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Validation of the recently developed aromaticity index D3BIA for benzenoid systems. Case study: acenes

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Abstract There are four types of aromaticity criteria: energetic, electronic, magnetic and geometric. The delocalization, density and degeneracy-based index of aromaticity, D3BIA, is an electronic aromaticity index from QTAIM that is not reference dependent and can be used for aromatic, homoaromatic, sigma aromatic and other aromatic systems with varying ring size containing hetereoatoms or not. We used B3LYP, MP2 and MP3 methods to search for linear relations between well-known aromaticity indices and D3BIA for a series of acenes. We found that the D3BIA versus FLU correlation exceeded 91 % and reasonably good correlations exist between D3BIA and HOMA and between D3BIA and PDI. Previous works have shown that D3BIA can be used for homoaromatic systems and tetrahedrane derivatives (sigma aromaticity), but no previous work has validated D3BIA for benzenoid systems. This is the first time we have shown that D3BIA can be used successfully for benzenoid systems, for example, acenes. This work supports and validates the use of D3BIA in classical aromatic systems.

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Introduction

Aromaticity is a key concept in chemistry due to its application to organic and inorganic molecules [1, 2], describing so-called aromatic, homoaromatic [3] and all-metal aromatic molecules [1, 4]. These molecules have distinctive geometrical [5], energetic [6] and magnetic [7–11] features as well as a unique reactivity behavior [5, 12]. Nonetheless, the definition of aromaticity lacks consensus [13] and some new attempts to account for this phenomenon have arisen, for instance, the ELF bifurcation value [14], the concept of π distorcivity from Shaik and collaborators [15, 16] and Nascimento's multicenter bond [17], in which π distorcivity has been proved experimentally [18]. Moreover, pure σ-aromaticity has been discovered recently in molecular systems such as Li clusters [19] and the tetrahedrane cage [20, 21], and the concepts of multifold aromaticity and conflicting aromaticity have emerged for metal clusters [22, 23].

An aromaticity index represents an attempt to quantify aromaticity based on a specific criterion (energetic, geometric, magnetic, reactivity or electronic). However, all the aromaticity indices proposed to date are somewhat arbitrary, which leads to a lack of agreement on the best aromaticity index. As a consequence, it is advisable to use two or more aromaticity indices to evaluate a set of aromatic molecules.

The harmonic oscillator model of aromaticity (HOMA) is a well-known geometric aromaticity index that quantifies aromaticity in comparison with a reference molecule (e.g., benzene) with highest bond length equalization [24]. HOMA values are derived from Eq. 1.

$$\text{HOMA} = 1 - \frac{\alpha}{n} \sum^{I} \left(R_{\text{opt}} - R_{\text{I}} \right)^2 \tag{1}$$

Where n is the number of chemical bonds; α is an empirical constant where HOMA disappears for hypothetical Kekulé structures and HOMA reaches its maximum value for structures with bond lengths similar to R_{opt} (α=257.7); R_I is the individual bond length, and R_{opt} is 1.388 Å.

Nucleus independent chemical shift (NICS) is one of the most used magnetic aromaticity indices [25] and exists in several variations in an attempt to improve its correlation with other aromaticity indices, e.g., NICS(1), NICS$_{zz}$, and so on [26].

More recently, electronic criteria have been developed for aromaticity quantification [27, 28], and several electronic aromaticity indices based on quantum theory of atoms in molecules (QTAIM) now exist [29, 30]. Most of these are dependent on the delocalization index (DI), which relates to the number of shared electrons between each atomic pair derived from the Fermi hole density [31, 32].

Based on the assumption that the DI between para-related carbon atoms is higher than that between meta-related carbon atoms in benzene, the para-DI (PDI) was developed as an aromaticity index. The PDI is an arithmetic average of all para-DI in six-membered-rings [33]; however, PDI can be applied only to six-membered rings.

In an attempt to find an aromaticity index that involved all DIs in the target ring, the aromatic fluctuation index (FLU) was developed [34]. Like HOMA, FLU depends on an aromatic molecule as reference. Its formula is shown in Eq. 2.

$$FLU = \frac{1}{n} \sum_{A-B}^{RING} \left[\left(\frac{\sum_{A \neq B} \delta(B,A)}{\sum_{B \neq A} \delta(A,B)} \right)^{\alpha} \left(\frac{\delta(A,B) - \delta_{ref}(A,B)}{\delta_{ref}(A,B)} \right) \right]^2 \therefore \quad (2)$$

$$\alpha = \begin{array}{l} 1 \ if \ \sum_{A \neq B} \delta(B,A) > \sum_{B \neq A} \delta(A,B) \\ -1 \ if \ \sum_{A \neq B} \delta(B,A) \leq \sum_{B \neq A} \delta(A,B) \end{array}$$

Where the summation involves all atomic pairs in the aromatic site and $\delta(A,B)$ is the DI value between atoms A and B.

Similarly, the delocalization, density and degeneracy-based index of aromaticity (D3BIA) is a QTAIM-based aromaticity index having the DI in its formula [35]. Like all other aromaticity indices, the D3BIA is an arbitrary aromaticity index, but has the advantage that it can be applied to all aromatic and homoaromatic systems with or without heteroatoms and it has no reference parameter. Early works have shown that D3BIA has very good correlation with NICS for a set of homoaromatic bisnoradamantenyl derivatives [36] and tetrahedranes derivatives [21]. However, no previous work has shown that D3BIA can be used to quantify the aromaticity of benzenoid systems.

In this work, we used a set of acenes in order to find correlations between D3BIA and some well-known aromaticity indices [37] (HOMA, NICS, FLU and PDI). Calculations in acenes were performed with different methods (B3LYP, MP2 and MP3) in order to investigate how these correlations change with the method used. There was a very good correlation between D3BIA and FLU and a reasonably good correlation between D3BIA and HOMA and between D3BIA and PDI for the studied acenes. For the first time, we have shown that D3BIA can be used for benzenoid systems. This work supports and validates the use of D3BIA for benzenoid systems.

Delocalization, density and degeneracy-based index of aromaticity

The D3BIA is based on three electronic factors: the electronic density within the aromatic ring; the uniformity of electronic delocalization in the aromatic ring; and the degree of degeneracy of the atoms in the aromatic ring [35]. The general formula of D3BIA is shown in Eq. (3).

$$D3BIA(\text{general formula}) = [RDF] \cdot [DIU] \cdot \delta \quad (3)$$

Where RDF stands for ring density formula; DIU stands for DI uniformity; and δ is related to the degeneracy of atoms in the aromatic site.

