

Aromaticity of Distorted Benzene Rings: Exploring the Validity of Different Indicators of Aromaticity

Ferran Feixas,[†] Eduard Matito,^{†,‡} Jordi Poater,[§] and Miquel Solà^{*,†}

Institut de Química Computacional and Departament de Química, Universitat de Girona, 17071 Girona, Catalonia, Spain, Instytut Fizyki, Uniwersytet Szczeciński, 70-451 Szczecin, Poland, and Afdeling Theoretische Chemie, Scheikundig Laboratorium der Vrije Universiteit, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands

Received: January 15, 2007; In Final Form: February 28, 2007

The effect of three in-plane (bond length alternation, bond length elongation, and clamping) and three out-of-plane deformations (boatlike, chairlike, and pyramidalization) on the aromaticity of the benzene molecule has been analyzed employing seven widely used indicators of aromaticity. It is shown that only the aromatic fluctuation index (FLU) is able to indicate the expected loss of aromaticity because of distortion from the equilibrium geometry in all deformations analyzed. As FLU has been shown previously to fail in other particular situations, we conclude that there is not yet a single indicator of aromaticity that works properly for all cases. Therefore, to reach safer conclusions, aromaticity analyses should be carried out employing a set of aromaticity descriptors on the basis of different physical manifestations of aromaticity.

1. Introduction

Discovered by Michael Faraday in 1825,¹ benzene is the archetype of a two-dimensional aromatic molecule that exhibits all typical structural and chemical manifestations of aromaticity as, for instance, substantial energy stabilization, bond length equalization, unusual reactivity, and characteristic spectroscopic features as well as distinctive magnetic properties related to strong induced ring currents.^{2–8}

Planarity and bond length equalization are two structural characteristics of benzene that are usually associated with its aromatic character. Yet, simple connection of benzene with another aromatic six-membered ring (6-MR) to form naphthalene destroys the perfect bond length equalization. Even more significant, C–C bond length alternation is achieved when the benzene ring is annelated with clamping groups such as the cyclopropa, cyclobuta, and cyclobutadieno clamps.^{9,10} However, as shown by Soncini et al., when only saturated clamping groups are used, the benzene ring current remains essentially unchanged.⁹ Thus, apparently the benzene molecule can suffer significant C–C bond length alternations (BLAs) without a substantial loss of its cyclic electron delocalization and its aromaticity.¹¹ This result is reinforced by resonance energy calculations of several BLA deformed benzene rings.^{12–14} However, aromaticity resists not only BLA in the benzene ring but also large out-of-plane distortions,^{15–19} a fact that has been well documented both experimentally and theoretically but that is usually overlooked by most organic chemistry textbooks.

From an experimental point of view, the suggestion that benzene possesses conformational ring flexibility is supported by the fact that the same molecule of deuterated benzene in its orthorhombic crystal structure suffers slight but non-negligible distortions caused by crystal packing forces that change the

symmetry of the molecule from D_{6h} to C_{3v} .²⁰ Moreover, the crystal structures of most acenes and their derivatives show some deviations from planarity.²¹ There is also other evidence of the flexibility of the benzene ring. A nonexhaustive list includes the following. First, $[n]$ para- and metacyclophanes^{15,16} and pyrenophanes^{17–19} can undergo severe distortions of the aromatic rings without significant loss of aromaticity in comparison with the undistorted benzene and pyrene molecules, respectively, as indicated by ¹H NMR signals, magnetic anisotropies, UV/vis spectra, X-ray molecular structures, and theoretical calculations.¹⁹ Second, severe out-of-plane distortions take place in the $C_{48}H_{24}$ and $C_{138}H_{42}$ structures that have D_{3d} symmetry instead of the expected D_{6h} geometries²² and, in general, all out-of-plane distortions that occur in sterically overcrowded polycyclic aromatic hydrocarbons,^{23,24} such as those found in the $[n]$ helicenes series for $n > 4$.^{25–28} For these species, it has been found that the aromaticity of their 6-MRs change only slightly when compared to the analogous rings in the planar $[n]$ phenacenes species.^{25,28} Third, most of the 6-MRs of fullerenes and buckybowls are known to be quite aromatic despite the important departure from planarity.^{29–36}

Theoretically, the flexibility of the benzene ring as well as the robustness of its π -electronic delocalization and aromatic character has been discussed in several works. Thus, Cyránski and Krygowski³⁷ analyzed the change in aromaticity of the benzene ring because of BLA (b_{2u} symmetry) and bond length elongation (BLE, a_{1g} symmetry) using the harmonic oscillator model of aromaticity (HOMA) index and the nucleus-independent chemical shifts (NICS) as indicators of aromaticity. NICS values indicated slight changes in the aromatic character of the 6-MR because of BLA and BLE, while HOMA results predicted larger variations. Krygowski³⁸ also analyzed with HOMA the change of aromaticity in metacyclophane with similar results. Moreover, some of us found that there is a small change in the local aromaticity of the 6-MR of pyracylene when going from planar to pyramidalized pyracylene according to different indicators of aromaticity.³⁹ Similar results have been reported

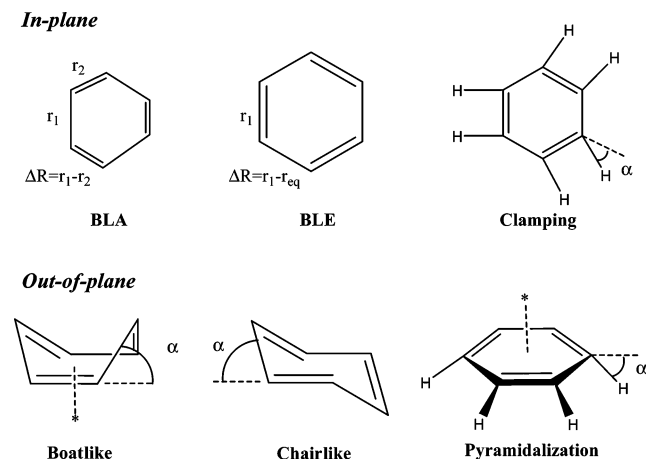
* To whom correspondence should be addressed. Phone: +34-972-418912. Fax: +34-972-418356. E-mail: miquel.sola@udg.es.

