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Density, Degeneracy, Delocalization-Based Index of Aromaticity (D_3BIA)

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A aromaticidade tem sido exaustivamente discutida e continua sendo um tema misterioso. Nesse trabalho é proposto um novo índice de aromaticidade chamado índice baseado na densidade-degenerescência-deslocalização ou, simplesmente, D_3BIA, numa tentativa de lançar nova introspecção sobre esse tema. Esse índice é baseado na teoria de átomos em moléculas (AIM) e, de certa forma, é suportado pela teoria dos spins acoplandos (SC). A aromaticidade diminui com o número de heteroátomos na molécula aromática, pois a degenerescência diminui, e diminui com o aumento do tamanho do anel do composto aromático porque desfavorece a sobreposição dos estados monoeletrônicos. A relação entre planaridade do anel, sua densidade eletrônica e aromaticidade é também observada. A interação atrativa da ressonância de 6 elétrons π no diânion ciclobutadieno compensa sua interação repulsiva carbono-carbono enquanto no seu parente dicatiônico a ressonância de 2 elétrons π é insuficiente para contrabalancear sua interação repulsiva e adota uma estrutura não-plana.

Aromaticity has been exhaustedly discussed for several years and it remains as a misterious issue. In this work it is proposed a new index of aromaticity named density, degeneracy and delocalization-based index of aromaticity or simply D_3BIA in an attempt to cast new insight and perspective over this theme. This index is based on AIM (atoms in molecules) theory and it is somewhat supported by SC (spin-coupled) theory. Aromaticity decreases as the number of heteroatoms in the aromatic molecule increases since degeneracy decreases and it decreases as the ring size of an aromatic compound increases because it disfavors overlap of single-electron states. The relation between planar structures, electron density and aromaticity is also observed. The attractive interaction of 6π-electron resonance in cyclobutadiene dianion compensate its carbon-to-carbon repulsive interaction while in its dicationic parent the 2π-electron resonance is insufficient to counterbalance its carbon-to-carbon repulsive interaction and it adopts a puckered structure.

Keywords: delocalization index; degeneracy; ring density; aromaticity

Introduction

In the nineteenth century benzene was the pivot of the aromatic empiricism.[1] After its early studies by Couper and Loschmidt,[2] Kekulé proposed the most important theory about benzene: the oscillation hypothesis.[3] Other theories at that time were Claus'centric hypothesis,[4] Bayer's reformulations of centric benzene,[5] Dewar's hypothesis[6] and Ingold's bridged formula.[7]

In the early twentieth century quantum theory study gave rise to a novel hypothesis for benzene. From a molecular orbital (MO) study of benzene and other unsaturated cyclic systems, Hückel[8] arrived at his famous rule for aromaticity. Two years later, Pauling and Wheland's[9] valence bond (VB) study of benzene (and naphtalene) gave the same result by following Hückel's premises and Slater method. Their simpler treatment was based on resonance[10] among independent Kekulé and Dewar canonical structures and became known as resonance hybrid hypothesis.[9] However, for cyclobutadiene both theories gave completely different results.[8,11] Hückel's MO study predicted the stability of other aromatic compounds and zero stability for conjugated cyclic systems such as cyclobutadiene.[8] The

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latter ones were ascribed by Breslow and Dewar to have anti-aromatic character.[12]

It was established that aromatic species have π electrons in delocalized bonds, uniform geometry and special stability with respect to an open chain referential. Conversely, anti-aromatic systems have π electrons in localized bonds and non-uniform geometries in alternate single and double bonds.[13] Several criteria to evaluate aromaticity were created so far: energetic criterion,[14] geometric criterion[15] and magnetic criterion.[16] However, Schleyer and Jiao[17] stated that magnetic susceptibility is the unique criterion applied to aromaticity. Schleyer *et al.*[18] also remarked that downfield proton chemical shifts are not a reliable aromaticity criterion and that aromaticity phenomenon can be statistically regarded as multi-dimensional.[19] Many different magnetic criteria have appeared so far, based on magnetic shielding or ring current.[20]