The D3BIA was inspired by Nascimento's statement that "the stabilization of benzene is brought about by a six-electron bond" based on benzene SCVB calculation and its quantum-dynamical type analysis for chemical bond [17], from which we associated the degree of degeneracy of atoms in the aromatic ring, δ, and the electronic density inside the aromatic ring, RDF. The third factor of D3BIA, DIU, on the other hand, was obtained empirically from the analysis of several aromatic molecules, including benzenoid, hetero and ionic aromatic systems, with varying ring size [35]. The DIU formula is shown in Eq. (4).

$$DIU = 100 - \left(\frac{100\sigma}{\overline{DI}} \right) \quad (4)$$

Where $\overline{DI}$ is the average of all DIs from the atoms of the aromatic ring and σ is the mean deviation of all DIs from the atoms in the aromatic ring.

The DIU formula was not inspired by HOMA and FLU; however, all have nearly the same grounding, i.e., the uniformity of bond length or DI, though their formulas are not mathematically equivalent. This close conceptual relation between HOMA, FLU and DIU corroborates the use of DIU in the D3BIA formula.

The D3BIA can be used for the analysis of aromatic and homoaromatic molecules. However, the RDF is different in

the two cases. The RDF formulas are shown bellow:

$$RDF = \left[\left(1 + \overline{\lambda_2} \right) \cdot \rho_{RCP} \right] \therefore For\ aromatic\ molecules \quad (5)$$

$$RDF = \left[\rho_{RCP/CCP} \right] \therefore For\ homoaromatic\ molecules \quad (6)$$

where $\overline{\lambda_2}$ is the average of all second eigenvalues from the Hessian matrix of the charge density, λ_2, of all bond critical points (BCP) in the aromatic ring, whose eigenvector, $\vec{u_2}$, points from the BCP belonging to the aromatic ring toward the center of the ring; ρ_{RCP} is the charge density of the ring critical point (RCP); and ρ_{CCP} is the charge density of the cage critical point (CCP).

For a series of heterobenzenoid systems, Ebrahimi and co-workers [38] used four topological data of the RCP as an aromaticity index, which yielded good correlations with several well-known aromaticity indices, including NICS. Although D3BIA was not inspired in RCP topological data as an aromaticity index, the latter corroborates the use of RDF in D3BIA.

The difference in the RDF formula for aromatic and homoaromatic rings arises from their distinct electronic structure, in which aromatic rings are planar rings without saturated linkages (e.g., sp^3 hybrid atoms) in the aromatic circuit, the homoaromatic systems are mostly non-planar and they have saturated linkages in the aromatic circuit. Hence, there are two D3BIA formulas shown in Eqs. (7) and (8).

$$D3BIA(a) = \left[\left(1 + \overline{\lambda_2} \right) \cdot \rho_{RCP} \right] \cdot [DIU] \cdot \delta \quad (7)$$

$$D3BIA(h) = \left[\rho_{CCP/RCP} \right] \cdot [DIU] \cdot \delta \quad (8)$$

Where D3BIA(a) is the D3BIA applied to aromatic systems, and D3BIA(h) is the D3BIA applied to homoaromatic systems and any other aromatic caged structures (e.g., tetrahedrane derivatives with sigma aromaticity or caged clusters with all-metal aromaticity). As one can see, the unique difference between D3BIA(a) and D3BIA(h) arises from the RDF, which is in accord with their particular geometric structure.

From QTAIM, it is possible to obtain the atomic energy according to the virial theorem [39, 40]. As a consequence, it is feasible to derive the degree of degeneracy of all atoms, δ, for an aromatic, homoaromatic or any other aromatic system. The reason for the δ component in the D3BIA formula is to evaluate the influence of heteroatom(s) on the aromatic site. For instance, Si_6H_6, N_6 and benzene have the same degree of degeneracy ($\delta=1$), while the values of degree of degeneracy in pyridine, pyrazine, 1,3,5-triazine, 1,2,4-triazine (less

symmetric) are 0.83, 0.67, 0.50 and 0.33, respectively [35], according to Eq. 9.

$$\delta = \frac{n}{N} \quad (9)$$

Where n is the number of atoms in the aromatic circuit that follow the rules for maximum degree of degeneracy shown below, and N is the total number of atoms in the aromatic circuit.

The rules for maximum degree of degeneracy for aromatic systems are shown below. Although these rules are arbitrary, they were obtained empirically from a large range of aromatic (neutral and ionic aromatic molecules, heteroaromatic molecules, aromatic molecules with varying ring size) and non-aromatic systems so that heteroaromatic systems have $\delta<1$.

(1) If all atoms of the ring are degenerate and if all of these atomic pairs have the same DIs, the molecule has the maximum degree of degeneracy ($\delta=1$).

(2) If all atoms of the aromatic ring are near-degenerate (within the range of 0.3 a.u.) and if their DIs are similar (where $\Delta DI \leq 0.50e$), the system also has a maximum degree of degeneracy ($\delta=1$).

In the case of homoaromatic systems, the degree of degeneracy was obtained empirically so that the influence of heteroatoms (and/or atoms of same chemical element but with very different atomic energies) in the aromatic circuit could be taken into account for evaluating the homoaromaticity [41]. The general formula for degree of degeneracy is also given by Eq. 9, where n is the number of atoms in the homoaromatic circuit whose $\Delta E(\Omega) \leq 0.009$ a.u. and N is the total number of participating atoms in the multicenter bond of the homoaromatic circuit. The minimum value for n is 1, where there is no atomic pair whose $\Delta E(\Omega) \leq 0.009$ a.u.

One correction is needed in relation to our first work [35] with D3BIA: when one reads λ_2 in D3BIA formula in reference [35], one should read $\overline{\lambda_2}$. In addition, the D3BIA values in ref. [35] were divided by 100 in order to normalize the percentage value given by DIU. However, this division was not shown explicitly in the D3BIA formula and yielded very small values for D3BIA. Thus, this normalization of D3BIA values was avoided in subsequent works [36, 41], including this latest study.

In our initial work with D3BIA [35], our main goal was to develop an aromaticity index that could encompass a large amount of neutral and ionic aromatic molecules with a varying ring size and varying number of heteroatoms. Thus, we obtained an aromaticity index (D3BIA) that was not reference dependent. However, due to the large and varying number of

aromatic systems (neutral and charged heteroaromatic molecules, aromatic molecules with varying ring size) analyzed in [35], we could not find, in our first work, any linear relationship between D3BIA and NICS, PDI, HOMA or FLU since NICS is size dependent [42], HOMA and FLU are reference dependent and PDI can be applied only to six-membered rings.

We have previously validated D3BIA for the analysis of homoaromaticity [36] and sigma aromaticity [21], but as mentioned above, no validation of D3BIA for benzenoid systems has been achieved to date. Thus, a new study is necessary to prove that D3BIA can be used for benzenoid systems, e.g., acenes.

Unlike homoaromatic and sigma aromatic systems, care should be taken with the minimum number of significant figures of D3BIA for benzenoid systems. In this work, we observed that D3BIA needs three significant figures for optimum correlation with other aromaticity indices.

