*J. Phys. Chem. A* **2007,** *111,* 6521−6525 **6521**

# Properties of Aromaticity Indices Based on the One-Electron Density Matrix[†]

**Jerzy Cioslowski,*,[‡] Eduard Matito,[‡] and Miquel Solà[§]**

*Institute of Physics, University of Szczecin, Wielkopolska 15, 70-451 Szczecin, Poland, and Institute of Computational Chemistry and Department of Chemistry, University of Girona, 17071 Girona, Catalonia, Spain*

*Received: February 27, 2007; In Final Form: April 26, 2007*

Proper normalization of two previously published indices yields aromaticity measures that, when computed within the Hückel molecular orbital (HMO) approximation, closely match the topological resonance energies per $\pi$ electron of aromatic annulenes and their ions. The normalized indices, which quantify aromaticity of individual rings in polycyclic systems, are equally applicable to homocyclic and heterocyclic compounds and can be readily computed from 1-matrices calculated at any level of electronic structure theory. However, only the index $I_{NG}$, derived from the Giambiagi formula, produces proper ordering of aromaticities of heterocyclic compounds, provided it is calculated from all-electron wavefunctions in conjunction with the atoms in molecule (AIM) partitioning. Its values are shown to be strongly affected by electron correlation effects. Because of its apparent inability to distinguish between anti- and nonaromatic systems, $I_{NG}$ should only be employed for aromatic species.

## Introduction

Despite its widespread use among both theoretical and experimental researchers, aromaticity remains one of the most ill defined chemical concepts. Unlike other quantities, such as bond ionicity and bond order, among others, aromaticity refers to not one but several properties that may or may not be mutually related.[1−3] For this reason, multiple definitions of aromaticity are both possible and necessary to exhaustively elucidate phenomena such as stability/reactivity, magnetic shielding/deshielding, and bond equalization/alternation that appear unusual from the localized point of view.

There has been a recent resurgence of interest in aromaticity indices, such as the para-delocalization index (PDI),[4] the aromatic fluctuation index (FLU),[5] ring current ($I_{ring}$),[6] and the multicenter index (MCI),[7,8] that rely solely on the electronic wavefunction or derived quantities, rather than on other properties, such as magnetic currents or bond lengths.[9] In this paper, we critically analyze properties of two such indices, namely, $I_{ring}$ and MCI, and test the performance of their normalized variants with several homocyclic and heterocyclic species.

## The Aromaticity Indices

**A. Definitions**. Consider the atomic-projected power of the spinless one-electron density matrix (the 1-matrix) $\Gamma(\mathbf{r}, \mathbf{r}')$, where $\mathscr{A}$ is an ordered set $\{A_1,...,A_N\}$ of $N$ atoms.

$$\gamma_{\mathscr{A}}(\mathbf{r}_1, \mathbf{r}_{N+1}) = \hat{A}_1(\mathbf{r}_1)\Gamma(\mathbf{r}_1, \mathbf{r}_2) \int ... \int \prod_{k=2}^{N} \hat{A}_k(\mathbf{r}_k)\Gamma(\mathbf{r}_k, \mathbf{r}_{k+1})\, \mathrm{d}\mathbf{r}_k \quad (1)$$

The projector operator $\hat{A}_k$, which pertains to the atom $A_k$, may be based upon either Hilbert- or Cartesian-space partitioning; the choice of eq 2 (the AIM partitioning[10]),

$$\hat{A}_k(\mathbf{r}) = \int_{\Omega(A_k)} \delta(\mathbf{r} - \mathbf{r}')\, \mathrm{d}\mathbf{r}' \quad (2)$$

where $\Omega(A_k)$ is the atomic basin of $A_k$, is the most natural one in the latter case. Quantities related to the trace of $\gamma_{\mathscr{A}}(\mathbf{r}_1, \mathbf{r}_{N+1})$ have recently been employed as aromaticity indices. In particular, for a singly determinantal wavefunction, Giambiagi et al.[6] defined the (unnormalized) ring index simply by eq 3:

$$I_G(\mathscr{A}) = \int \gamma_{\mathscr{A}}(\mathbf{r}, \mathbf{r})\, \mathrm{d}\mathbf{r} \quad (3)$$

where $\mathscr{A}$ is ordered according to the adjacency of the atoms constituting the $N$-membered ring in question. This index is known in the chemical literature as $I_{ring}$.