[†] Universitat de Girona.

[‡] Uniwersytet Szczeciński.

[§] Scheikundig Laboratorium der Vrije Universiteit.

CHART 1: Schematic Representation of the Six Distortions of the Benzene Ring Analyzed Indicating the Main Parameter Changed in Each Case^a



for cyclophanes.^{40,41} Two studies, the first by Dijkstra and van Lenthe⁴² and the second by Jenneskens et al.,⁴³ of boat-shaped benzenes, which mimic the distortions of the 6-MR in cyclophanes, showed that the benzene ring can experience deviations from planarity up to 25 degrees without a substantial loss of electron conjugation. In addition, resonance energies obtained by Datta and Patti indicate that the benzene ring retains its aromatic stabilization even for severe chair and boat distortions.⁴⁴ The high conformational out-of-plane flexibility of aromatic systems has been also analyzed in two recent works reporting that changes of about 20° in torsion angles result in an energy increase of about only 2–3 kcal·mol⁻¹.^{45,46} Interestingly, according to Shishkin and co-workers,^{45–47} the energy of the out-of-plane deformations of the ring can be used as a measure of aromaticity. In addition, as a clear indication of the flexibility of the 6-MR, Moran et al.⁴⁸ have shown recently that several ab initio correlated methods give nonplanar equilibrium structures for benzene. Finally, let us mention the work by Bader et al.⁴⁹ who studied the effect of BLA and BLE distortions on the delocalization of π electrons in benzene. They found that there is no significant change in the delocalization pattern because of BLE distortions. However, the π electronic delocalization between para-related carbon atoms is clearly reduced because of BLA deformations. This property has been used by some of us to define an index of aromaticity named para-delocalization index (PDI)⁵⁰ (vide infra).

In the present paper, we extend the previous investigations by Cyrński and Krygowski³⁷ on BLA and BLE deformations to clamping and several out-of-plane distortions of the ring employing the HOMA and NICS indexes used by these authors as well as other descriptors of aromaticity on the basis of the analysis of the electronic structure such as the para-delocalization index (PDI),⁵⁰ the fluctuation aromaticity (FLU) index,⁵¹ the six-center index (SCI),⁵² and the hardness (η).⁵³ The main aim of the present paper is to discuss the behavior of the aforementioned descriptors to analyze the changes of aromaticity because of different deformations of the benzene ring (see Chart 1). In particular, we have studied three in-plane distortions (BLA, BLE, and clamping) and three out-of-plane deformations (boatlike, chairlike, and pyramidalization). Here, we anticipate that only the FLU index of aromaticity is able to reproduce the expected result, namely, a decrease in the aromatic character

of the ring with the increase of deformation for any of the six possible distortions analyzed. As a byproduct of this work, our results confirm the previously reported resistance of the benzene ring to the loss of aromaticity when distorted in several ways.

2. Descriptors of Aromaticity

The evaluation of aromaticity is usually performed by analyzing its manifestations, and this leads to the classical structural, magnetic, energetic, electronic, and reactivity-based measures of aromaticity.^{2,54} Despite several aromaticity indicators that have been put forward, we must note the important contribution by Katritzky and co-workers and Krygowski and co-workers who found, by means of principal component analyses, that aromaticity is a multidimensional property and, as a consequence, aromatic compounds are better characterized using a set of indexes on the basis of different physical properties.^{54–58}

As a structure-based measure, we have made use of the harmonic oscillator model of aromaticity (HOMA) index, defined by Kruszewski and Krygowski as^{38,59}

$$\text{HOMA} = 1 - \frac{\alpha}{n} \sum_{i=1}^n (R_{\text{opt}} - R_i)^2 \quad (1)$$

where n is the number of bonds considered, and α is an empirical constant (for C–C bonds $\alpha = 257.7$) fixed to give HOMA = 0 for a model nonaromatic system, and HOMA = 1 for a system with all bonds equal to an optimal value R_{opt} (1.388 Å for C–C bonds), assumed to be achieved for fully aromatic systems. R_i stands for a running bond length. This index is one of the most effective structural indicators of aromaticity.^{8,57} In 1996, Krygowski and Cyrński^{57,60,61} split the HOMA into the energetic (EN) and geometric (GEO) contributions according to the relation HOMA = 1 – EN – GEO. The GEO contribution measures the decrease/increase in bond length alternation as follows:

$$\text{GEO} = \frac{\alpha}{n} \sum_{i=1}^n (R_{\text{av}} - R_i)^2 \quad (2)$$

where R_{av} is the mean C–C bond length of the ring. On the other hand, the EN term takes into account the lengthening/shortening of the mean bond lengths of the ring and is given by

$$\text{EN} = \alpha(R_{\text{opt}} - R_{\text{av}})^2 \quad \text{for } R_{\text{av}} > R_{\text{opt}} \quad (3a)$$

and

$$\text{EN} = -\alpha(R_{\text{opt}} - R_{\text{av}})^2 \quad \text{for } R_{\text{av}} < R_{\text{opt}} \quad (3b)$$

In this 1996 reformulation,^{57,60,61} the HOMA index can be larger than 1 for systems with $R_{\text{av}} < R_{\text{opt}}$.