Computational details

The geometries of the studied species were optimized according to the Berny algorithm using energy-represented direct inversion in the iterative subspace [43, 44]. Calculations were performed with B3LYP/6-311++G(2d,2p), MP2/6-311++G(d,p) and B3LYP/6-311++G(2d,2p)//MP3/6-311++G(d,p) levels of theory [45–48]. The MP3 single point calculations were run from B3LYP-optimized geometries instead of MP2 optimization since the former has more precise bond lengths compared to experimental conditions (see Table 1). The calculations were run in the Gaussian 09 package [49]. All topological data for D3BIA calculation were derived from Bader's QTAIM [50]. Further QTAIM analysis of the density matrix of the optimized molecules was performed by means of AIMALL Professional package [51]. NICS calculations [52] were performed by employing the GIAO (gauge-independent atomic orbital) method at 1 Å above the geometric center of the ring.

Table 1 Coefficients of determination of linear relations between experimental and theoretical bond length data; theoretical data were obtained from B3LYP/6-311++G(2d,2p) and MP2/6-311++G(d,p) levels of theory (MP2 values in square brackets)

Acenes	R^2
Benzene	1 [1]
Naphthalene	0.990 (0.965)
Anthracene	0.920 (0.876)
Pyrene	0.985 [0.966]
Chrysene	0.847 [0.812]

**Table 2** The values of charge density of the ring critical point (ρ_{RCP}); average of all second eigenvalues from the Hessian matrix of the charge density ($\overline{\lambda_2}$); delocalization index uniformity (DIU); and delocalization, density and degeneracy-based index of aromaticity (D3BIA) of all studied acenes using B3LYP/6-311++G(2d,2p), MP2/6-311++G(d,p), in parentheses, and B3LYP/6-311++G(2d,2p)//MP3/6-311++G(d,p), in square brackets. $\overline{DI}$; ring density formula (RDF); $\overline{DI}$;

Molecule	$\overline{\lambda_2}$	ρ_{rcp}	RDF	$\overline{DI}$	DIU	D3BIA
Benzene	-0.586 (-0.546) [-0.557]	0.0220 (0.0203) [0.0209]	0.00961 (0.00921) [0.00927]	1.387 (1.388) [1.389]	99.981 (99.993) [99.976]	0.960 (0.921) [0.927]
Naphthalene	-0.575 (-0.541) [-0.551]	0.0224 (0.0197) [0.0203]	0.00950 (0.00905) [0.00910]	1.329 (1.335) [1.337]	91.960 (91.345) [91.103]	0.874 (0.826) [0.829]
Anthracene (ring A)	-0.571 (-0.540) [-0.549]	0.0220 (0.0195) [0.0200]	0.00946 (0.00896) [0.00901]	1.315 (1.320) [1.321]	89.148 (88.023) [87.454]	0.843 (0.789) [0.788]
Anthracene (ring B)	-0.568 (-0.536) [-0.546]	0.0218 (0.0192) [0.0197]	0.00943 (0.00889) [0.00896]	1.280 (1.292) [1.296]	94.330 (94.906) [94.927]	0.889 (0.844) [0.851]
Phenanthrene (ring A)	-0.577 (-0.540) [-0.551]	0.0226 (0.0199) [0.0205]	0.00958 (0.00916) [0.00922]	1.339 (1.347) [1.349]	94.369 (94.156) [94.131]	0.904 (0.863) [0.868]
Phenanthrene (ring B)	-0.559 (-0.535) [-0.542]	0.0211 (0.0188) [0.0191]	0.00931 (0.00874) [0.00876]	1.263 (1.271) [1.273]	91.949 (90.922) [90.475]	0.856 (0.795) [0.793]
Pentacene (ring A)	-0.567 (-0.541) [-0.549]	0.0218 (0.0194) [0.0198]	0.00942 (0.00891) [0.00893]	1.306 (1.310) [1.308]	87.216 (85.780) [84.651]	0.822 (0.764) [0.756]
Pentacene (ring B)	-0.564 (-0.535) [-0.544]	0.0215 (0.0189) [0.0194]	0.00938 (0.00879) [0.00886]	1.264 (1.274) [1.277]	93.101 (92.672) [91.667]	0.873 (0.815) [0.812]
Pentacene (ring C)	-0.563 (-0.533) [-0.544]	0.0215 (0.0187) [0.0194]	0.00937 (0.00875) [0.00884]	1.259 (1.269) [1.274]	93.152 (93.576) [93.702]	0.873 (0.819) [0.828]
Tetracene (ring A)	-0.568 (-0.541) [-0.549]	0.0219 (0.0194) [0.0199]	0.00943 (0.00893) [0.00896]	1.309 (1.313) [1.313]	87.877 (86.483) [85.648]	0.829 (0.773) [0.768]
Tetracene (ring B)	-0.565 (-0.535) [-0.545]	0.0216 (0.0190) [0.0196]	0.00940 (0.00884) [0.00890]	1.269 (1.280) [1.284]	93.568 (94.014) [93.786]	0.879 (0.831) [0.834]
Pyrene (ring A)	-0.574 (-0.538) [-0.549]	0.0223 (0.0195) [0.0202]	0.00949 (0.00902) [0.00909]	1.309 (1.320) [1.323]	95.442 (95.817) [95.922]	0.906 (0.864) [0.872]
Pyrene (ring B)	-0.564 (-0.540) [-0.548]	0.0214 (0.0190) [0.0194]	0.00933 (0.00874) [0.00878]	1.265 (1.268) [1.268]	91.871 (91.021) [90.766]	0.858 (0.796) [0.797]
Chrysene (ring A)	-0.533 (-0.508) [-0.547]	0.0212 (0.0213) [0.0203]	0.00988 (0.01048) [0.00918]	1.337 (1.126) [1.344]	93.548 (94.456) [93.062]	0.924 (0.989) [0.854]
Chrysene (ring B)	-0.523 (-0.500) [-0.538]	0.0201 (0.0204) [0.0192]	0.00957 (0.01021) [0.00886]	1.277 (1.079) [1.289]	92.494 (93.868) [91.134]	0.885 (0.958) [0.808]