On the other hand, Bultinck et al.[7] extensively studied the (unnormalized) multicenter index given by eq 4:

$$I_B(\mathscr{A}) = \sum_{\mathscr{P}(\mathscr{A})} \gamma_{\mathscr{P}(\mathscr{A})}(\mathbf{r}, \mathbf{r})\, \mathrm{d}\mathbf{r} \quad (4)$$

where the sum runs over all the possible permutations $\mathscr{P}(\mathscr{A})$ of $\mathscr{A}$, that had also been considered for similar purposes by Ponec et al.[11] and Giambiagi et al.[12,13] The MCI[7,8] is proportional to $I_B$.

The 1-matrices that enter the above equations are readily available from modern electronic structure calculations. When such calculations are carried out at correlated levels of theory, it is preferable, for the sake of size consistency, to employ the energy-derivative $\Gamma(\mathbf{r}, \mathbf{r}')$ computed with methods such as

---

[†] This paper is dedicated to the memory of our friend and colleague Dr. Xavier Gironés who passed away in November 2005.

* To whom the correspondence should be addressed. E-mail: jerzy@kyoko.chem.fsu.edu.

[‡] University of Szczecin.

[§] University of Girona.

10.1021/jp0716132 CCC: $37.00

second-order Møller-Plesset perturbation (MP2) or coupled cluster singles and doubles (CCSD). Conversely, the use of the non-interacting $\Gamma(\mathbf{r}, \mathbf{r}')$ constructed from occupied Kohn−Sham orbitals should be discouraged, as the resulting aromaticity indices do not properly account for electron correlation effects.[14]

It is important to emphasize that the original expressions for $I_G$ and $I_B$ were based upon the multicenter indices formulated with 1-matrices at the Hartree−Fock level of theory by Giambiagi et al.[15] Subsequently, these formulas were generalized in terms of higher-order densities (the $n$-matrices),[16,17] but the actual quantities were still computed with single-determinantal wavefunctions. Only recently have values for multicenter indices based upon the 3-matrices of multideterminantal wavefunctions been quoted.[18] However, as the electronic Hamiltonian contains only one- and two-particle operators, the $n$-matrices cannot be obtained as energy derivates for $n > 2$, and thus are bound to lack size consistency unless computed from the prohibitively expensive full configuration interaction (FCI) calculations. In light of these facts, the use of (correlated or uncorrelated) 1-matrices in eqs 3 and 4 remains the sole practical option.[19]

The actual computations of $I_G(\mathcal{A})$ and $I_B(\mathcal{A})$ are most conveniently carried out in the basis of natural orbitals $\{\psi_j\}$ to yield eq 5:

$$I_G(\mathcal{A}) = \sum_{j_1} \ldots \sum_{j_N} \prod_{k=1}^{N} n_{j_k} \langle j_k | j_{k-1} \rangle_{A_k} \tag{5}$$

where $A_0 \equiv A_N$, $\{n_j\}$ are the occupancies of $\{\psi_j\}$, and $\langle j | j' \rangle_{A_k}$ are elements of the atomic overlap matrix given by eq 6:

$$\langle j | j' \rangle_{A_k} = \int \psi_j^*(\mathbf{r}) \hat{A}_k(\mathbf{r}) \psi_{j'}(\mathbf{r}) \, d\mathbf{r} \tag{6}$$

The computation of $I_B(\mathcal{A})$ proceeds in an analogous manner.

**B. The HMO Approximation and Normalization of the Indices.** Within the Hückel molecular orbital (HMO) approximation,[20,21] only the $\pi$ orbitals contribute to the aromaticity indices. Moreover, one has eq 7:

$$\langle j_k | j_{k-1} \rangle_{A_k} = c^*_{A_k j_k} c_{A_k j_{k-1}} \tag{7}$$

where $\{c_{A,j}\}$ are the atomic orbital (AO) coefficients of the HMOs. Consequently, we have eq 8:

$$I_G(\mathcal{A}) = \prod_{k=1}^{N} P_{A_{k-1} A_k} \tag{8}$$

where $P_{AB}$ is the Coulson $\pi$ -electron bond order between atoms A and B.[22] Thus, $I_G(\mathcal{A})^{1/N}$ is equal to the geometric mean of the orders of bonds constituting the ring in question. For annulenes and their ions with $N$ carbon atoms and $N_\pi$ $\pi$ electrons, this observation leads to eq 9:

$$I_G(\mathcal{A})^{1/N} = \frac{2}{N} F(N, N_\pi) \frac{\sin(\pi N_\pi / 2N)}{\sin(\pi / N)} \tag{9}$$