Magnetic indices of aromaticity are based on the π -electron ring current that is induced when the system is exposed to external magnetic fields. In this work, we have used the NICS, proposed by Schleyer and co-workers,^{7,62} as a magnetic descriptor of aromaticity. It is defined as the negative value of the absolute shielding computed at a ring center or at some other interesting point of the system. Rings with large negative NICS values are considered aromatic. The more negative the NICS value, the more aromatic the ring is.

Three aromaticity criteria based on electron delocalization measures have been employed.^{63,64} These indexes try to measure

the cyclic electron delocalization of mobile electrons in aromatic rings. First, the para-delocalization index (PDI),^{35,50} which is obtained using the delocalization index (DI)^{65,66} as defined in the framework of the atoms in molecules (AIM) theory of Bader,^{67–69} is an average of all DI of para-related carbon atoms in a given 6-MR. The DI value between atoms A and B, $\delta(A, B)$, is obtained by double integration of the exchange-correlation density ($\Gamma_{XC}(\vec{r}_1, \vec{r}_2)$) over the basins of atoms A and B, which are defined from the condition of zero-flux gradient in the one-electron density, $\rho(\mathbf{r})$:^{67–69}

$$\delta(A, B) = -2 \int_A \int_B \Gamma_{XC}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (4)$$

For monodeterminantal closed-shell wavefunctions one obtains

$$\delta(A, B) = 4 \sum_{ij}^{N/2} S_{ij}(A) S_{ij}(B) \quad (5)$$

The summations in eq 5 run over all the $N/2$ occupied molecular orbitals. $S_{ij}(A)$ is the overlap between molecular orbitals i and j within the basin of atom A. $\delta(A, B)$ provides a quantitative idea of the number of electron pairs delocalized or shared between atoms A and B. Therefore, the PDI is clearly related to the idea of electron delocalization so often found in textbook definitions of aromaticity. Previous works^{35,50} have shown that for a series of planar and curved polycyclic aromatic hydrocarbons there is a satisfactory correlation between NICS, HOMA, and PDI.

Second is the aromatic fluctuation index (FLU),⁵¹ which describes the fluctuation of electronic charge between adjacent atoms in a given ring. The FLU index is based on the fact that aromaticity is related to the cyclic delocalized circulation of π electrons, and it is constructed not only considering the amount of electron sharing between contiguous atoms, which should be substantial in aromatic molecules, but also taking into account the similarity of electron sharing between adjacent atoms. It is defined as

$$\text{FLU} = \frac{1}{n} \sum_{A-B}^{\text{RING}} \left[\left(\frac{V(B)}{V(A)} \right)^\alpha \left(\frac{\delta(A, B) - \delta_{\text{ref}}(A, B)}{\delta_{\text{ref}}(A, B)} \right) \right]^2 \quad (6)$$

with the sum running over all adjacent pairs of atoms around the ring, n being equal to the number of members in the ring, $\delta_{\text{ref}}(C, C) = 1.389e$ (the $\delta(C, C)$ value in benzene at the B3LYP/6-311++G(d,p) level), and $V(A)$ is the global delocalization of atom A given by

$$V(A) = \sum_{B \neq A} \delta(A, B) \quad (7)$$

Finally, α is a simple function to make sure that the first term in eq 6 is always greater or equal to 1, so it takes the values

$$\alpha = \begin{cases} 1 & V(B) > V(A) \\ -1 & V(B) \leq V(A) \end{cases} \quad (8)$$

FLU is close to 0 in aromatic species and differs from it in nonaromatic ones.

Third, multicenter indexes have been recently used as a measure of aromaticity in a given ring. Giambiagi et al. have extensively used these indexes to characterize the aromaticity. For a closed-shell monodeterminantal wavefunction of a 6-MR

molecule, Giambiagi's proposal of aromaticity index reads⁷⁰

$$\text{KSCI} = 24 \sum_{i,j,k,l,m,n} S_{ij}(A) S_{jk}(B) S_{kl}(C) S_{lm}(D) S_{mn}(E) S_{ni}(F) \quad (9)$$

Recently, Bultinck et al. have worked on a particular extension of the latter index. According to these authors, summing up all the KSCI resulting from the permutations of indexes A,B...F defines a new index of aromaticity, in the case of 6-MR, the so-called six-center index (SCI).⁵² The particular expression of SCI for a decomposition of the molecular space into atomic basins, in the case of a monodeterminantal closed-shell wavefunction, reads as follows:

$$\text{SCI} = \frac{16}{3} \sum_{\alpha} \sum_{i,j,k,l,m,n} \Gamma_{\alpha} [S_{ij}(A) S_{jk}(B) S_{kl}(C) S_{lm}(D) S_{mn}(E) S_{ni}(F)] \quad (10)$$

where Γ_{α} stands for a permutation operator which interchanges the atomic labels A,B...F to generate up to 6! combinations. Generally, the values of SCI and KSCI are in tight correlation because the dominant contribution to SCI is the Kekulé structure, nonetheless some exceptions may arise.⁷¹

Finally, we have also computed the hardness, which was reported as a good indicator of global aromaticity by Zhou and Parr.⁵³ For the indexes used, we have that the more negative the NICS, the lower the FLU index, and the higher the HOMA, PDI, KSCI, SCI, and η values, the more aromatic the rings are.

