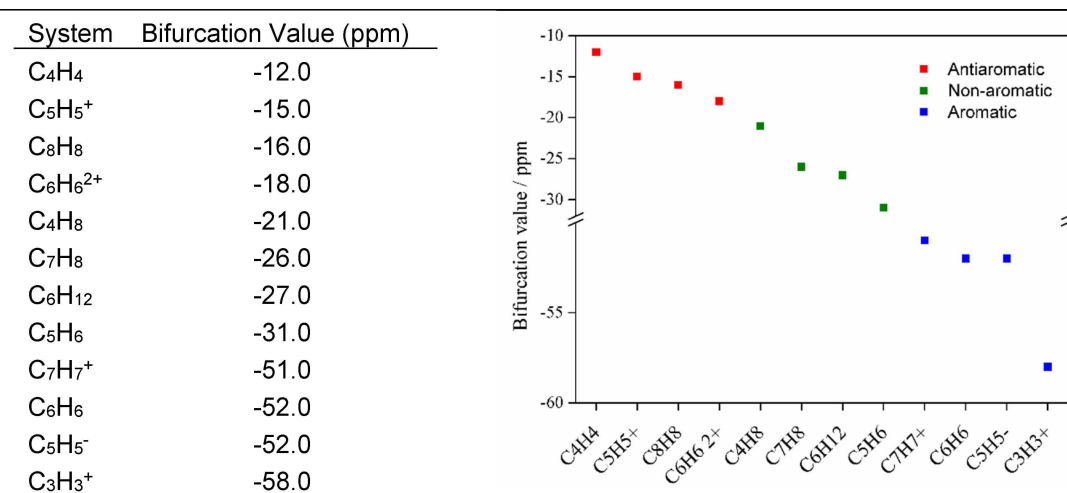


Figure 3. Bifurcation values for monocyclic systems studied in this work. For antiaromatic molecules (in red) it is considered the outer ring-shaped domain and, for nonaromatic and aromatic molecules (in green and blue, respectively) it is considered the inner ring-shaped domain (see Figure 2).

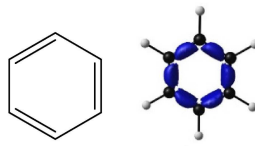
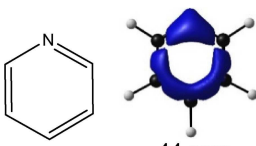
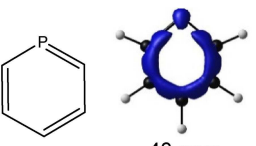
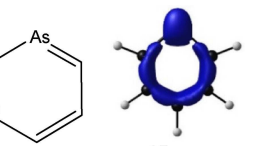
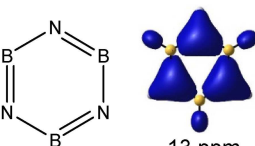
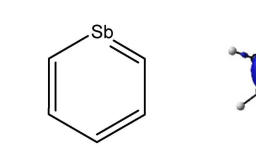
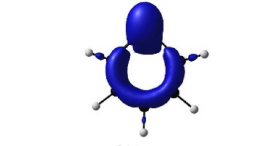
Benzene	Pyridine	Phosphorine	Arsinine
 -53 ppm	 -44 ppm	 -43 ppm	 -45 ppm
Borazine	Stibine	Bismine	
 -13 ppm	 -36 ppm	 -35 ppm	

Figure 4. Bifurcation values of heterocyclic analogues of benzene studied in this work.

$C_5H_5^+ > C_8H_8 > C_6H_6^{2+}$ is in agreement with Poater et. al results by means of delocalization criteria.^[24] Additionally, the aromatic character of the studied monocycles is summarized in Figure 3 (Right).

Heterocycles analogues of benzene. With the aim of assessing the performance of the B_z^{ind} bifurcation analysis in molecular rings different to hydrocarbons, we have evaluated a series of heterocycles, analogues of benzene (specifically those resulting by replacement of one CH on benzene by one group 15 elements N, P, As, Sb and Bi). Previous studies, based on ring currents strengths and NICS_{zz} evaluations, suggest that all pnictogen heterobenzenes are strongly aromatic; moreover, their aromaticity decreases as the heteroatom size increases.^[25] As we can see in Figure 4, all the C_5H_5X (where $X = N, P, As, Sb, Bi$) systems are less aromatic than benzene, but they remain strongly aromatic with bifurcation values between -35 and -45 ppm for bismine and arsinine, respectively. However, the order of aromaticity (predicted by the bifurcation value) does not follow a periodic trend. It is possible that the size of the heteroatom, and its consequent local contribution to the B_z^{ind} , also affect the bifurcation value. The magnitude of this effect is not evaluated in this work and should be the object of study in the near future. Finally, borazine is also considered in this set of heterocycles; the bifurcation value for this system classifies it as a non-aromatic system, in agreement with most recent studies based on current density and induced magnetic field analysis.^[8c,d,26]