where $F(N, N_\pi)$ equals either 1 for $N_\pi = 2,6,10,\ldots$ (aromatic systems) or $\cos(\pi/N)$ for $N_\pi = 4,8,12,\ldots$ (antiaromatic systems). On the other hand, the topological resonance energy per $\pi$ electron[23] of such species is given by eq 10:

$$E_{\mathrm{TRPE}} = \frac{2}{N_\pi} \sin(\pi N_\pi / 2N) \left[ \frac{2F(N, N_\pi)}{\sin(\pi/N)} - \frac{1}{\sin(\pi/2N)} \right] \tag{10}$$

which implies the relationship shown in eq 11:

$$E_{\mathrm{TRPE}} = \frac{2N}{N_\pi} I_G(\mathcal{A})^{1/N} \left[ 1 - \frac{\cos(\pi/2N)}{F(N, N_\pi)} \right] \tag{11}$$

The expression in square brackets of eq 11 is very closely approximated by $(\pi^2/8)N^{-2}G(N_\pi)$, where $G(N_\pi)$ equals 1 and −3 for aromatic and antiaromatic systems, respectively. Therefore, for annulenes and their ions, the values of the normalized index[24] (eq 12) are expected to closely follow those of $E_{\mathrm{TRPE}}$.

$$I_{NG}(\mathcal{A}) = \frac{\pi^2}{4} \frac{G(N_\pi)}{N N_\pi} I_G(\mathcal{A})^{1/N} \tag{12}$$

This conclusion is confirmed by the actual data computed for 12 species with ring sizes ranging between 4 and 9 (Figure 1).

The relationship derived above is no longer valid when permutations are applied to the ordered set $\mathcal{A}$. In fact, the analytical formulas for $I_B(\mathcal{A})$ of annulenes and their ions involve polynomials in $\sin(\pi N_\pi/2N)$ and $\cos(\pi N_\pi/2N)$ that rapidly increase in complexity with the ring size. It appears that these polynomials cannot be converted to a simple expression applicable to all combinations of $N$ and $N_\pi$. For this reason, any attempt to normalize $I_B(\mathcal{A})$ has to rely upon purely numerical observations. Surprisingly, eq 13 is an expression analogous to eq 12:[24]

$$I_{NB}(\mathcal{A}) = C \frac{G(N_\pi)}{N N_\pi} I_B(\mathcal{A})^{1/N} \tag{13}$$

where the proportionality constant $C = 3^{5/3} \cdot 2^{5/6}(4 - 2^{1/2} - 6^{1/2}) \approx 1.5155$ follows from the requirement that the values of $I_{NB}$ and $E_{\mathrm{TRPE}}$ coincide for benzene [for which $I_B = 128/81$ and $E_{TRPE} = (1/3)(4 - 2^{1/2} - 6^{1/2})$], and it yields a normalized aromaticity index that matches $I_{NG}$ in its extent of correlation with the topological resonance energy per $\pi$ electron (Figure 2).

In light of the above discussion, $I_{NG}$ and $I_{NB}$ emerge as properly normalized aromaticity indices that are equally suited for describing annulenes and their ions within the HMO approximation. Unfortunately, both indices share the serious disadvantage of relying upon the sign factor $G(N_\pi)$ to distinguish between the aromatic and antiaromatic species.

**C. The Topological and Geometric Contributions to the Normalized Indices**. Aromaticity indices calculated within the HMO approximation solely reflect the topology of chemical bonds and ignore the contribution of $\sigma$ orbitals to electron delocalization. Although stabilities of planar aromatic hydrocarbons are indeed determined by their molecular topologies, flexible species of nominally antiaromatic character (such as planar cyclooctatetraene) readily adopt nonaromatic conformations that exhibit bond alternation and ring puckering. For this reason, it is instructive to compare the HMO values of the $I_{NG}$ and $I_{NB}$ indices with those computed from all-electron wavefunctions and to assess the sensitivity of the latter to conformational changes. Such a comparison is especially interesting for annulenes and their anions, for which the indices are expected to follow predictable patterns (see the previous section).