Table 3 D3BIA, aromatic fluctuation index (FLU), nucleus independent chemical shift (NICS)(1), NICS(1)$_{zz}$, para delocalization index (PDI) and harmonic oscillator model of aromaticity (HOMA) of the studied acenes from B3LYP/6-311++G(2d,2p), MP2/6-311++G(d,p), in parentheses, and B3LYP/6-311++G(2d,2p)//MP3/6-311++G(d,p), in square brackets

| Molecule	D3BIA	FLU	NICS(1)	NICS(1)$_{zz}$	PDI	HOMA
Benzene	0.960 (0.921) [0.927]	8.7E-05 (6.8E-05) [6.7E-05]	−10.2 (−10.2)	−29.3 (−29.8)	0.103 (0.099) [0.099]	0.983 (1.000)
Naphthalene	0.874 (0.826) [0.829]	0.0093 (0.0099) [0.0101]	−10.4 (−11.5)	−29.6 (−31.2)	0.075 (0.072) [0.072]	0.861 (0.867)
Anthracene (ring A)	0.843 (0.789) [0.788]	0.0155 (0.0193) [0.0189]	−9.5 (−10.3)	−26.6 (−27.2)	0.066 (0.061) [0.060]	0.735 (0.772)
Anthracene (ring B)	0.889 (0.844) [0.851]	0.0104 (0.0085) [0.0080]	−12.7 (−14.2)	−35.4 (−38.1)	0.065 (0.066) [0.066]	0.855 (0.814)
Phenanthrene (ring A)	0.904 (0.863) [0.868]	0.0053 (0.0052) [0.0050]	−7.9 (−11.5)	−20.8 (−31.1)	0.081 (0.080) [0.080]	0.923 (0.920)
Phenanthrene (ring B)	0.856 (0.794) [0.793]	0.0199 (0.0213) [0.0219]	−10.5 (−8.8)	−20.9 (−21.6)	0.047 (0.044) [0.044]	0.654 (0.653)
Pentacene (ring A)	0.822 (0.764) [0.756]	0.0207 (0.0244) [0.0275]	−7.8 (−8.4)	−21.4 (−21.3)	0.059 (0.053) [0.050]	0.615 (0.723)
Pentacene (ring B)	0.873 (0.815) [0.812]	0.0152 (0.0144) [0.0150]	−12.2 (−13.6)	−33.9 (−35.9)	0.059 (0.058) [0.057]	0.733 (0.723)
Pentacene (ring C)	0.873 (0.819) [0.828]	0.0144 (0.0128) [0.0118]	−13.5 (−15.2)	−37.8 (−40.5)	0.060 (0.059) [0.060]	0.759 (0.679)
Tetracene (ring A)	0.829 (0.773) [0.768]	0.0189 (0.0222) [0.0242]	−8.5 (−9.1)	−23.7 (−23.7)	0.061 (0.056) [0.054]	0.660 (0.735)
Tetracene (ring B)	0.879 (0.831) [0.834]	0.0145 (0.0119) [0.0166]	−12.6 (−14.1)	−35.3 (−37.7)	0.062 (0.061) [0.061]	0.788 (0.752)
Pyrene (ring A)	0.906 (0.864) [0.872]	0.0065 (0.0054) [0.0048]	−12.8 (−14.2)	−36.2 (−38.6)	0.069 (0.071) [0.072]	0.941 (0.907)
Pyrene (ring B)	0.858 (0.796) [0.797]	0.0195 (0.0216) [0.0223]	−6.8 (−7.6)	−17.1 (−17.8)	0.044 (0.039) [0.039]	0.744 (0.743)
Chrysene (ring A)	0.924 (0.989) [0.854]	0.0065 (0.0066) [0.0066]	−10.74 (−11.47)	−28.37 (−30.71)	0.079 (0.078) [0.078]	0.903 (0.907)
Chrysene (ring B)	0.885 (0.958) [0.808]	0.0156 (0.0140) [0.0167]	−9.02 (−9.07)	−22.51 (−23.96)	0.053 (0.052) [0.052]	0.723 (0.727)
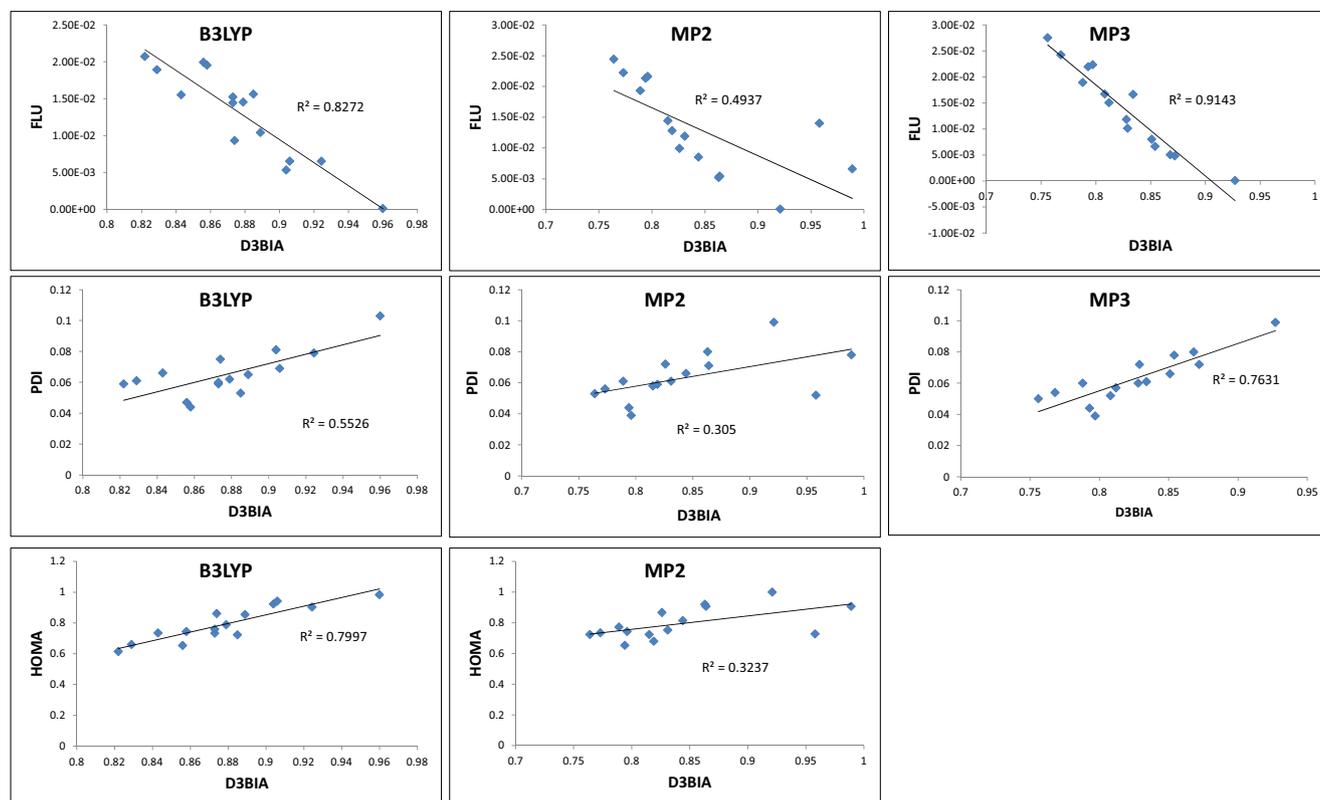
Fig. 1 Plots and coefficient of determination from correlations between delocalization, density and degeneracy-based index of aromaticity (D3BIA) and aromatic fluctuation index (FLU), D3BIA and para delocalization index (PDI), and D3BIA and harmonic oscillator model of aromaticity (HOMA) from the studied acenes calculated from B3LYP/6-311++G(2d,2p), MP2/6-311++G(d,p) and B3LYP/6-311++G(2d,2p)//MP3/6-311++G(d,p) level of theory