3. Computational Details

All calculations have been performed with the Gaussian 03⁷² and AIMPACK⁷³ packages of programs at the B3LYP level of theory^{74–76} with the 6-311++G(d,p) basis set.^{77,78} All aromaticity criteria have also been evaluated at the same B3LYP/6-311++G(d,p) level of theory.

The GIAO method⁷⁹ has been used to perform calculations of NICS at ring centers (NICS(0)) determined by the non-weighted mean of the heavy atom coordinates and at 1 Å above or below the center of the ring taken into analysis (NICS(1)). It has been postulated that NICS(1) better reflects aromaticity patterns because at 1 Å the effects of the π -electron ring current are dominant and local σ -bonding contributions are diminished.^{80,81} We have also analyzed the out-of-plane component of the NICS(1), the NICS(1)_{zz}, which was found to be (together with the so-called NICS(0) _{π zz}) the best NICS-based indicator of aromaticity.^{81,82}

Calculation of atomic overlap matrices (AOM) and computation of DI, KSCI, and SCI were performed with the AIMPACK⁷³ and ESI-3D⁸³ collection of programs. Calculation of these DIs with the density functional theory (DFT) cannot be performed exactly because the electron-pair density is not available at this level of theory.⁸⁴ As an approximation, we have used the Kohn–Sham orbitals obtained from a DFT calculation to compute Hartree–Fock-like DIs through eq 5, which does not account for electron correlation effects. In practice, the values of the DIs obtained using this approximation are generally closer to the Hartree–Fock values than correlated DIs obtained with a configuration interaction method.^{84,85} The numerical accuracy of the AIM calculations has been assessed using two criteria: (1) The integration of the Laplacian of the electron density ($\nabla^2 \rho(\mathbf{r})$) within an atomic basin must be close to zero and (2) the number of electrons in a molecule must be equal to the sum of all the electron populations of the molecule and also equal to

TABLE 1: B3LYP/6-311++G(d,p) HOMA, NICS (ppm), PDI (Electrons), FLU, SCI (Electrons), KSCI (Electrons), and η (Hartrees) for the In-Plane Distortions

ΔR	HOMA	NICS(0)	NICS(1)	NICS(1) _{zz}	PDI	FLU ^{1/2}	SCI	KSCI	η
BLA									
0	0.989	-8.045	-10.216	-29.248	0.103	0.000	0.072	0.0179	0.24216
0.05	0.827	-7.913	-10.069	-28.787	0.102	0.045	0.070	0.0175	0.24326
0.1	0.344	-7.541	-9.651	-27.471	0.099	0.088	0.064	0.0163	0.24566
0.15	-0.461	-6.996	-9.020	-25.483	0.094	0.130	0.056	0.0146	0.24956
0.2	-1.588	-6.373	-8.257	-23.076	0.088	0.168	0.046	0.0125	0.25487
0.25	-3.038	-5.782	-7.453	-20.523	0.082	0.204	0.037	0.0105	0.26146
BLE									
-0.15	6.295	-7.576	-10.285	-33.173	0.107	0.017	0.068	0.0171	0.27076
-0.1	3.245	-7.832	-10.361	-31.925	0.105	0.011	0.069	0.0173	0.26416
-0.05	1.484	-7.988	-10.335	-30.607	0.104	0.006	0.070	0.0176	0.25826
0	0.989	-8.045	-10.216	-29.248	0.103	0.000	0.072	0.0179	0.24216
0.05	0.173	-8.029	-10.019	-27.861	0.102	0.006	0.073	0.0182	0.22647
0.1	-1.932	-7.937	-9.754	-26.468	0.101	0.012	0.074	0.0186	0.21163
0.15	-5.325	-7.773	-9.431	-25.085	0.101	0.018	0.076	0.0189	0.19786
α	HOMA	NICS(0)	NICS(1)	NICS(1) _{zz}	PDI	FLU ^{1/2}	SCI	KSCI	η
Clamping									
0	0.989	-8.045	-10.216	-29.248	0.103	0.000	0.072	0.0179	0.24216
5	0.970	-8.057	-10.208	-29.190	0.103	0.014	0.072	0.0179	0.24243
10	0.905	-8.080	-10.178	-28.993	0.103	0.029	0.071	0.0179	0.24236
15	0.761	-8.088	-10.097	-28.574	0.104	0.047	0.071	0.0177	0.24222
20	0.457	-8.035	-9.918	-27.761	0.104	0.071	0.069	0.0174	0.24198
25	-0.193	-7.852	-9.566	-26.258	0.104	0.103	0.065	0.0167	0.24163

the sum of all the localization indices and half of the delocalization indices in the molecule. For all atomic calculations, integrated absolute values of $\nabla^2\rho(r)$ were always less than 0.001 au. For all molecules, errors in the calculated number of electrons were always less than 0.01 au.