Within MO theory, the aromatic character of benzene is explained through delocalized orbitals. Nevertheless by using the spin coupled valence bond theory (SCVB), Gerratt *et al.*[21] established that all the six π electrons of benzene are localized and symmetrically distorted towards neighboring carbon atoms on each side and possess the same energy and shape. Other studied aromatic molecules have similar features.[22] Within the description SCVB, the stability of aromatic systems is ascribed to the modes of coupling the electron spins which resembles Pauling's resonance structures.[21,23] Hiberty *et al.*[24] demonstrated that delocalization of the π-electrons in benzene is energetically unfavorable and the σ-framework determines the structural symmetry of benzene. They[25] stated that π electronic system distorts benzene to D_{3h} symmetry while σ-framework keeps it in D_{6h}, although Havenith *et al.*[14f] have established the necessity of resonance to obtain a fully symmetric benzene molecule. Havenith[26a] demonstrated that resonance between Kekulé structures does not influence the magnetic and electric properties of benzene and that ring currents exist in its D_{3h} symmetry.[26] Within modern VB scope Cooper *et al.*[27] obtained the following order of degree of aromaticity: $C_6H_6 \sim B_6 > N_6 > Al_6 \sim Si_6H_6 > P_6$.

Atoms in molecules (AIM) theory has also been applied to study aromaticity.[30] Bader *et al.*[28] found out a greater π density delocalization in cyclic unsaturated hydrocarbons than that in acyclic ones. Solà *et al.*[29] related the delocalization index[30] (DI) to different aromatic criteria. They introduced a new local aromatic criterion: the paradelocalization index (PDI). Hernández-Trujillo and Matta[31] also proposed a geometric criterion that takes into account the DI as a measure of electron-sharing alternation.

From the AIM theory,[32] we propose a new criterion for aromaticity based on the electronic density in the ring, on the degree of delocalization uniformity and on the degree of degeneracy of atoms in the ring, named D_3BIA (density, degeneracy and delocalization-based index of aromaticity). This criterion casts new light on the way aromaticity has been reasoned.

Computational Methods

All calculations were performed using the GAUSSIAN 2003 package.[33] The geometries were optimized in DFT level employing Becke three-parameter interchange functional[34] (B3) in conjunction with Lee-Yang-Parr[35] correlation functional (LYP) and the split valence basis set[36] 6-311++G**.

The AIM 2000 software[37] was used for charge density calculations from the electronic densities (ρ) obtained at B3LYP/6-311++G** level.

Rationale

Rationale on D_3BIA index was influenced by modern (VB) studies on aromaticity and particularities of some aromatic compounds.[38] The similarities of results between AIM and SC encouraged us to use the former since it provides us important and complementary information. The coherence between AIM and SC can be noticed from AIM results of benzene. The DI between carbon atoms in benzene is 1.39. Since DI between carbon atoms in ethane is 1.0, it is established that 0.39 e. from π system is delocalized in each C-C bond of benzene ring. This means that 0.61 from each $2p_z$ electron is localized in each carbon atom in benzene. This result matches with the SC one in which a $2p_z$ electron of benzene is localized and symmetrically distorted towards neighboring carbon atoms on each side.[21] Moreover, Gerratt *et al.*[21] remarked that distortion effects of $C(2p_z)$ orbitals are not larger than those of C-C π bonds in conjugated systems. From AIM calculations, DI's for hexatriene are 1.74 (double bond) and 1.14 (single bond). This indicates another convergence of results between SC and AIM theories since the latter shows that delocalization index in double bonds in acyclic conjugated systems is greater than that in benzene.

Pauling and Wheland[9] stated that benzene is represented by a linear combination of five independent canonical structures. This view is emphasized by SC theory,[21,23] in which a two-electrons spin coupling allows the description of the different possible resonance structures and generates the stability of aromatic systems.