Table 4   Experimental and theoretical bond lengths (in Ångstroms) of chrysene

Bond (chrysene)	Bond length		
	Experimental[a]	B3LYP	MP2
AB	1.468	1.452	1.450
BC	1.409	1.417	1.420
CD	1.381	1.379	1.388
DE	1.394	1.408	1.412
EF	1.363	1.377	1.385
FG	1.428	1.415	1.418
GH	1.421	1.426	1.427
HI	1.368	1.362	1.372
IJ	1.428	1.430	1.431
AJ	1.401	1.415	1.423
BG	1.409	1.425	1.430

[a] From ref. [55]
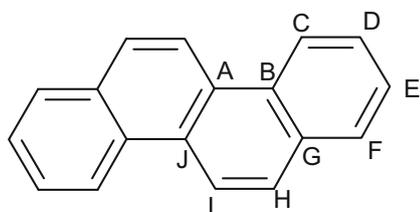
Results and discussion

Table 1 shows the linear relationship between experimental and theoretical bond lengths for benzene [53], naphthalene [54], anthracene [55], pyrene [56], and chrysene [55]. Analysis of R^2 in Table 1 indicates that B3LYP-optimized geometries are closer to experimental data than those from MP2 for these selected acenes. As a consequence, we chose B3LYP-optimized geometries to obtain MP3 single point and electronic density.

Table 2 shows the B3LYP, MP2 and MP3 values of ρ_{RCP}, $\overline{\lambda_2}$, RDF, $\overline{DI}$, DIU that are used for obtaining D3BIA according to Eqs. (4), (5) and (7) for all studied acenes. We kept three significant figures in all topological data in order to guarantee a considerable precision for D3BIA. A lower number of significant figures decreases the R^2 between D3BIA and other indices.

For the studied acenes, all carbon atoms in each ring were regarded as degenerate since they have close atomic energies and all DI(CC)<0.5e. As a consequence, all bezenoid rings from the studied acenes follow either rule I or rule II of degree of degeneracy, and all have δ=1.

Table 3 shows the aromaticity indices (D3BIA, FLU, NICS(1), NICS(1)$_{zz}$, PDI and HOMA) for all studied acenes from the three levels of theory in which FLU values change three-fold, on average, more than those from D3BIA, while

variation in PDI values when changing the level of theory were slightly higher than those from D3BIA.

Figure 1 shows plots of the linear (or not) relationships involving D3BIA and FLU, D3BIA and HOMA, and D3BIA and PDI aromaticity indices derived from B3LYP, MP2 and MP3 methods. The linear relations between D3BIA and FLU and between D3BIA and HOMA from the B3LYP method gave good correlations (79.97 % and 82.7 %, respectively). The aromaticity indices PDI and D3BIA did not correlate with the B3LYP method. On the other hand, a reasonably good correlation was found between PDI and D3BIA with the MP3 method (correlation 76.3 %). With both B3LYP and MP3 methods, the FLU aromaticity index presented the best correlation with D3BIA, in which the FLU / D3BIA coefficient of determination from MP3 was 0.9143.

Table 4 shows the experimental [55] and theoretical (from B3LYP and MP2 methods) bond lengths for chrysene. We see that variation between B3LYP and experimental bond lengths is smaller than that between MP2 and experimental data. In addition, the bond lengths in B3LYP and experimental data present a higher alternation than those from MP2.

Figure 2 shows the linear relations for D3BIA / FLU and D3BIA / PDI from MP2 and MP3 methods plus D3BIA / HOMA for the MP2 method without considering aromaticity data from chrysene rings. The coefficients of determination obtained from the MP2 method improve considerably when removing chrysene aromaticity data from D3BIA, FLU, HOMA and PDI. However, the D3BIA / FLU and D3BIA / PDI coefficients of determination display no significant change when chrysene aromaticity data are not considered in MP3 method.

Except for chrysene, all D3BIA values from MP2 and MP3 were very similar [Δ D3BIA$_{(from\ MP2\ and\ MP3)}$ varies within the range from 0.001 to 0.009]. By comparing D3BIA from chrysene rings and that from other acenes, this difference is much higher [Δ D3BIA$_{(from\ MP2\ and\ MP3)}$=0.135 and 0.150 comparing rings A and B of chrysene with other acenes, respectively]. This discrepancy can be ascribed mainly to the comparatively lower $\overline{\lambda_2}$ and higher DIU from MP2 in chrysene.