For the analysis of the BLE distortion, we will for the first time compute SCI and the KSCI indexes at a correlated level with the MP2 method. To this aim, providing the calculation of the six-order density matrix is completely unaffordable, our choice of the (K)SCI formula has been one that reduces to existing formulas at monodeterminantal level, and at the same time, excepting for a numerical factor, provides the correlated version of the Mayer–Wiberg bond order in the case of two-center indexes. The same formula as that in eqs 9 and 10 can be used but performing the following substitution:

$$S_{ij}(A) \rightarrow \frac{\sqrt{n_i n_j} S_{ij}^{NO}(A)}{2} \quad (11)$$

where $S_{ij}(A)$ is now the AOM of atom A in terms of natural orbitals and the summations run over the whole set of natural orbitals instead of only the occupied molecular orbitals. At the correlated level, the SCI indexes become much more computationally expensive (and susceptible to numerical errors) than at the monodeterminantal level, obviously because of the larger size of AOM in eq 11. Yet 6-MR can be calculated without problems, but addressing larger size rings may become rather cumbersome.

In the framework of the conceptual DFT,⁸⁶ the hardness is the second derivative of the energy with respect to the number of electrons at a constant external potential. The combination of the finite differences approximation and Koopmans' theorem⁸⁷ leads to the expression used in this work for the calculation of the hardness:

$$\eta = \epsilon_L - \epsilon_H \quad (12)$$

where ϵ_H and ϵ_L are the energies of the HOMO and LUMO molecular orbitals, respectively.

4. Results

The B3LYP/6-311++G(d,p) optimization of benzene leads to a C–C bond length of 1.395 Å to be compared with the experimental²⁰ and CCSD/TZ2P⁸⁸ results of 1.390 and 1.392 Å, respectively. Chart 1 represents the six distortions of the benzene ring considered in the present work together with the main parameter changed in each deformation. Three distortions keep the planar structure of the ring (in-plane deformations) while the rest break the planarity of the molecule (out-of-plane deformations).

In-Plane Deformations. Table 1 encloses the corresponding HOMA, NICS, PDI, FLU^{1/2}, KSCI, SCI, and η values for the different in-plane distortions. Obviously, being FLU is a positive quantity, the conclusions derived from the FLU or FLU^{1/2} values are exactly the same. However, we have preferred in Table 1 to list FLU^{1/2} instead of FLU because FLU^{1/2} values are scattered over a wider range and, therefore, the trends derived are clearer. In addition, we have recently shown that FLU^{1/2} presents better correlations with classical aromaticity indexes.⁸⁹ For the studied in-plane BLA and BLE distortions, we have introduced the deformation with consecutive steps of 0.05 Å without further reoptimization of the distorted benzene ring geometry. For the in-plane clamping distortion, we have modified the α angle (see Chart 1) up to 25° with consecutive steps of 5°, and we have reoptimized the remaining geometrical parameters of the ring at every point. For the different deformations analyzed, Figures S1–S6 in the Supporting Information contain the graphical representation of the results obtained conveniently transformed into dimensionless quantities and normalized.

The in-plane BLA distortion of b_{2u} symmetry, which connects the symmetric D_{6h} benzene with a Kekulé-like D_{3h} symmetry structure, breaks the bond length equalization in benzene and leads to a more localized π system and, therefore, to a less aromatic ring.⁹⁰ All indices studied acknowledge this fact, with the exception of the hardness. As already reported by some of us, the b_{2u} BLA vibrational mode is a nontotally symmetric vibration that breaks the maximum hardness (MHP) and minimum polarizability principles (MPP).^{91,92} So, not unexpectedly, we find that a larger BLA deformation goes with an

increase of the hardness. On the other hand, the magnetic (NICS) and electronic indexes (PDI, FLU, KSCI, and SCI) predict a relatively small change in the aromaticity of the benzene ring with BLA distortions as large as 0.25 Å. This result is in line with the findings by Soncini et al. that the benzene ring current remains almost unchanged despite significant bond alternation introduced by several clamping groups.⁹ On the contrary, HOMA yields an important change in the aromatic character of the ring with HOMA values that are negative already for $\Delta R = 0.15$ Å. It seems that HOMA overemphasizes the loss of aromaticity because of BLA distortions. Indeed, Krygowski and Cyrński have already warned about the use of geometry-based aromaticity indexes in too much strained systems.⁵⁷ Obviously, the EN component of the HOMA index is equal to zero in the BLA deformation while the GEO term steeply increases when the deformation builds up. The BLA is a relatively easy deformation from an energetic point of view.⁹³ For instance, it only costs about 11 kcal·mol⁻¹ to reach a deformation of $\Delta R = 0.15$ Å as compared to the approximately 60 kcal·mol⁻¹ needed to produce a BLE deformation of the same amount.

The in-plane BLE distortion of a_{1g} symmetry elongates/shortens the C–C bonds simultaneously, whereas C–H distances are kept constant. Therefore, both planarity and bond length equalization are preserved and, consequently, one would expect a loss of aromaticity smaller than in the BLA deformation. Moreover, at variance with all other distortions studied, in the BLE distortion the D_{6h} symmetry is preserved, and consequently our hypothesis that aromaticity reaches a maximum value in the optimal geometry of benzene is at least arguable. The indexes NICS(0), PDI, and FLU, for $\Delta R > 0$ at the B3LYP/6-311++G(d,p) level, indicate the anticipated small loss of aromaticity because of BLE distortion. In contrast, although HOMA, NICS(1)_{zz}, and η correctly predict a loss of aromaticity, they show a larger change for BLE than in BLA distortions. In this kind of deformations, the change in HOMA is due entirely to the EN component, the GEO term being exactly zero. As stated for the BLA deformation, apparently the HOMA also overemphasizes the loss of aromaticity because of BLE distortions with $\Delta R > 0$. For positive ΔR , all indexes point out that the aromatic character of the ring decreases as ΔR increases, with the only exception of the KSCI and SCI index that fail to indicate the expected loss of aromaticity in this case. For $\Delta R < 0$, HOMA, NICS(1), NICS(1)_{zz}, PDI, and η give the trend exactly opposite to our KSCI and SCI results, indicating a regular increase in the aromatic character as the C–C bond lengths decrease, in contradiction with the expected behavior. For $\Delta R < 0$, the HOMA values are larger than 1, a result that must be attributed to the particular expression of the EN term in eq 3b, indicating an unexpected increase of the aromatic character of the ring. Therefore, all indexes excepting FLU and NICS(0) fail to predict a decrease of aromaticity, either for $\Delta R < 0$ or $\Delta R > 0$. Because of this general failure, we have analyzed in greater detail the electronic structure of benzene under the BLE deformation within the AIM partition to shed light into this issue. The following results hold regardless if we optimize C–H distance in each point or not, indicating that the relaxation of C–H has no effect on the aromaticity from an electronic viewpoint.