From a more rigorous quantum mechanical standpoint,[39] benzene has no resonance[40] since there is no intersection of degenerate point group states. It means that benzene (D_{6h} symmetry) cannot be related to Kekulé (D_{3h} symmetry) or Dewar (D_{2h}) structures (see Electronic Supplementary Information). In this case, benzene stability is ascribed to maximum overlap among six degenerate single-electron states.[41]

Then, the existence of resonance in benzene depends on the rigor of the theory applied to it. By spin coupling π electrons, within same D_{6h} symmetry in SC, it is possible to associate the obtained stability with resonance of hybrid structures.[21] Otherwise, benzene molecule cannot be represented by "hybrids" of symmetries D_{3h} and D_{2h} since it is forbidden by point group symmetry rules.[42]

The index D_3BIA is based on the density in the ring, the degeneracy and the delocalization index of atoms in the ring. With respect to AIM theory, degeneracy is the similar energy of basins. Delocalization index (DI) is a measure of the number of electrons that are shared between two atoms or basins. All data are obtained from AIM theory.

Results and Discussion

All studied compounds are depicted in Scheme 1.

For an aromatic system, according to modern VB theory, the degeneracy of single-electron states plays an important role on aromaticity.[41] In AIM theory, the degeneracy can be reasoned in terms of energy of each atomic basin of atoms in the aromatic ring and also associated with its delocalization indexes of each atomic pair im the aromatic ring. The greater the uniformity of atomic energy and the DIs among atoms in the ring is, the greater is the degeneracy of atoms of the aromatic system.

The importance of the electron density in aromaticity arises from the following points: *(i)* the relative stability of three-membered rings is related to the electron density in the ring;[30] *(ii)* the overlap among (near) degenerate p_z single-electron states can be correlated to the electron density in the ring; *(iii)* the spin coupling to form Dewar structures can be correlated to the electron density in the ring.

The D_3BIA formula is:

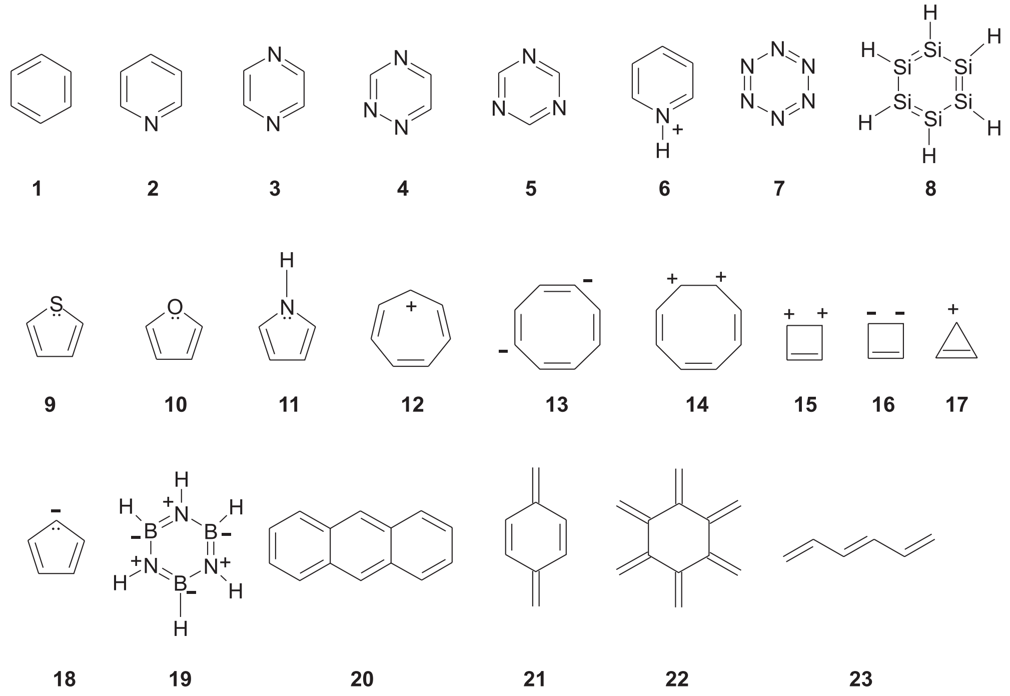
$$D_3\text{BIA} = [\text{RDF}][\text{DIU}]\delta \qquad (1)$$