Inspection of Table 1 reveals that the values of $I_{NG}$ computed for seven aromatic annulenes and their ions at the HF/6-311++G** level of theory are consistently lower than their HMO counterparts. However, in spite of the entirely different nature of the atomic projection operators employed in the two approaches in question, the HMO and HF/6-311++G** data correlate rather well; the only exception is the highly strained

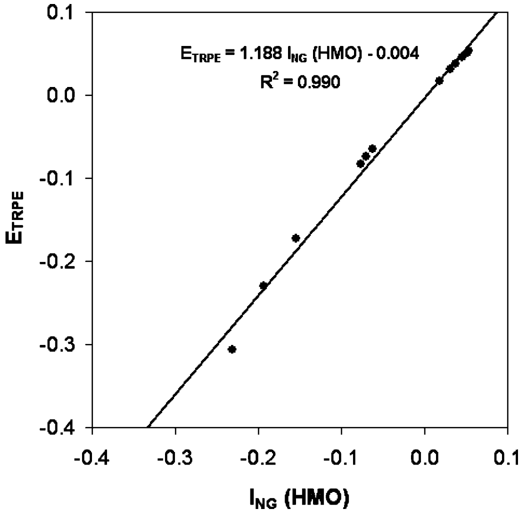

**Figure 1.** The correlation between the HMO values of $I_{NG}$ and $E_{TRPE}$ for 12 annulenes and their ions (the species, ordered according to the increasing values of $I_{NG}$, are as follows: $C_4H_4$, $C_5H_5^+$, $C_6H_6^{2+}$, $C_7H_7^-$, $C_8H_8$, $C_9H_9^+$, $C_9H_9^-$, $C_8H_8^{2+}$, $C_7H_7^+$, $C_6H_6$, $C_4H_4^{2-}$, and $C_5H_5^-$).

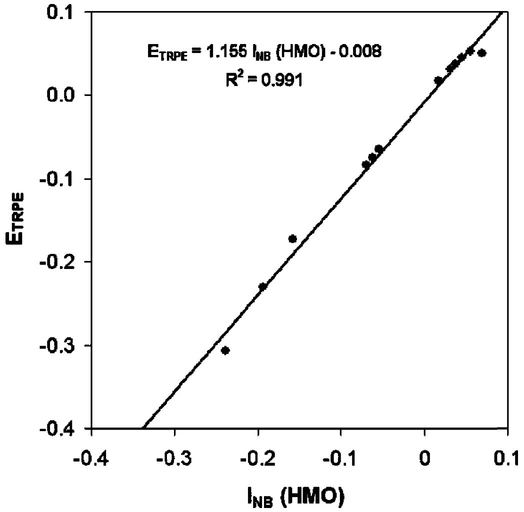

**Figure 2.** The correlation between the HMO values of $I_{NB}$ and $E_{TRPE}$ for 12 annulenes and their ions (the species, ordered according to the increasing values of $I_{NB}$, are as follows: $C_4H_4$, $C_5H_5^+$, $C_6H_6^{2+}$, $C_7H_7^-$, $C_8H_8$, $C_9H_9^+$, $C_9H_9^-$, $C_8H_8^{2+}$, $C_7H_7^+$, $C_6H_6$, $C_5H_5^-$ and $C_4H_4^{2-}$).

**TABLE 1: Values of $E_{TRPE}$, $I_{NG}$, and $I_{NB}$ for Selected Annulenes and Their Ions[a]**

| | | $I_{NG}$ | | $I_{NB}$ | |
|---|---|---|---|---|---|
| species | $E_{TRPE}$ | HMO | HF[b] | HMO | HF[b] |
| $C_4H_4^{2-}$ | 50.8 | 51.4 | 31.2 | 69.9 | 46.8 |
| $C_5H_5^-$ | 52.8 | 53.2 | 43.9 | 55.8 | 46.0 |
| $C_6H_6$ | 45.4 | 45.7 | 40.9 | 45.4 | 40.7 |
| $C_7H_7^{2-}$ | 37.6 | 37.7 | 35.0 | 37.3 | 34.8 |
| $C_8H_8^{2+}$ | 30.9 | 31.0 | 29.4 | 31.3 | 29.9 |
| $C_8H_8$ | n/a | n/a | −47.0 | n/a | −55.2 |
| $C_8H_8$ (planar) | −74.4 | −69.8 | −51.0 | −82.5 | −55.2 |
| $C_8H_8^{2-}$ | 18.6 | 18.6 | 14.7 | 18.8 | 15.4 |
| $C_9H_9^-$ | 17.5 | 17.5 | 15.0 | 16.6 | 14.4 |

[a] All values are multiplied by 1000. [b] HF/6-311++G** fully optimized geometries[25] and AIM partitioning.[26]

$C_4H_4^{2-}$ dianion (Figure 3). Quite surprisingly, in the case of the cyclooctatetraene molecule, little change in $I_{NG}$ is observed upon relaxation of the planarity constraint. It is apparent that ring puckering and the accompanying significant bond alternation have little effect upon the aromaticity index.