Comparing the electron density of the benzene for different R values, we can observe how as R increases there is a constant increment on the size of C basin at the expense of the decrease of H basin. It is a direct consequence of the larger distance between C and the bond critical point (BCP) connecting this atom with the nearest H. The only effect that it has in the

TABLE 2: MP2/6-311++G(d,p) SCI (Electrons) and KSCI (Electrons) for the BLE Distortion

ΔR	SCI	KSCI
-0.15	0.0493	0.0127
-0.1	0.0491	0.0126
-0.05	0.0489	0.0126
0	0.0486	0.0125
0.05	0.0481	0.0124
0.1	0.0475	0.0123
0.15	0.0468	0.0121

population of these atomic basins is σ -charge transfer from hydrogen to carbon as the value of R increases. One can deduce the latter from the perfect correlation between C and H σ -population. Therefore, BLE distortion undergoes important σ -electron distribution and subtle π -electron reorganization. This is of course not completely unexpected, since the BLE is an in-plane distortion. To gather the effects that this distortion has on electron localization, we will focus on the integrated values of the exchange-correlation density (XCD) function. A sum of all DIs in the system may provide a global measure of electron delocalization. Not unexpectedly, our calculations indicate a linear increment of the electron delocalization with R . This delocalization comes from σ charge placed in the C atoms and affects the σ -electron sharing with other carbon atoms: adjacent, para-related, and meta-related carbon atoms. However, the effects are completely different. For adjacent atoms, σ -electron sharing keeps constant as $\Delta R > 0$ though decreases slightly as $\Delta R < 0$. The para-related atoms electron sharing shows opposite trends for σ - and π -electron sharing; while the former decreases considerably with R , the latter increases slightly, all together leading to a global para-related electron sharing decrease with R . The meta-related atoms electron sharing decreases with R , as one would expect, and the same occurs with its π counterpart. An amazing result is found for σ -electron sharing of atoms in meta-position: it increases as the structure deviates from benzene either shortening or increasing R . This is the only component of electron sharing which is able to recover the expected changes of aromaticity because of BLE distortion. It seems as the meta-related atoms σ -electron sharing goes with lower aromaticity. Besides, the KSCI and the SCI indexes were also separated into their σ and π components; providing both lead to the same conclusions, we will only focus on SCI results. In the same line of the results given by Bultinck for a Mulliken partition,⁹⁴ the SCI_π decreases while SCI_σ increases with R . However, the increase of the SCI_π is much more notorious with the AIM partition, leading to a general increase of SCI with R , just the opposite which was found with Mulliken partition.⁹⁴ This SCI failure is somewhat surprising since one would expect a larger delocalization for smaller C–C distances as it is found for all two-center DIs. Interestingly, the B3LYP/6-311++G(d,p) SCI values for a BLE distortion increase until $\Delta R \approx 0.9$ and then it decreases abruptly, probably because of a sudden change in the wavefunction of the electronic ground state.

To validate our B3LYP calculations, we have also performed MP2/6-311++G(d,p) calculations of AIM properties of benzene under the BLE distortion. At the MP2/6-311++G(d,p) level, the general tendency holds but the charge transfer from H to C is less than half of the value found with the B3LYP method; exactly the same exaggeration effect of B3LYP is observed in the meta-related electron sharing. However, the reduction of adjacent atoms and para-related atoms electron sharing is of the same magnitude as that of B3LYP, which leads to the same qualitative results for FLU and PDI measures. On the other hand, the KSCI and the SCI indexes reverse their trend according to

TABLE 3: B3LYP/6-311++G(d,p) HOMA, NICS (ppm), PDI (Electrons), FLU, SCI (Electrons), KSCI (Electrons), and η (Hartrees) for the Out-of-Plane Distortions