The higher DIU from MP2 in chrysene rings is a consequence of the smaller bond length alternation from MP2 (see Table 4) compared to that from experimental and B3LYP, which yields lower DIU for B3LYP and MP3 from B3LYP optimized geometries). Table 3 reveals that FLU and HOMA from chrysene rings are very similar regardless of the method used, unlike when comparing D3BIA from chrysene rings between MP2 and other methods. Then, DIU and D3BIA are more sensitive to bond length alternation in chrysene (from MP2) than the corresponding HOMA and FLU values, which are also influenced by bond length and DI, respectively. As a consequence, the higher DIU in
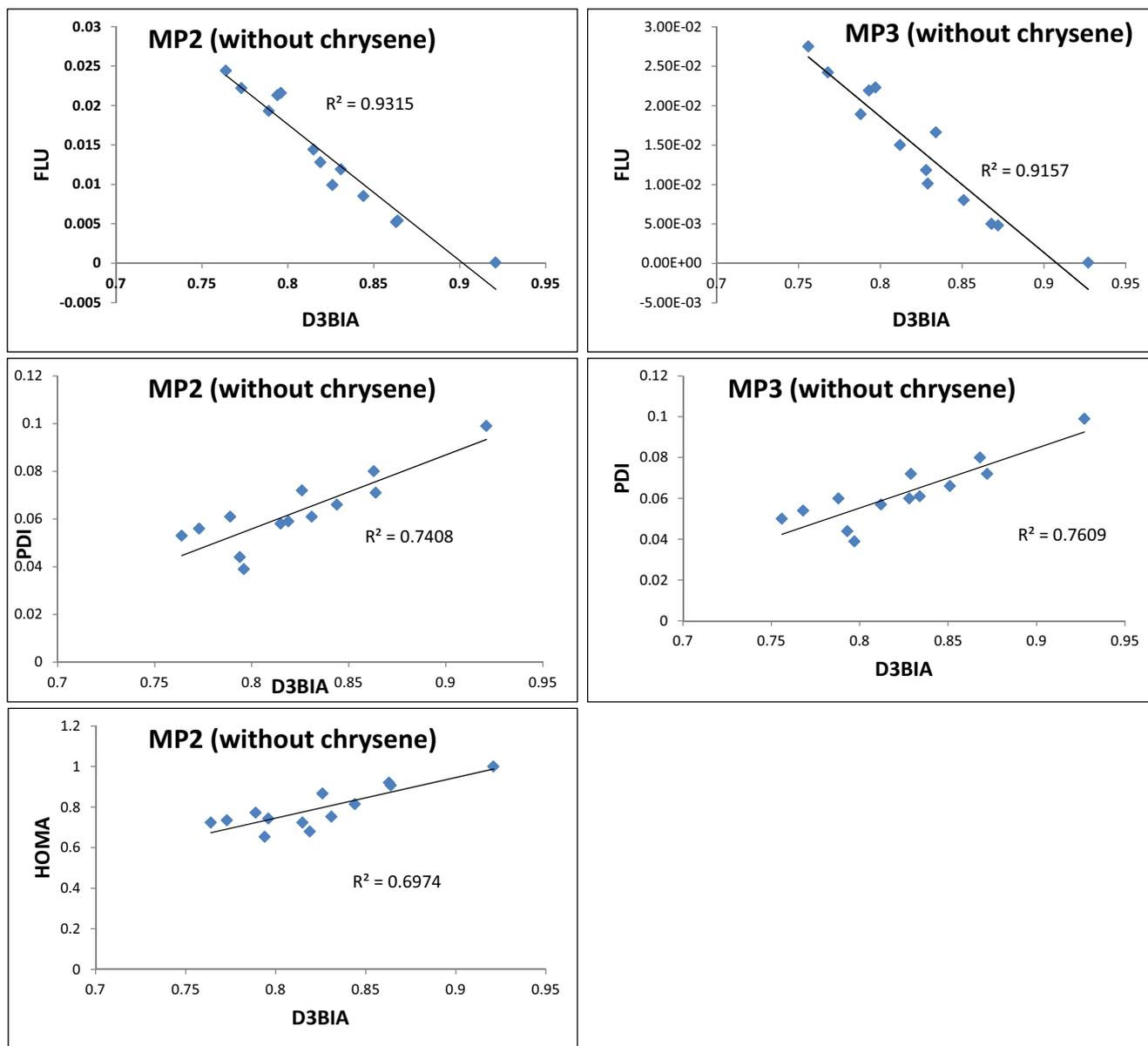
Fig. 2 Plots and coefficient of determination from correlations between D3BIA and FLU, D3BIA and PDI and D3BIA and HOMA from the studied acenes calculated excluding aromaticity data from chrysene from MP2/6-311++G(d,p) and B3LYP/6-311++G(2d,2p)//MP3/6-311++G(d,p)

Fig. 3 Plots of D3BIA and FLU from the MP3 method versus **a** external ring from linear acenes, and **b** external and internal rings from linear and non-linear acenes

(A)

(B)
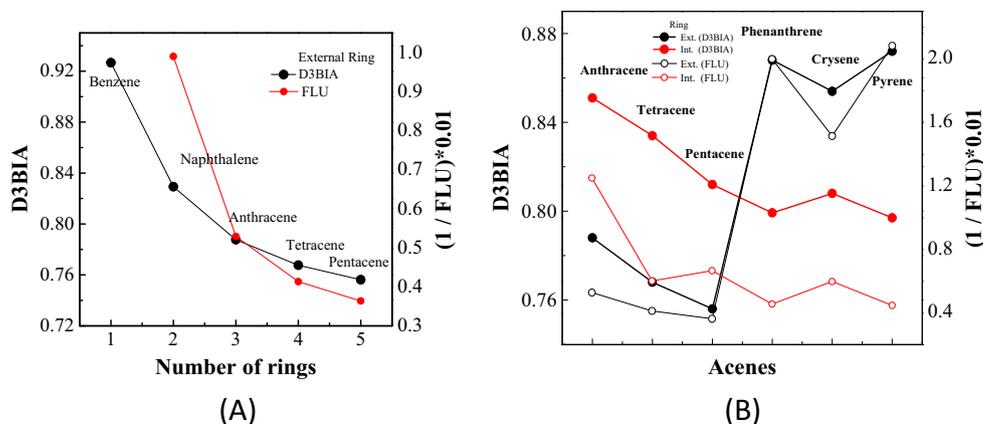
chrysene rings from the MP2 method gives rise to divergent trends when comparing their corresponding D3BIA with FLU and HOMA.

Moreover, discrepancies in D3BIA values from chrysene when comparing MP2 with MP3 or B3LYP are also attributed to a comparatively lower $\overline{\lambda_2}$ in chrysene with the MP2 method. As a consequence of Eq. (5), the RDF values of chrysene rings from MP2 method are higher than those from MP3 and B3LYP methods. The $\overline{\lambda_2}$ discrepancy is 0.04 a.u. for chrysene rings involving all methods. This discrepancy is twice as high as the highest $\overline{\lambda_2}$ discrepancy for all other acenes from all methods.

As a consequence, we plotted linear relationships excluding chrysene aromaticity data. Consequently, D3BIA versus FLU/HOMA/PDI coefficients of determination from the MP2 method improve significantly while only a slight difference occurs in the same coefficients of determination without chrysene from the MP3 method.

Figure 3 shows that both D3BIA and FLU display the same trends for aromaticity of external and internal rings of the studied acenes. According to D3BIA and FLU (Fig. 3a), aromaticity of external rings from linear acenes (benzene, naphthalene, anthracene, tetracene and pentacene) decreases from benzene to pentacene following a power equation (e.g., D3BIA$=0.9488N^{0.098}$, where N is the number of rings of the linear acene). When including non-linear acenes, the aromaticity of external rings does not follow any particular trend, according to both aromaticity indices (Fig. 3b). However, D3BIA indicates a decreasing trend of aromaticity for internal rings regarding linear and non-linear acenes (Fig. 3b).

Table 5 shows all coefficients of determination involving correlation between all studied aromaticity indices for acenes from B3LYP, MP2 and MP3 methods. Excluding the correlation between NICS(1) and NICS(1)$_{zz}$, the highest R^2 values are the linear relationships between FLU and D3BIA and

between FLU and HOMA. Moreover, D3BIA gave the second best correlation with HOMA ($R^2=0.800$), along with that between HOMA and PDI, and D3BIA correlated fairly well with PDI ($R^2=0.763$). However, D3BIA had no linear relationship with NICS(1) and NICS(1)$_{zz}$. Likewise, FLU, PDI and HOMA also have no linear relationships with either of the NICS indices. Similar poor correlations were also found for NICS versus HOMA, NICS versus PDI, NICS versus FLU and HOMA versus PDI for a series of acenes using HF/6-31G(d) level of theory [57].