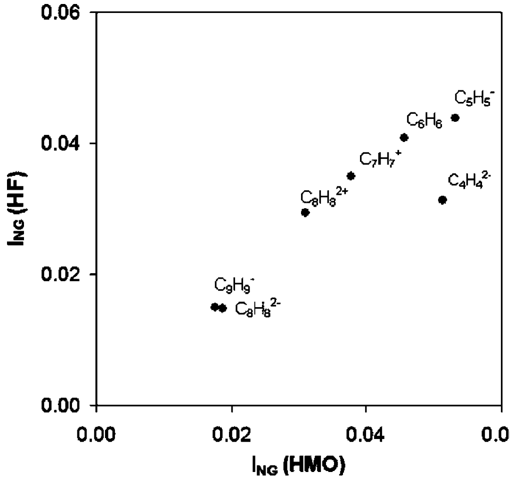

**Figure 3.** The HMO vs the HF/6-311++G** values of the $I_{NG}$ index for 7 aromatic annulenes and their ions.

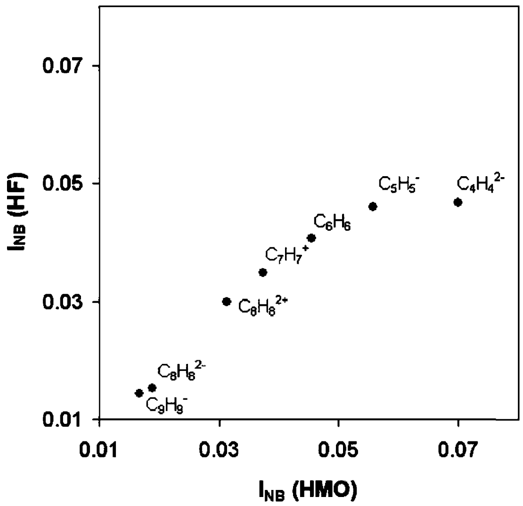

**Figure 4.** The HMO vs the HF/6-311++G** values of the $I_{NB}$ index for 7 aromatic annulenes and their ions.

Similar observations pertain to the $I_{NB}$ index as its HF/6-311++G** values turn out to be quite close to the $I_{NG}$ ones, with the exception of $C_4H_4^{2-}$. Consequently, the extent of the correlation between the $I_{NB}$ indices computed at the HMO and the HF/6-311++G** levels of theory (Figure 4) is comparable to that found for the $I_{NG}$ data. In the case of the cyclooctatetraene molecule, the computed $I_{NB}$ is largely independent of the ring conformation (Table 1).

The insensitivity of relative aromaticities to the level of electronic structure theory is a desirable property of both indices. However, the results obtained for the cyclooctatetraene molecule indicate that $I_{NG}$ may be incapable of distinguishing between antiaromatic and nonaromatic species (i.e., those with $E_{TRPE} < 0$ and $E_{TRPE} \approx 0$, respectively).

**D. Relative Aromaticities of Five- and Six-Membered Heterocycles.** Because any extension of the HMO approximation to heteroatoms has to rely upon empirical parameters, the assessment of aromaticity of heterocyclic compounds calls for abandoning the concept of the topological resonance energy per $\pi$ electron in favor of more sophisticated indices. For this reason, benchmarking of aromaticity indices with a set of simple heterocycles provides useful information on their overall reliability. The results of such testing are presented in Table 2.

Two sets of values of the $I_{NG}$ index, computed respectively at the PM3 and HF/6-311++G** levels of theory, markedly

**TABLE 2: Values of $E_{\mathrm{TRPE}}$, $I_{\mathrm{NG}}$, and $I_{\mathrm{NB}}$ for Selected Heterocycles**[a]

| | | $I_{\mathrm{NG}}$ | | | | $I_{\mathrm{NB}}$ | | |
|---|---|---|---|---|---|---|---|---|
| species | $E_{\mathrm{TRPE}}$[b] | PM3[c] | HF[d] | MP2[e] | CCSD[f] | HF[d] | MP2[e] | CCSD[f] |
| pyrrole | 40.0 | 51.5 | 37.2 | 38.7 | 37.6 | 38.4 | 40.1 | 38.9 |
| thiophene | 33.0 | 48.3 | 38.1 | 39.5 | 37.9 | 38.3 | 40.6 | 38.5 |
| furan | 7.0 | 45.9 | 33.1 | 36.7 | 34.8 | 32.0 | 37.4 | 34.8 |
| pyridine | 38.0 | 45.7 | 39.9 | 38.6 | 38.3 | 39.6 | 38.1 | 37.9 |
| pyridazine | n/a | 45.7 | 40.0 | 38.5 | 38.3 | 39.4 | 38.0 | 37.8 |
| pyrimidine | 32.0 | 45.6 | 38.9 | 38.5 | 38.0 | 38.6 | 38.1 | 37.5 |
| pyrazine | 22.0 | 45.7 | 39.2 | 38.0 | 37.9 | 39.1 | 37.6 | 37.5 |
| 1,3,5-triazine | n/a | 45.4 | 37.7 | 38.5 | 37.7 | 37.3 | 38.1 | 37.2 |