α	HOMA	NICS(0)	NICS(1)	NICS(1) _{zz}	PDI	FLU ^{1/2}	SCI	KSCI	η
Boat									
0	0.989	-8.045	-10.216	-29.248	0.103	0.000	0.072	0.0179	0.24216
5	0.987	-8.000	-10.130	-29.254	0.103	0.000	0.072	0.0179	0.24142
10	0.986	-7.907	-10.023	-29.287	0.103	0.000	0.071	0.0178	0.23850
15	0.982	-7.781	-9.898	-29.309	0.104	0.001	0.070	0.0176	0.23401
20	0.976	-7.595	-9.744	-29.299	0.104	0.003	0.070	0.0174	0.22816
25	0.965	-7.311	-9.546	-29.241	0.105	0.004	0.069	0.0172	0.22105
Chair									
0	0.989	-8.045	-10.216	-29.248	0.103	0.000	0.072	0.0179	0.24216
5	0.988	-7.877	-10.145	-29.158	0.103	0.000	0.072	0.0179	0.24178
10	0.984	-7.588	-10.021	-28.903	0.103	0.001	0.071	0.0178	0.23978
15	0.967	-7.139	-9.834	-28.478	0.103	0.003	0.070	0.0176	0.23660
20	0.955	-6.529	-9.593	-27.889	0.103	0.005	0.069	0.0173	0.23237
25	0.951	-5.766	-9.060	-26.832	0.104	0.007	0.068	0.0171	0.22718
Pyramidalization									
0	0.989	-8.045	-10.216	-29.248	0.103	0.000	0.072	0.0179	0.24216
5	0.988	-7.981	-9.357	-26.909	0.103	0.000	0.072	0.0179	0.24194
10	0.986	-7.809	-8.382	-24.284	0.103	0.000	0.071	0.0179	0.24052
15	0.983	-7.559	-7.311	-21.421	0.103	0.001	0.071	0.0178	0.23817
20	0.977	-7.256	-6.167	-18.368	0.104	0.002	0.071	0.0177	0.23502
25	0.969	-6.918	-4.964	-15.169	0.104	0.003	0.071	0.0176	0.23074

our MP2 calculations (see Table 2). While SCI and KSCI are seriously affected by the correlation, FLU or PDI are not. Although some authors argue that PDI can be regarded as a cheap alternative to SCI, this is yet another example that they measure different characteristics of aromaticity and are differently affected by the method and the molecular partition. Failure to find a decrease of aromaticity for $\Delta R < 0$ is probably less relevant than for $\Delta R > 0$ since the most common experimental BLE distortions of the benzene ring are those with $\Delta R > 0$. Remarkably, only the FLU and NICS(0) indexes are able to indicate the loss of aromaticity for both positive and negative ΔR values. Let us briefly add that as for the DIs, the SCI and KSCI correlated indexes are lower than the uncorrelated ones.

Finally, for the in-plane deformation that simulates the effect of clamping groups on the benzene ring, all indexes show a reduction of aromaticity when α increases, with the only exceptions of PDI that remains practically constant, slightly increasing with α , and NICS(0) and η that present some oscillations. As said before, Soncini et al. found that the ring current in benzene is essentially unchanged when saturated clamping groups are used.⁹ In accordance with this result, all indexes, except HOMA, predict a relatively small change in the aromaticity of the benzene ring with clamping distortions as large as 25°.

Out-of-Plane Deformations. Table 3 lists the corresponding HOMA, NICS, PDI, FLU^{1/2}, KSCI, SCI, and η values for the three out-of-plane distortions analyzed. The change in aromaticity for the out-of-plane deformations was studied by scanning the α angle (see Chart 1) up to 25° with consecutive steps of 5°, and by optimizations of the remaining geometrical parameters of the molecules at every point.

Boatlike deformations are those suffered by benzene rings in [*n*]para- and metacyclophanes^{15,16} and pyrenophanes.^{17–19} Table 3 shows that, for the boatlike out-of-plane deformation, all indexes analyzed indicate a minor loss of aromaticity, with the exceptions of the PDI that points to a minor increase in the aromatic character of the ring and NICS(1)_{zz} that has for small deformations an oscillatory behavior. However, the observed increase in the PDI value can be very large in case of a large (~80°) boatlike out-of-plane deformation.⁹⁴ The failure of this index to show the expected reduction of aromaticity can be attributed to the fact that in this boatlike deformation two para-

related carbon atoms come close to each other. To analyze further the breakdown of the PDI in this boatlike distortion, we have decomposed the PDI into the different molecular orbital contributions.⁹⁵ As some of us have shown previously,⁹⁵ the PDI in benzene is mainly the result of a positive contribution of the doubly degenerated e_{1g} HOMO orbitals of about 0.18 e and a negative component coming from the a_{2u} π -orbital of approximately -0.09 e. This means that the two electrons in a_{2u} MO reduce the delocalization between para-related carbon atoms in benzene. The main reason for the increase of the PDI value in a boatlike out-of-plane deformation is that the negative contribution from the a_{2u} π -orbital is significantly reduced. This is a consequence of the fact that the overlap between the e_{1g} and a_{2u} π -orbitals in the basin of a given carbon atom is reduced because of pyramidalization of the C atoms. This results in a reduction in absolute value of the negative products $S_{a_{2u}e_{1g}}(C_1)S_{a_{2u}e_{1g}}(C_4)$, $S_{a_{2u}e_{1g}}(C_2)S_{a_{2u}e_{1g}}(C_5)$, and $S_{a_{2u}e_{1g}}(C_3)S_{a_{2u}e_{1g}}(C_6)$ involved in the calculation of the PDI component of the a_{2u} π -orbital, thus justifying the increase of the PDI in a boatlike distortion. The results obtained with the rest of the indexes for this boatlike distortion are in line with previous experimental^{15–19} and theoretical^{40–43,45} studies showing a slight loss of aromaticity with bending. Finally, despite the failure of PDI to show the expected reduction of aromaticity in boatlike distortions, unlike NICS the PDI correctly indicated the loss of aromaticity of the six-membered rings when going from planar to pyramidalized pyracylene.³⁹

For the chairlike out-of-plane distortion, the trends are almost the same. There is a small reduction of aromaticity when increasing the deformation according to all indexes, except the PDI which indicates that the aromaticity remains almost unchanged with the distortion. All indexes, with the exception of the hardness, show a somewhat larger loss of aromaticity for the chairlike as compared to the boatlike out-of-plane deformations.