Al_4^{2-} cluster and its derivatives. Clusters Al_4^{2-} and Al_4^{4-} have been classified as aromatic and antiaromatic species, respectively.^[27] Despite Al_4^{2-} was initially classified as doubly aromatic (σ and π), more recent studies have concluded that this species is mainly σ -aromatic considering its contribution to ring currents and induced magnetic fields. As we can see in Figure 5, the B_z^{ind} of Al_4^{2-} , $LiAl_4^-$ and Li_2Al_4 do not present a bifurcation pattern similar to benzene; instead, four localized p_z -like domains (at each Al atom) bifurcate from an irreducible domain placed at the center of the Al_4 ring at -55 , -55 and -52 ppm, respectively. This information suggests that these aromatic clusters do not behave similarly to benzene. However,

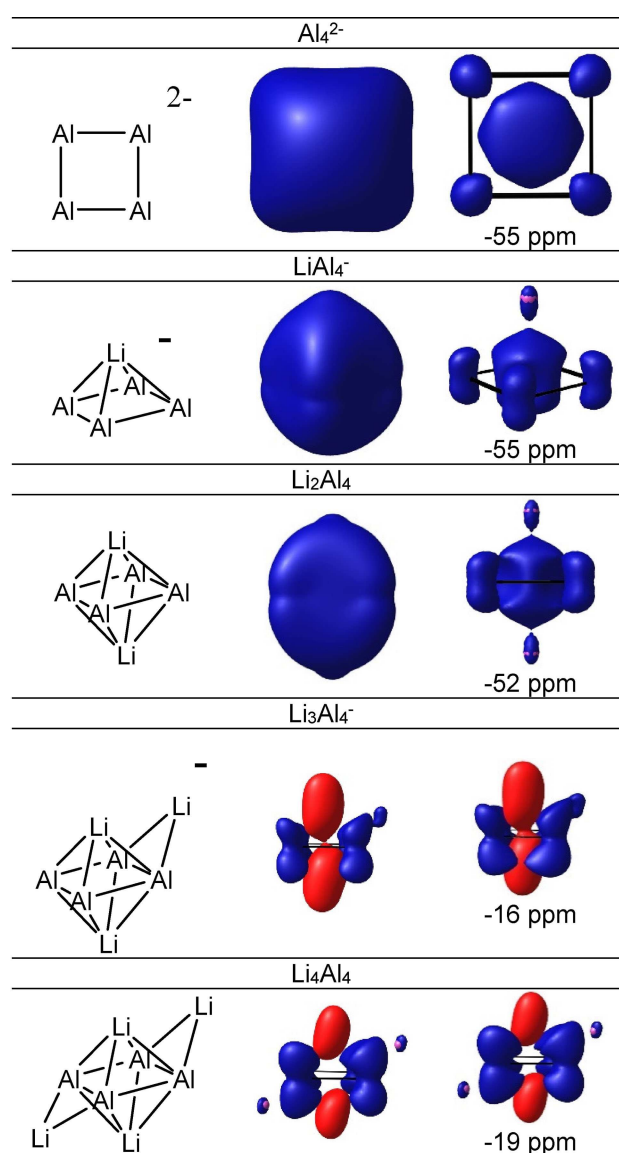


Figure 5. Isosurfaces of the B_z^{ind} at ± 20 ppm (left side) and isosurfaces at bifurcation values (right side) of Al_4^{2-} cluster and its derivatives.