Thus, B3LYP/6-311++G(2d,2p)//MP3/6-311++G(d,p) level of theory gave the best correlations of D3BIA with FLU and PDI, showing that more precise electron correlation calculation improves correlation between D3BIA and other QTAIM aromaticity indices. On the other hand, B3LYP/6-311++G(2d, 2p) gave the best correlation of D3BIA with HOMA, which can be attributed to the more precise geometric data from B3LYP than those available from MP2 (Table 1).

In this work we showed for the first time that the recently developed aromaticity index, D3BIA, can be used successfully for benzenoid systems along with HOMA and FLU. No previous work has proved this before. Thus, the most important chemical and physical insight of this work is the validation of D3BIA for quantifying the aromaticity of benzenoid systems, giving a new alternative for the study of aromaticity.

The D3BIA has the advantage that it can be used for any aromatic, homoaromatic, sigma aromatic and all-metal aromatic systems (and will be adopted in our future work). This is because D3BIA is not reference- and ring-size-dependent. On the other hand, HOMA and FLU can be used only for aromatic systems without heteroatoms (since they are reference dependent) and PDI for six-membered rings [28]. Another advantage of D3BIA is its very good correlation with NICS for homoaromatic and sigma aromatic systems and its very good correlation with FLU and fairly good correlation

Table 5 Coefficient of determination (R^2) for correlations between studied aromatic indices for acenes. The results were obtained within B3LYP/6-311++G(2d,2p), MP2/6-311++G(d,p) (in parentheses), without chrysene data, and B3LYP/6-311++G(2d,2p)// MP3/6-311++G(d,p) (in square brackets)

	D3BIA	FLU[a]	NICS(1)$_{iso}$	NICS(1)$_{zz}$[b]	PDI[c]	HOMA[d]
D3BIA	1	0.827 (0.931)[e] [0.914]	0.100 (0.174)	0.113 (0.267)	0.553 (0.741) [0.763]	0.800 (0.697)
FLU		1	0.0771 (0.328)	0.142 (0.444)	0.811 (0.776)	0.936 (0.690)
NICS(1)$_{iso}$			1	0.887 (0.979)	0.0119 (0.0942)	0.0863 (0.0135)
NICS(1)$_{zz}$				1	0.0683 (0.193)	0.0153 (0.0568)
PDI					1	0.632 (0.798)
HOMA						1

[a] Best correlations of FLU are D3BIA $\cong$ HOMA > PDI

[b] Best correlation of NICS(1)$_{zz}$ is NICS(1)

[c] Best correlations of PDI are FLU > HOMA > D3BIA

[d] Best correlations of HOMA are FLU > D3BIA $\cong$ PDI

[e] Without chrysene data for MP2/6-311++G(d,p) calculations

with HOMA in acenes (and probably other benzenoid systems). While FLU and HOMA also have a very good correlation, D3BIA is much simpler to calculate than FLU.

Conclusions

The newly developed D3BIA aromaticity index can be used to quantify the aromaticity of acenes and other benzenoid systems. No previous work has shown this before. This work proves that D3BIA is a successful aromaticity index (like HOMA and FLU) for analyzing benzenoid systems.

The D3BIA can be compared successfully with FLU for analyzing aromaticity trends of acenes in which the D3BIA versus FLU correlation exceeded 91 %. Moreover, good or fairly good correlations were found between D3BIA and HOMA and between D3BIA and PDI.

As for the linear relationships of FLU versus D3BIA and PDI versus D3BIA, the MP3 method (from B3LYP/6-311++G(2d,2p)//MP3/6-311++G(d,p) level of theory) gave the best correlations compared to those obtained from the MP2 (including chrysene aromaticity data) and B3LYP methods, showing that the linear relationship of D3BIA with other electronic aromaticity indices improves when increasing the level of theory. On the other hand, the B3LYP method gave the best correlation between HOMA and D3BIA compared to that from the MP2 method (with or without chrysene aromaticity data).

The D3BIA is neither reference dependent (unlike HOMA and FLU) nor ring size dependent (unlike NICS and PDI) but, when searching for correlation with other aromaticity indices in classical aromatic systems, care should be taken when considering the level of theory and minimum number of significant figures (at least, three) for D3BIA analysis.

References

1. Boldyrev AI, Wang LS (2005) All-metal aromaticity and antiaromaticity. Chem Rev 105:3716–3757
2. Tsipis CA (2005) DFT study of "all-metal" aromatic compounds. Coord Chem Rev 249:2740–2762
3. Williams RV (2001) Homoaromaticity. Chem Rev 101:1185–1204
4. Mercero JM, Boldyrev AI, Merino G, Ugalde JM (2015) Recent developments and future prospects of all-metal aromatic compounds. Chem Soc Rev. doi: 10.1039/C5CS00341E
5. Krygowski TM, Cyranski MK (2001) Structural aspects of aromaticity. Chem Rev 101:1385–1419
6. Schaad LJ, Andes Hess Jr B (2001) Dewar resonance energy. Chem Rev 101:1465–1476
7. Mitchell RH (2001) Measuring aromaticity by NMR. Chem Rev 101:1301–1315
8. Gomes JANF, Mallion RB (2001) Aromaticity and ring currents. Chem Rev 101:1349–1383
9. Islas R, Heine T, Merino G (2012) The induced magnetic field. Acc Chem Res 45:215–228
10. Merino G, Heine T, Seifert G (2004) The induced magnetic field in cyclic molecules. Chem Eur J 10:4367–4371
11. Torres-Vega JJ, Vasquez-Espinal A, Caballero J, Valenzuela ML, Alvarez-Thon L, Osorio E, Tiznado W. Minimizing the risk of reporting false aromaticity and antiaromaticity in inorganic heterocycles following magnetic criteria. Inorg Chem 53:3579–3585
12. Garratt PJ (1986) Aromaticity, 1st edn. Wiley, New York
13. Stanger A (2009) What is aromaticity: a critique of the concept of aromaticity—can it really be defined? Chem Commun 2009:1939–1947
14. Santos JC, Tiznado W, Contreras R, Fuentealba P (2004) Sigma-pi separation of the electron localization function and aromaticity. J Chem Phys 120:1670–1673
15. Shaik S, Shurki A, Danovich D, Hiberty PC (2001) A different story of π-delocalization—the distortivity of π-electrons and its chemical manifestations. Chem Rev 101:1501–1539
16. Shaik SS, Hiberty PC, Lefour JM, Ohanessian G (1987) Is delocalization a driving force in chemistry? Benzene, allyl radical, cyclobutadiene, and their isoelectronic species. J Am Chem Soc 109:363–374
17. Nascimento MAC (2008) The nature of the chemical bond. J Braz Chem Soc 19:245–256
18. Haas Y, Zilberg S (1995) The.nu.14(b2u) mode of benzene in S0 and S1 and the distortive nature of the .pi. electron system: theory and experiment. J Am Chem Soc 117:5387–5388
19. Alexandrova AN, Boldyrev AI (2003) σ-aromaticity and σ-antiaromaticity in alkali metal and alkaline earth metal small clusters. J Phys Chem A 107:554–560
20. Nemirowski A, Reisenauer HP, Schreiner PR (2006) Tetrahedrane—dossier of an unknown. Chem Eur J 12:7411–7420
21. Monteiro NKV, De Oliveira JF, Firme CL (2014) Stability and electronic structures of substituted tetrahedranes, silicon and germanium parents-a DFT, ADMP, QTAIM and GVB study. New J Chem 38:5892–5904
22. Sergeeva AP, Averkiev BB, Boldyrev AI. All-transition metal aromaticity and antiaromaticity. Struct Bond 136:275–306
23. Galeev TR, Boldyrev AI (2011) Recent advances in aromaticity and antiaromaticity in transition-metal systems. Annu Rep Sect C 107: 124–147
24. Kruszewski J, Krygowski TM (1972) Definition of aromaticity basing on harmonic oscillator model. Tetrahedron Lett 13:3839–3842
25. Chen ZF, Wannere CS, Corminboeuf C, Puchta R, Schleyer PV (2005) Nucleus-independent chemical shifts (NICS) as an aromaticity criterion. Chem Rev 105:3842–3888
26. Fallah-Bagher-Shaidaei H, Wannere CS, Corminboeuf C, Puchta R, Schleyer PV (2006) Which NICS aromaticity index for planar pi rings is best? Org Lett 8:863–866
27. Poater J, Duran M, Solà M, Silvi B (2005) Chem Rev 105:3911–3947
28. Feixas F, Matito E, Poater J, Sola M (2015) Quantifying aromaticity with electron delocalisation measures. Chem Soc Rev. doi:10.1039/C5CS00066A
29. Matta CF, Boyd RJ (2007) Front matter. In: Matta CF, Boyd RJ (eds) The quantum theory of atoms in molecules—from solid to DNA and drug design. Wiley-VCH, Weinheim, pp 1–34
30. Merino G, Vela A, Heine T (2005) Description of electron delocalization via the analysis of molecular fields. Chem Rev 105:3812–3841