The ring density factor (RDF) formula is:

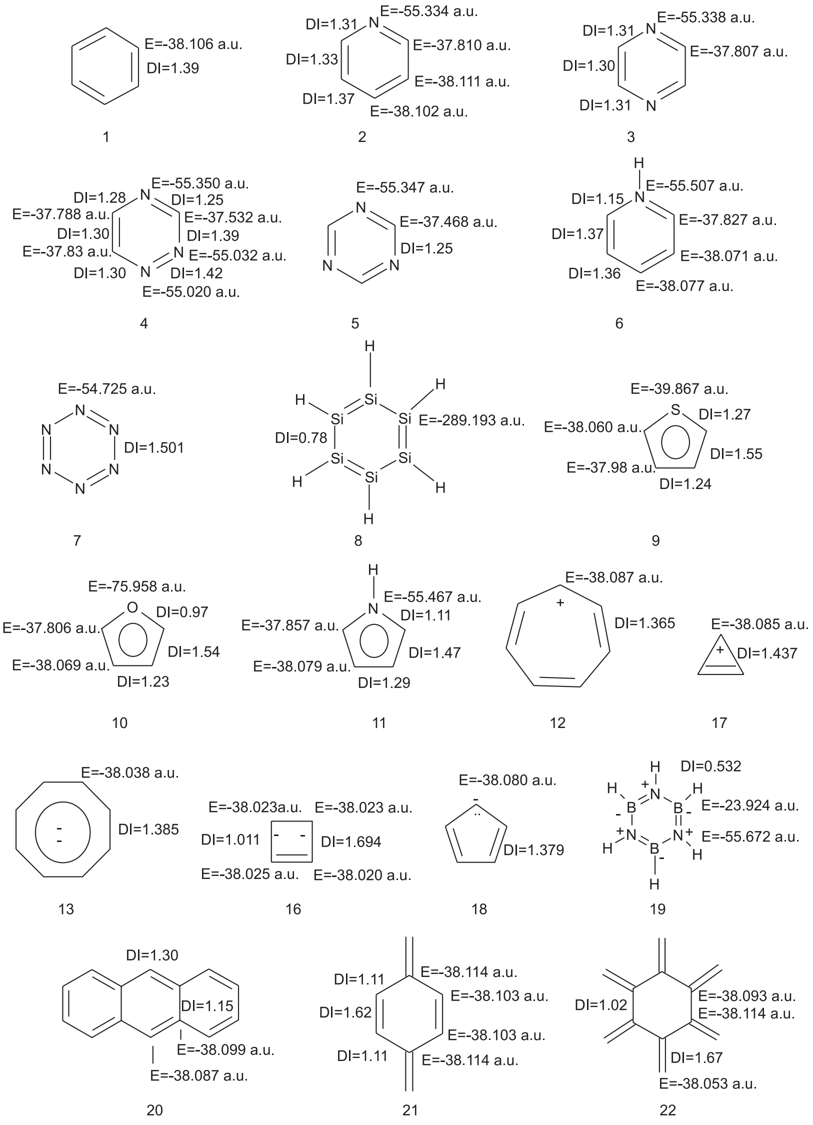
$$\text{RDF} = (1+ \lambda_2)\, \rho_{\text{RCP}} \qquad (2)$$

Where λ_2 is the mean eigenvalue of the density Hessian matrix from the bond critical point (BCP) towards the ring critical point (RCP) and ρ_{RCP} is the density value of ring critical point. One can see that the more negative is λ_2 the steeper is the curvature of the surface of the density at this direction.