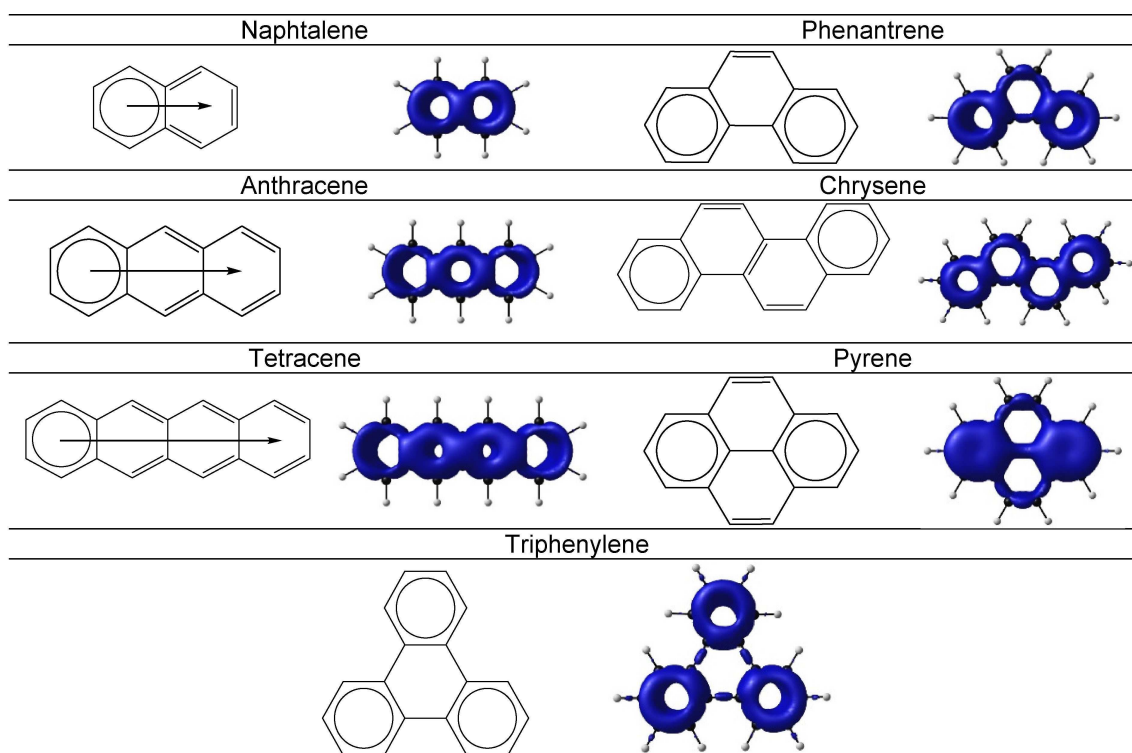


Figure 6. Clar structures and B_z^{ind} isosurfaces of the PAHs studied in this work at ± 35 ppm isovalue. Blue color represents negative (diatropic) values.

the degree of their σ -aromaticity could not be rationalized in terms of the bifurcation patterns. This suggests the need of systematic studies of B_z^{ind} topology for σ -(anti) aromatic systems.

For the case of the antiaromatic species Li_3Al_4^- and Li_4Al_4 , an external ring shaped diatropic ring is evidenced, similar to that of $\text{C}_6\text{H}_6^{2+}$ (see Figure 2), which bifurcates at -16 and -19 ppm for Li_3Al_4^- and Li_4Al_4 , respectively, classifying them as antiaromatic species.

Polycyclic Aromatic Hydrocarbons (PAHs). A classical model for the study of aromaticity in PAHs is the Clar's rule,^[28] proposed in 1972. It states that Kekulé resonance structure with the largest number of disjoint aromatic π -sextets (benzene like rings) is the most important feature for the characterization of PAHs properties. It can be observed that B_z^{ind} isosurfaces (Figure 6) show the disjoint benzene type structures according to the model; for example: in the case of Phenanthrene, the first bifurcation of a ring-shaped domain (-39.5 ppm) occurs in the central ring (which coincides with his reactivity), while a second ring-shaped domain bifurcation occurs in the peripheral rings and has a value of -48.0 ppm, preserving its *benzenoid* nature. Chrysene, pyrene and triphenylene present a similar behaviour to phenanthrene. The first bifurcation of a ring-shaped domain occurs in the central rings, with values of -41.5 , -36.0 and -31.5 ppm, respectively. While the external rings retain their aromaticity with bifurcation values of -47.5 , -55.0 and -46.0 ppm, respectively. The structures known to have migrant sextets, naphthalene, anthracene and naphthacene, show a first bifurcation of a ring-shaped domain in the peripheral rings, which present values of -48.0 , -44.0 and -41.5 ppm,

respectively. Anthracene and naphthacene depict a second ring-shaped domain located in the central rings that bifurcates at -50.5 and -49.5 ppm, respectively. This is in agreement with previous studies based on magnetic criteria^[29] and electronic delocalization^[30] that indicate that the central ring is the most aromatic one. Also, it is supported the high stability of phenanthrene compared with anthracene, in agreement with Bickelhaupt et al.^[31] results, which indicates that the greater stability of the former is due to a greater stabilization interaction between the π electrons of the system (two vs one aromatic rings). B_z^{ind} isosurfaces at each bifurcation value are reported in the supporting information.

Conclusions

The topological analysis of the z-component of the induced magnetic field in molecular rings allows to identify the presence of ring-shaped reducible domains. The aromatic and non-aromatic molecules present two concentric reducible domains: the inner (diatropic), placed around the molecular backbone, and the outer (paratropic), around the global molecule. In the case of the antiaromatic molecules, only the outer reducible domain is present (diatropic in this case). An ellipsoidal irreducible domain (paratropic) appears inside the molecular ring. The bifurcation value of these ring-shaped domains adequately classifies the analyzed molecules according to their (anti)aromatic character. However, in the case of the heterocycle's analogues to benzene, the order of aromaticity (pre-

dicted by the bifurcation value) does not follow a periodic trend. This is possible due to the local contribution of the core, core and lone pairs of the heteroatom to B_{2z}^{ind} . In addition, this analysis was applied to a series of Polycyclic Aromatic Hydrocarbons (PAHs). The bifurcation values of the ring-shaped domains made it possible to describe the local aromaticity of the different hexagonal rings in complete agreement with the classical rationalization based on Clar's sextets.

It is important to note that in heteroatomic species, bifurcation values do not follow aromaticity trends and present some inconsistencies in comparison to ring currents strengths, showing that this approximation provides only a qualitative estimation about (anti)aromaticity.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: aromaticity · magnetic criteria · induced magnetic field · topological analysis · bifurcation analysis

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