Finally, similar results are obtained when the carbon atoms of the ring are pyramidalized, simulating the situation found in buckybowls and fullerenes. Such deformation introduces a lot of strain energy. Indeed, this is the most energetically costly out-of-plane deformation among the three analyzed. However, only a minor loss of aromaticity is found because of pyramidalization according to all indexes. This is in line with previous

results found for the 6-MRs of a series of pyramidalized pyracylene molecules.³⁹ The two exceptions to this general rule are the PDI that indicates a small increase in aromaticity because of pyramidalization and the NICS(1) and NICS(1)_{zz} descriptors which give an important loss of the aromatic character of the ring with the distortion.

5. Discussion and Concluding Remarks

If one considers that the aromatic character of the benzene ring is the largest at its optimized geometry (except for the BLE distortion, this is an assumption that can be easily accepted), then we have shown in the previous section that only the FLU index is able to account for the loss of aromaticity in the six distortions of the benzene ring that we have analyzed. This is not completely unexpected, because FLU is indeed measuring the degree of electronic similarity with respect to benzene.⁹⁶ In this sense, it is only proving the change of aromaticity comes together with the change of adjacent atoms electron sharing. The HOMA index overestimates the loss of aromaticity for the BLA and clamping deformations and fails for the BLE deformation indicating an increase of aromaticity for negative ΔR values. It is noteworthy the superior behavior of FLU as compared to HOMA despite the similarity in the definition of these two indexes. Thus, while FLU compares the C–C delocalization index with that of benzene, HOMA takes into account the differences between the C–C bond lengths in the ring with those of the optimized benzene molecule. The KSCI, SCI, NICS(1), and NICS(1)_{zz} indexes only fail to detect the reduction of aromaticity in BLE deformations for positive and negative ΔR values, while NICS(0) only falls short in the clamping deformation. The hardness indicator does not succeed for the BLA deformations and for the BLE distortions with negative ΔR values. Moreover, it presents oscillatory behavior for the clamping deformation. Finally, the PDI gives incorrect trends for all distortions analyzed except the BLA one, although, in general, the PDI remains almost unaffected by the different ring deformations analyzed.

BLE is by far the most difficult distortion for the current measures of aromaticity. Neither the global delocalization nor the π - or σ -electron sharing between adjacent, meta-related, or para-related atoms succeeds to explain the evolution of the aromatic character of the BLE deformed benzene rings. The use of the electron sharing of benzene as a reference explains the success of FLU to detect the change of aromaticity in BLE distortions. It is not possible to uncover the effects of BLE in aromaticity using adjacent electron sharing. Unhopefully, the same is true for atoms in para-related positions: σ - and π -electron sharing exhibit opposite behavior as R increases, being predominant the effect of the σ -electron sharing. Surprisingly, only the meta-related σ -electron sharing follows exactly the opposite trend to be expected in an aromaticity index when benzene is under BLE distortion, though it may be a mere coincidence. Finally, MP2 results have proved that the trend yield by the SCI and KSCI indexes depends on the method of calculation.

In our opinion, it is very important to know the limitations of the different methods to analyze aromaticity. To this end, simple systems such as distorted benzene are good starting points. As a summary, we have found that only the FLU index does well for all distortions of the benzene ring analyzed. Despite the excellent behavior of the FLU indicator of aromaticity for these distortions, this index may fail in other situations. For instance, we have found that FLU is unable to detect the aromaticity of the transition state of the Diels–Alder reaction.⁹⁷

A similar situation occurs for the NICS index that behaves notably well for the distortions analyzed but has well-known problems in condensed benzenoid species.^{28,39,98–101} These results show that there is not yet a single indicator of aromaticity that works properly for all cases. Since aromaticity refers to a nonobservable physical property and, consequently, it is a vaguely defined concept, it may happen that such an indicator valid for all situations simply does not exist. However, exploring the successes and breakdowns of the different descriptors of aromaticity is relevant not only for its own sake but as a way to get ideas of how to improve present indicators of aromaticity and to define new indices that correlate better with chemical intuition for most of the cases. For the moment, with the current descriptors available, our results emphasize the need of using more than a single index to analyze aromaticity.^{102,103} Thus, chemists wishing to use indicators of aromaticity should be aware that more than one aromaticity parameter must be used. Even in this case, if different methods provide different answers, it is not possible to reach a definite conclusion on the relative local aromaticity of the rings in these compounds.

Acknowledgment. This paper is dedicated to the memory of our appreciated friend and colleague Prof. Dr. Lorenzo Pueyo who passed away on March 18, 2007. Financial help has been furnished by the Spanish MEC Project No. CTQ2005-08797-C02-01/BQU and by the catalan Departament d'Universitats, Recerca i Societat de la Informació (DURSI) through project No. 2005SGR-00238. F. F. and E. M. thank the MEC for the doctoral fellowships no. AP2005-2997 and AP2002-0581, respectively, and J. P. acknowledges the European Union for a Marie Curie fellowship. We thank the Centre de Supercomputació de Catalunya (CESCA) for partial funding of computer time. Finally, we are grateful for Professor J. Cioslowski and the two referees for helpful suggestions.

Supporting Information Available: Table S1 with the B3LYP/6-311++G(d,p) optimized Cartesian xyz coordinates of all analyzed species and Figures S1–S6 with the normalized values of the aromaticity indexes analyzed for all distortions studied. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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