[a] All values multiplied by 1000. [b] Ref 23. The value for benzene is 45.7. [c] Computed from values compiled in ref 6. [d] HF/6-311++G** fully optimized geometries[25] and AIM partitioning.[26] [e] MP2/6-311++G** fully optimized geometries[25] and AIM partitioning.[26] [f] CCSD/6-311++G** fully optimized geometries[25] and AIM partitioning.[26]

**TABLE 3: Values of $I_{\mathrm{NG}}$ and $I_{\mathrm{NB}}$ for Selected Polycyclic Aromatic Hydrocarbons**[a]

| | $I_{\mathrm{NG}}$ | | | $I_{\mathrm{NB}}$ | |
|---|---|---|---|---|---|
| species | HMO | PM3[b] | HF[c] | HMO | HF[c] |
| naphthalene | 41.7 | 41.6 | 37.3 | 41.1 | 36.7 |
| anthracene[d] | 40.8 | 38.8 | 34.8 | 40.1 | 34.0 |
| anthracene[e] | 38.6 | 41.0 | 36.5 | 37.9 | 35.9 |
| phenanthrene[d] | 42.5 | 43.3 | 38.7 | 42.0 | 38.2 |
| phenanthrene[e] | 37.5 | 35.9 | 32.7 | 36.6 | 31.6 |

[a] All values multiplied by 1000. [b] Computed from values compiled in ref 6. [c] HF/6-311++G** fully optimized geometries,[25] AIM partitioning.[26] [d] The outer ring. [e] The inner ring.

**TABLE 4: Values of $I_{\mathrm{NG}}$ and $I_{\mathrm{NB}}$ for the Rings of Anthracene**[a]

| | $I_{\mathrm{NG}}$ | | | $I_{\mathrm{NB}}$ | | |
|---|---|---|---|---|---|---|
| ring | HF | B3LYP | MP2 | HF | B3LYP | MP2 |
| outer | 34.8 | 36.2 | 34.2 | 34.0 | 35.3 | 33.3 |
| inner | 36.5 | 35.6 | 33.3 | 35.9 | 34.8 | 32.4 |

[a] All values (multiplied by 1000) have been computed with the 6-311++G** basis set and the AIM partitioning[26] at geometries fully optimized at their respective levels of theory.[25]

**TABLE 5: Values of $I_{\mathrm{NG}}$ and $I_{\mathrm{NB}}$ for the Benzene Molecule with Uniformly Compressed/Stretched Carbon−Carbon Bonds**[a]

| | $I_{\mathrm{NG}}$ | | | | $I_{\mathrm{NB}}$ | | | |
|---|---|---|---|---|---|---|---|---|
| $\Delta R_{\mathrm{CC}}$ (Å) | HF | B3LYP | MP2 | CCSD | HF | B3LYP | MP2 | CCSD |
| −0.15 | 40.6 | 40.9 | 39.0 | 38.9 | 40.3 | 40.7 | 38.6 | 38.6 |
| −0.10 | 40.7 | 41.1 | 38.9 | 38.9 | 40.4 | 40.8 | 38.5 | 38.5 |
| −0.05 | 40.8 | 41.2 | 38.9 | 38.8 | 40.6 | 40.9 | 38.5 | 38.4 |
| 0.00 | 40.9 | 41.3 | 38.9 | 38.7 | 40.7 | 41.1 | 38.5 | 38.3 |
| 0.05 | 41.0 | 41.4 | 38.8 | 38.6 | 40.8 | 41.2 | 38.4 | 38.2 |
| 0.10 | 41.1 | 41.5 | 38.8 | 38.5 | 40.9 | 41.3 | 38.3 | 38.1 |
| 0.15 | 41.2 | 41.7 | 38.7 | 38.3 | 41.0 | 41.4 | 38.2 | 37.9 |

[a] All values (multiplied by 1000) have been computed with the 6-311++G** basis set and the AIM partitioning.[26] The carbon−carbon bond lengths are relative to those at the geometries fully optimized at the respective levels of theory.[25]

differ in their predictions of relative aromaticities. The semiempirical calculations, used in conjunction with the Hilbert-space partitioning, find pyrrole to be much more aromatic than thiophene and also find furan to be slightly more aromatic than benzene. Such findings are in obvious contradiction with the known experimental observations (such as those concerning relative stabilities and reactivities) of the molecules in question. However, the HF/6-311++G** values of $I_{\mathrm{NG}}$ decrease as follows: benzene > pyridazine > pyridine > pyrazine > pyrimidine > thiophene >1,3,5-triazine > pyrrole > furan, which is in agreement with the commonly accepted ordering of relative aromaticities.