AIM provides a delocalization index for each bond between vicinal atoms.[30,37] The delocalization index uniformity (*DIU*) can be correlated to the efficiency of the single-electron states interaction (or overlap). The



Scheme 1.



Scheme 2.

maximum degree of delocalization uniformity parallels the maximum overlap among single-electron states, which can be verified in benzene (**1**) (Scheme 2).

The delocalization index of uniformity (DIU) formula is:

$$DIU = 100 - \left(\frac{100\sigma}{\overline{DI}}\right) \tag{3}$$

Where σ is mean deviation and $\overline{\text{DI}}$ is mean DI of the ring.

The uniformity of delocalization is also taken into account in the degree of degeneracy to fine tune this parameter because a molecule may have atoms nearly degenerate, but with completely different delocalization indexes (see *p*-xylylene (**21**) in Scheme 2). Then, uniformity of delocalization is used to adjust the degree of degeneracy.

The formula of the degree of degeneracy (δ) is the number of degenerate atoms divided by the number of atoms in the ring. The δ takes into account the following requisites: *(i)* if all atoms of the ring are degenerate and if all of these atomic pairs have same delocalization indexes, the molecule has the maximum degree of degeneracy (δ=1); *(ii)* if the atoms of the atomic ring are near-degenerate (within range of 0.3 a.u.) and have near delocalization indexes (within range of 0.05) they may be regarded degenerate; *(iii)* if all atoms of the ring are near-degenerate and have completely different delocalization indexes (ΔI > 0.3) the molecule has the minimum degree of degeneracy (δ=0), where ΔI is the difference between DI's.

From D_3BIA formula (equation 1) *p*-xylylene (**21**) does not have aromaticity since it has δ=0 (requisite III). Hexaradialene (**22**) has no aromaticity either. It has no planar structure and no π electrons between C-C bonds in the ring (Scheme 2), as can be seen by its DI values (similar to single bonds).

In Table 1 it is depicted either the values of the individual parameters and D_3BIA values. Energy and DI values are also depicted in Scheme 2.

By analyzing D_3BIA values of compounds **1** to **4** in Table 1 it is remarkable that the decrease of degeneracy of single-electron states and aromaticity of the respective compound are related to the number of heteroatoms in the aromatic molecule. The more heteroatoms in the ring then, the smaller are the degeneracy and the aromaticity. The heteroatoms break uniformity of the electron density in the ring as one can see Figure 1. It is known from literature that benzene has different aromaticity from the corresponding aromatic compounds containing nitrogen atoms, *e.g.*, pyridine.[43] One also can see that D_3BIA value of 1,3,5-triazine (**5**) is greater than that from 1,2,4-triazine (**4**) since the former is more symmetric than the latter. Moreover, the pyridinium (**6**) has smaller D_3BIA value than that from non-protonated species (**2**) because the former lost some of delocalization index uniformity (DIU) and degree of degeneracy (δ) (see Scheme 2).

From the analysis of D_3BIA values (Table 1) of compounds **1**, **12** and **13** one can also notice that ring size and aromaticity are inversely related, where other parameters are kept constant. Moreover, compound **8** has smaller D_3BIA than that from compound **1** where C-C bond length (1.394 Å) in compound **1** is smaller than Si-Si bond length (2.219 Å) in compound **8**. However, Si_6H_6 is not a minimum in the potential energy surface. This reverse relation is probably due to decrease of the density in the ring which disfavors overlap of single-electron states.[41] In Figure 1 it is possible to see how electronic interaction inside the ring is stronger in benzene than in compounds **8** and **13** since there is only one Laplacian line inside benzene ring unlike **8** and **13**.

