Bonding in Polycyclic Aromatic Hydrocarbons in Terms of the Electron Density and of Electron Delocalization

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We show that the delocalization indices calculated within the framework of the quantum theory of atoms in molecules provide an excellent basis for the definition of a bond order in polycyclic aromatic hydrocarbons. We show that the two-electron information contained within the delocalization index can be estimated from the electron density at the bond critical point, a mapping that has no a priori reason to exist. The mapping between the bond order and the electron density at the bond critical point can be exploited to provide a fast estimate of bond orders from theoretical or experimental electron densities. Bond orders in these molecules are shown to be associated to other one-electron properties. We provide evidence to the strong coupling of the σ and π contributions to the electron density at the bond critical point, a nonseparability by virtue of which the electron density at the bond critical point reflects both contributions. Another remarkable finding is that the delocalization indices between bonded carbon atoms are also strongly negatively correlated to the electronic energy density at the bond critical point, the latter being another example of a two electron property. In this manner, bond order is associated to a stabilizing effect quantified by the electronic energy density at the bond critical point. Because aromaticity is rooted in electron delocalization within a ring system, the delocalization index is used to define an aromaticity index that measures alternation in the delocalization of electrons within a ring of a polycyclic aromatic hydrocarbon. The proposed aromaticity index represents a "local aromaticity measure". We have analyzed in detail the effects of ring annealation on bond orders and on the aromatic character of a ring and explored its correlation with independent measures of aromaticity such as NICS and HOMA.

I. Introduction

The polycyclic aromatic hydrocarbons (PAHs) have been the focus of continual attention for several decades in view of their rich chemistry and of the environmental carcinogenic hazard posed by some. Nowadays, there is a surge in interest in this class of molecules because they represent the basic building blocks of nanostructures such as carbon nanotubes and bucky balls, the bedrock of a burgeoning nanotechnology. As part of our ongoing interest in understanding the properties of the electron density and of the electron pair density of the PAHs, we have recently reported on a new type of stabilizing hydrogen−hydrogen bonding interaction in angular PAHs, interactions that are absent in the corresponding linear isomers.[1] We have also studied electron delocalization between the hydrogen atoms of PAHs and used the electron delocalization indices (defined below) to construct a linear statistical model which accurately fits ($r^2 = 0.99$) the experimental proton spin−spin coupling constants of several representatives of these molecules.[2] Thus, our previous work focused on the properties of the electron density and of the pair density of the hydrogen atoms in the PAHs, a necessary step shedding light on several important aspects of the reactivity and stability of these molecules. The purpose of the present paper is to build on, and complete, our previous work by shifting the emphasis to the carbon skeleton of the PAHs. The properties of the carbon−carbon bonding in some prototypical PAHs will be explored in this study using the properties of the one-electron density $\rho(\mathbf{r})$ and those of the electron-pair density $\rho(\mathbf{r},\mathbf{r}')$. Unless a clear distinction is to be emphasized, in the present paper, $\rho(\mathbf{r})$ and $\rho(\mathbf{r},\mathbf{r}')$ will be referred to simply as "density" and "pair density", respectively.

An elegant and rigorous method of increasing popularity to analyze these densities in real three-dimensional space is the quantum theory of atoms in molecules (QTAIM), developed by Bader and co-workers.[3] We will use the terminology and parlance of QTAIM without definitions because those have been amply reviewed elsewhere,[3,4] along with a review of the concepts related to electron delocalization within QTAIM.[2]

Coulson used molecular orbital theory to define a bond order involving a summation of products of coefficients of atom centered basis functions over the π molecular orbitals.[5−7] Coulson's definition relates delocalization to a property determined by *all* of the occupied orbitals. Indeed, *every* occupied orbital contributes to the pair density, the density that determines electron localization and delocalization. Salem[8] noted that Coulson's definition of a mobile bond order[9] in the molecular orbital theory of conjugated systems serves as a link between Fermi correlation and electron delocalization. Within this theory,