Inclusion of electron correlation effects within the MP2 approximation gives rise to the incorrect predictions of thiophene being more aromatic than benzene and of pyrrole being more aromatic than pyridine. However, the proper ordering of relative aromaticities is restored once the more accurate CCSD approach is employed. In fact, the only difference between the HF and the CCSD predictions occurs for the pyrazine/pyrimidine pair of molecules.

Keeping in mind the overall similarity between the respective values of $I_{\mathrm{NG}}$ and $I_{\mathrm{NB}}$ for annulenes and their ions, it comes as a surprise that the latter index predicts an incorrect ordering of relative aromaticities, namely, pyrrole > thiophene >1,3,5-triazine (Table 2). The inclusion of electron correlation effects within either the MP2 or CCSD aproximation does not rectify this problem. In conclusion, only the $I_{\mathrm{NG}}$ index can be regarded as a reliable aromaticity measure, provided it is computed from all-electron wavefunctions with the help of the AIM projector operators and that the electron correlation effects are handled in a proper manner.

**E. Local Aromaticities of Rings in Polycondensed Benzenoid Hydrocarbons.** Although incapable of quantifying electron delocalization phenomena in entire polycyclic molecules, the two indices under study measure aromaticities of individual rings. In the simplest polycyclic aromatic hydrocarbons, the rings turn out to be less aromatic than that in benzene at all levels of theory (Table 3). As expected, a similar agreement is observed among the relative aromaticities of the rings in the phenanthrene molecule. The inner ring is uniformly predicted to be much less aromatic than the outer ones. However, no consensus is found in the case of anthracene. The HMO values of both indices favor the outer rings, whereas the PM3 and HF/6-311++G** ones rule in favor of the inner hexagon. The latter prediction appears to be an artifact of the Hartree−Fock approximation, as the inclusion of electron correlation (either within the MP2 approach or through the improper use of the non-interacting Kohn−Sham 1-matrix) reverses the ordering of aromaticities (Table 4), and thus confirming the results of earlier calculations.[8]

The sensitivity of the computed indices to contraction/expansion of the bonds constituting the ring in question is also of interest.[27] In the case of the benzene molecule, the decrease of both indices upon uniform stretching of the C−C bonds is observed at the correlated (MP2 and CCSD) levels of theory (Table 5). Surprisingly, a counterintuitive trend is predicted within the Hartree−Fock approximation and when the non-interacting 1-matrices computed with the B3LYP functional are used. This finding underscores the need for the inclusion of correlation effects, which can be accomplished at present only with correlated 1-matrices (see the discussion above).

## Conclusions

Proper normalization of two previously published indices yields aromaticity measures that, when computed within the HMO approximation, closely match the topological resonance energies per $\pi$ electron of aromatic annulenes and their ions. The normalized indices, which quantify aromaticity of individual rings in polycyclic systems, are equally applicable to homocyclic and heterocyclic compounds, and they can be readily computed from 1-matrices calculated at any level of electronic structure theory. However, a detailed examination of their performance reveals that only the index $I_{NG}$, derived from the Giambiagi formula, produces the proper ordering of aromaticities of heterocyclic compounds, provided it is calculated from all-electron wavefunctions in conjunction with the AIM partitioning. Consequently, the use of the $I_{NB}$ index is not recommended, as it is more expensive to compute, not readily amenable to mathematical analysis, and yields far less satisfactory results in the case of heterocycles.

The index $I_{NG}$ is found to be quite sensitive to the quality of the underlying wavefunction. Its values are shown to be affected by the inclusion of electron correlation. In some cases, the resulting changes in relative aromaticities are of a qualitative nature, which implies that values of $I_{NG}$ or $I_{NB}$ produced by lower-level calculations have to be treated with caution. It should be also stressed that because of its apparent inability to distinguish between anti- and nonaromatic systems, $I_{NG}$ should be employed only for aromatic species.