Table 1. Charge density of the ring critical point (ρ_{RCP}), eingenvalue of density Hessian matrix from BCP towards RCP ring (λ_2), ring density factor (RDF), degree of delocalization index uniformity (DIU), degree of degeneracy (δ), D_3BIA

Entry	RCP × 10^3 (a.u.)	λ_2	RDF × 10^3 (a.u.^{2})	DIU	δ	D_3BIA × 10^3
1	21.5	-0.54	9.9	1.000	1.00	9.9
2	23.5	-0.57	10.1	0.980	0.83	8.2
3	26.1	-0.62	9.9	0.996	0.67	6.6
4	26.9	-0.69	8.3	0.936	0.33	2.6
5	29.0	-0.69	9.0	1.000	0.50	4.5
6	22.0	-0.57	9.5	0.913	0.50	4.3
7	25.0	-0.92	2.0	1.000	1.00	2.0
8	3.7	-0.07	3.4	1.000	1.00	3.4
9	39.0	-0.42	22.6	0.887	0.40	8.0
10	53.0	-0.49	27.0	0.776	0.40	8.4
11	51.0	-0.50	25.5	0.860	0.40	8.8
12	9.2	-0.57	4.0	1.000	1.00	4.0
13	3.8	-0.48	2.0	1.000	1.00	2.0
16	98.5	-0.44	55.2	0.747	0.50	20.6
17	62.0 [b]	-0.47	32.9	1.000	1.00	32.9 [c]
18	48.2	-0.48	25.1	1.000	1.00	25.1
19	19.7	-0.44	11.0	1.000	0.50	5.5
20 [a]	20.0	-0.52	9.6	0.938	0.67	6.0

[a] Data from central ring; [b] Densities of ring critical point in cyclopropane and in cyclopropenyl cation are 0.195 a.u. and 0.257 a.u., respectively, and difference between them represents the electron density in RCP from p electrons without influence of r electrons. However, it remains a partial r electron influence in the density of RCP since C-C bond lengths in cyclopropenyl cation are smaller than those in cyclopropane; [c] Imprecise value of D3BIA as there exists an influence of r electrons which cannot be excluded.

The difference among D_3BIA values of thiophene (**9**), furane (**10**) and pyrrole (**11**) is not so large (Table 1). One can also realize that the expected smaller aromaticity of anthracene (**20**) with respect to benzene (**1**) is supported by their D_3BIA values (Table 1).

In Scheme 2 one can see that from all ionic aromatic species, cyclobutadiene dianion (**16**) is the unique with non-uniform delocalization indexes involving its C-C bonds and non-degeneracy among all carbon atoms. One can also see in Scheme 2 that delocalization indexes involving carbon and nitrogen atoms are quite similar in pyridine and pyrazine unlike 1,3,4-triazine where they are completely different. Furthermore, the carbon atoms in the ring of *p*-xylylene (**21**) are near-degenerate but they have different delocalization indexes which shows the importance of uniformity of the delocalization index, of all atomic pairs belonging to the aromatic ring, in aromaticity (Scheme 2).

Optimization calculations were performed for the dicationic species **14** and **15**, but they gave no planar structures as it is supported experimentally[38] and computationally.[44] On the other hand, their dianion parents, cyclooctetraene dianion (**13**) and cyclobutadiene dianion (**16**), respectively, have planar structures.[45]

The high D_3BIA value of **16** might explain its planar structure since its 6π-electron resonance compensates its carbon-to-carbon repulsive interaction in which each carbon atom has a charge of -0.5 a.u. Its parent dication (**15**) probably has a puckered structure because the 2π-electron resonance does not compensate its carbon-to-carbon repulsive interaction (with 0.5 a.u. positively charged carbons). Accordingly, the puckered structure of cyclooctatetraenyl dication (**14**) is probably due to its overall 2.0 a.u. charge and ineffective 6π-electron resonance in an eight-membered ring while its dianion parent (**13**) has planar structure because of its 10π-electron resonance.

From all studied ionic aromatic species the cyclopentadiene anion (**18**) is the most aromatic system since the D_3BIA value of **17** (Table 1) is overestimated because it is not possible to eliminate thoroughly the influence of its C-C ρ electrons.