31. Bader RFW, Stephens ME (1975) Spatial localization of the electronic pair and number distributions in molecules. J Am Chem Soc 97:7391–7399

32. Bader RFW, Streitwieser A, Neuhaus A, Laidig KE, Speers P (1996) Electron delocalization and the fermi hole. J Am Chem Soc 118:4959–4965

33. Poater J, Fradera X, Duran M, SolÃ M (2003) The delocalization index as an electronic aromaticity criterion: application to a series of planar polycyclic aromatic hydrocarbons. Chem Eur J 9:400–406

34. Matito E, Duran M, Sola M (2005) The aromatic fluctuation index (FLU): a new aromaticity index based on electron delocalization. J Chem Phys 122:014109

35. Firme CL, Galembeck SE, Antunesa OAC, Esteves PM (2007) Density, degeneracy, delocalization-based index of aromaticity (D 3BIA). J Braz Chem Soc 18:1397–1404

36. Firme CL, Da Costa TF, Da Penha ET, Esteves PM (2013) Electronic structures of bisnoradamantenyl and bisnoradamantanyl dications and related species. J Mol Model 19:2485–2497

37. Ghosh D, Periyasamy G, Pati SK (2011) Density functional theoretical investigation of the aromatic nature of BN substituted benzene and four ring polyaromatic hydrocarbons. Phys Chem Chem Phys 13:20627–20636

38. Ebrahimi AA, Ghiasi R, Foroutan-Nejad C (2010) Topological characteristics of the Ring Critical Points and the aromaticity of groups IIIA to VIA hetero-benzenes. J Mol Struct (THEOCHEM) 941:47–52

39. Slater JC (1933) The virial and molecular structure. J Chem Phys 1: 687–691

40. Hernandez-Trujillo J, Cortes-Guzman F, Fang DC, Bader RFW (2007) Forces in molecules. Faraday Discuss 135:79–95

41. Firme CL, Antunes OAC, Esteves PM (2008) Electronic nature of the aromatic adamantanediyl ions and its analogues. J Braz Chem Soc 19:140–149

42. Foroutan-Nejad C, Shahbazian S, Rashidi-Ranjbar P (2010) The electron density vs. NICS scan: a new approach to assess aromaticity in molecules with different ring sizes. Phys Chem Chem Phys 12:12630–12637

43. Pulay P, Fogarasi G (1992) Geometry optimization in redundant internal coordinates. J Chem Phys 96:2856

44. Li X, Frisch MJ (2006) Energy-represented direct inversion in the iterative subspace within a hybrid geometry optimization method. J Chem Theory Comput 2:835–839

45. Becke AD (1993) Density-functional thermochemistry.3. the role of exact exchange. J Chem Phys 98:5648–5652

46. Lee C, Yang W, Parr RG (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys Rev B 37:785

47. Pople JA, Binkley JS, Seeger R (1976) Theoretical models incorporating electron correlation. Int J Quantum Chem 10:1–19

48. Head-Gordon M, Pople JA, Frisch MJ (1988) MP2 energy evaluation by direct methods. Chem Phys Lett 153:503–506

49. Frisch MJ, Trucks GW, Schegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery JA Jr., Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas Ö, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2009) Gaussian 09. Revision A.01. Wallingford

50. Bader RFW (1994) Atoms in molecules a quantum theory. International Series of Monographs on Chemistry (Book 22). Oxford University Press, Oxford

51. Keith TA (2013) AIMAll. TK Gristmill Software, Overland Park, KS, http://aim.tkgristmill.com

52. Schleyer PV, Maerker C, Dransfeld A, Jiao HJ, Hommes N (1996) Nucleus-independent chemical shifts: a simple and efficient aromaticity probe. J Am Chem Soc 118:6317–6318

53. Johnson-III RD (2013) NIST Standard Reference Database Number 101. NIST Computational Chemistry Comparison and Benchmark Database

54. Hellwege K, Hellwege A (eds) (1976) Structure data of free polyatomic molecules. Springer, Berlin

55. Cruickshank DWJ, Sparks RA (1960) Experimental and theoretical determinations of bond lengths in naphthalene, anthracene and other hydrocarbons. Proc R Soc Lond A 258:270–285

56. Frampton CS, Knight KS, Shankland N, Shankland K (2000) Single-crystal X-ray diffraction analysis of pyrene II at 93K. J Mol Struct 520:29–32

57. Matito E, Poater J, Solà M (2007) Aromaticity analysis by means of the quantum theory of atoms in molecules. In: Matta CF, Boyd RJ (eds) The quantum theory of atoms in molecules—from solid state to DNA and drug design. Wiley-VCH, Weinheim