**Acknowledgment.** Financial help has been provided by the Spanish Ministerio de Educación y Cultura (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. E.M. thanks the MEC for the doctoral fellowship No. AP2002-0581. We also thank the Centre de Supercomputació de Catalunya (CESCA) for partial funding of computer time.

## References and Notes

(1) Katritzky, A. R.; Barczynski, P.; Musumarra, P.; Pisano, P.; Szafran, M. *J. Am. Chem. Soc.* **1989**, *111*, 7.

(2) Katritzky, A. R.; Karelson, M.; Sild, S.; Krygowski, T. M.; Jug, K. *J. Org. Chem.* **1998**, *63*, 5228.

(3) Schleyer, P. v. R.; Freeman, P. K.; Jiao, H.; Goldfuss, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 337.

(4) Poater, J.; Fradera, X.; Duran, M.; Solà, M. *Chem.—Eur. J.* **2003**, *9*, 1113.

(5) Matito, E.; Duran, M.; Solà, M. *J. Chem. Phys.* **2005**, *122*, 014109.

(6) Giambiagi, M.; de Giambiagi, M. S.; dos Santos Silca, C. D.; de Figuereido, A. P. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3381.

(7) Bultinck, P.; Ponec, R.; Van Damme, S. *J. Phys. Org. Chem.* **2005**, *18*, 706.

(8) Bultinck, P.; Rafat, M.; Ponec, R.; Gheluwe, B.; Carbó-Dorca, R.; Popelier, P. *J. Phys. Chem. A* **2006**, *110*, 7642 and references therein.

(9) Poater, J.; Duran, M.; Solà, M.; Silvi, B. *Chem. Rev.* **2005**, *105*, 3911.

(10) Bader, R. *Atoms in Molecules: A Quantum Theory*; Clarendon: Oxford, 1990.

(11) Ponec, R.; Cooper, D. L. *Int. J. Quantum Chem.* **2004**, *97*, 1002.

(12) Bollini, G. C.; Giambiagi, M.; de Giambiagi, M. S.; de Figuereido, A. P. *J. Math. Chem.* **2000**, *28*, 71.

(13) Bollini, G. C.; Giambiagi, M.; de Giambiagi, M. S.; de Figuereido, A. P. *Struct. Chem.* **2001**, *12*, 113.

(14) Matito, E.; Solà, M.; Salvador, P.; Duran, M. *Faraday Discuss.* **2007**, *135*, 325.

(15) Giambiagi, M.; de Giambiagi, M. S.; Mundim, K. C. *Struct. Chem.* **1990**, *1*, 423.

(16) Bochicchio, R.; Lain, L.; Torre, A.; Ponec, R. J. *J. Math. Chem.* **2000**, *28*, 83.

(17) Bochicchio, R.; Ponec, R.; Torre, A.; Lain, L. *Theor. Chem. Acc.* **2001**, *105*, 292.

(18) Ponec, R.; Cooper, D. L. *Int. J. Quantum Chem.* **2004**, *97*, 1002.

(19) Lain, L.; Torre, A.; Bochicchio, R. *J. Phys. Chem. A* **2004**, *108*, 4132.

(20) Hückel, E. *Z. Phys.* **1931**, *70*, 204.

(21) Hückel, E. *Z. Phys.* **1932**, *76*, 628.

(22) Coulson, C. A. *Proc. Roy. Soc. A* **1939**, *169*, 413.

(23) Gutman, I.; Milun, M.; Trinajstić, N. *J. Am. Chem. Soc.* **1977**, *99*, 1692.

(24) Note that in all the cases considered in this paper, the unnormalized indices $I_G$ and $I_B$ assume positive values and produce real-valued $I_{NG}$ and $I_{NB}$.

(25) All calculations were carried out with the Gaussian 03 suite of programs (ref 28). In all cases, core orbitals were frozen at the correlated levels of theory.

(26) Programs PROAIM and ESI-3D (refs 29 and 30, respectively) have been employed in the integrations over atomic domains and calculations of aromaticity indices, respectively.

(27) Feixas, F.; Matito, E.; Poater, J.; Solà, M. *J. Phys. Chem. A.* **2007**, *111*, 4513.

(28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Katao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyeve, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortia, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keit. *Gaussian 03*; Gaussian, Inc.: Pittsburgh, PA, 2003.

(29) Biegler-Konig, F.; Bader, R.; Tang, T.-H. *J. Comp. Chem.* **1982**, *3*, 317.

(30) Matito, E. *Electron Sharing Indexes Program for 3D Molecular Space Partitioning*. http://iqc.udg.es/~eduard/ESI, Institute of Computational Chemistry, Girona, 2006.