Borazine[46] (**19**) D_3BIA value higher than those from triazines, N_6H_6 and Si_6H_6 but smaller value than those from other six-membered and five-membered aromatic compounds as one might expect.

Other examples of application of D$_3$BIA can be found in the Electronic Supplementary Information section.

Another important analysis from AIM theory is the Laplacian of the charge density. It is defined as the sum of the three principal curvatures of the function at each point of the space. The density is locally concentrated in those regions where $L(r)>0$, since $\nabla^2 \rho<0$ when $\rho(r)$ is a local maximum. Likewise, the density is locally depleted in those regions where $L(r)<0$, since $\nabla^2 \rho<0$ when $\rho(r)$ is a local minimum.[30]

In Figure 1, one can see that the inner part of benzene ring is surrounded by only one $L(r)<0$ Laplacian line (first green line within the ring) while compounds **8** and **13** have another inner concentric $L(r)<0$ Laplacian lines within their rings. This means that the electronic interaction inside the ring is stronger in benzene than in compounds **8** and **13**. As for 1,3,4-tryazine (**4**) one can realize that the $L(r)<0$ Laplacian lines inside its ring are not concentric. This demonstrates how heteroatoms impair a uniform electronic interaction.

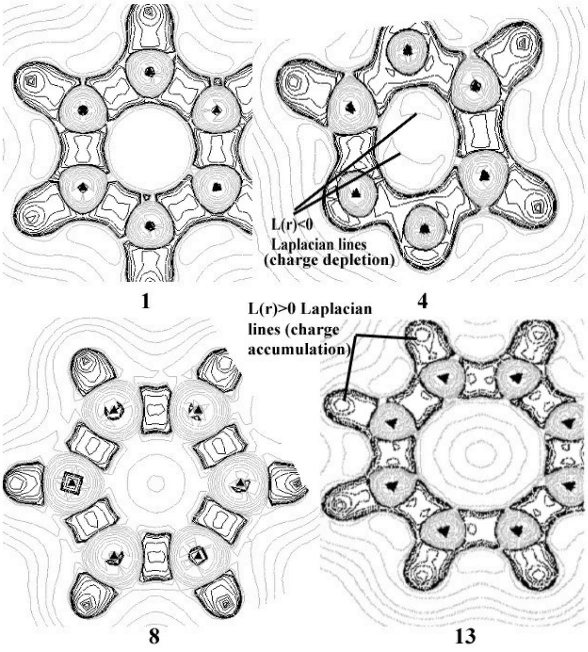


Figure 1. Contour maps of the negative of the Laplacian distribution of the electronic charge density for compounds **1**, **4**, **8**, **13** within the ring plane. The green curves are related to charge depletion, while the black lines are charge concentration.

Conclusions

We have proposed an index for quantifying aromaticity (D$_3$BIA). This index shows that aromaticity decreases as the number of heteroatoms in the aromatic molecule increases, since the degeneracy of single-electron states decreases. The ring size of an aromatic compound and aromaticity are inversely related, because the decrease of the charge density in the ring which disfavors the overlap of single-electron states.

The attractive interaction of 6ρ-electron resonance in cyclobutadiene dianion compensate its carbon-to-carbon repulsive interaction, while in its dicationic parent the 2π-electron resonance is insufficient to counterbalance its carbon-to-carbon repulsive interaction and it adopts a puckered structure. Accordingly, the puckered structure of cyclooctatetraenyl dication is probably due to its overall 2.0 a.u. charge and ineffective 6π-electron resonance in an eight-membered ring while its dianion parent has planar structure because of its 10π-electron resonance.

Cyclopentadiene anion is the most aromatic molecule of all studied ionic aromatic species.

Acknowledgments

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Supplementary Information

Examples of application of D$_3$BIA and other data are available free of charge at http://jbcs.sbq.org.br/, as PDF file.

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