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atomic charges and bond orders are determined by the products of coefficients of the carbon atomic π orbitals (AOs) obtained when a given MO is squared to obtain an expression for its density, the products of the AOs themselves being equated to unity. A product of coefficients is identified with an atomic charge when both AOs refer to the same atom and with a bond order when they are on different carbons. When these products are summed over all MOs, one obtains q_r, the atomic charge for atom r and p_{rs}, the mobile bond order for atoms r and s. Quoting Salem, "The square of the bond order between atoms r and s represents the extent of the *total correlation between two electrons with parallel spin*, one at r, the other at s". The total correlation is Fermi correlation, and it equals the exchange of electrons between r and s. Bader and Stephens[10] showed that the spatial pairing of electrons and their localization is a consequence of the Fermi correlation determined by the electron pair density. They demonstrated that the extent to which electrons are spatially localized or delocalized is determined by the corresponding spatial extent of the density of the Fermi hole, as measured by the exchange of same-spin electrons. It has since been proposed[11] that the spatial distribution of the Fermi correlation be used to provide a common, quantitative basis for the concept of electron delocalization. Electron delocalization as well as the electronic energy density are two important examples of two-electron properties which are studied in this paper and which are shown to be highly correlated.

It is often recognized that bond order is reflected in the properties of the density at the bond critical point (BCP or bcp), ρ_{bcp}. For example, Wiberg[12] reported linear correlations between ρ_{bcp} at the carbon−carbon bond critical point and the ellipticity and the bond length in PAHs. Knop, Boyd, and their co-workers studied several correlations between bond properties and each other, and between bond properties and bond length in sulfur−sulfur[13] and in hydrogen bonding interactions.[14,15] Popelier and O'Brien[16−18] used several bond properties to define a bond critical point Eucledian space in which distances are utilized as a measure of molecular similarity. These workers studied the correlations between several one-electron bond properties and carbon−carbon and carbon−oxygen bond lengths in the 20 naturally occurring amino acids.[17] Howard and Krygowski[19] found strong correlations between the bond and ring critical point properties and empirical aromaticity indices based on bond lengths[20−23] and on absolute magnetic shielding at the geometric ring centers (NICS).[24,25] The present paper explores the link between the two-electron indices and both the geometric as well as the one-electron properties. One of our goals is to find *one-electron* properties that would yield essentially the same information about the sharing of electrons between two bonded carbon atoms as that provided by the two-electron measure of electron delocalization (δ(C,C)). The mapping between a two-electron property such as the delocalization index, which requires integration of the Fermi hole density over the basins of the two atoms in question, and one-electron properties determined at a single point in space (the BCP) is of considerable theoretical interest in itself. In addition, this mapping would provide a fast alternative to estimate electron delocalization and bond order. Furthermore, with such a correlation at hand, one can estimate delocalization indices, a two-electron property, from experimentally determined electron densities.

In addition to our main focus on bonding and bond order in PAHs, we will apply our findings to explore certain aspects of the oft-treated phenomenon of aromaticity.[26] Attempts to quantify aromaticity include the use of energetic,[27] structural,[21,23,28] and magnetic[29] criteria. Recently, Poater et al. [30,31] proposed the average of the *para*-carbon−carbon delocalization indices [average $\delta(\text{C}^1,\text{C}^4)$] within a six-membered ring as a measure of local aromaticity in PAHs, and they used the differences in $\delta(\text{C},\text{C}')$ between formal double and single bonds as a measure of aromaticity in substituted cyclopentadienyl compounds. These workers obtained good correlation with other independent aromaticity measures[30] such as HOMA and NICS and applied their indices to study local aromaticity in fullerenes.[31] HOMA is a bond alternation based index defined as HOMA $= 1 - (\beta/n)\ \sum_i(R_{\text{opt}} - R_i)$.[2] In this expression, individual bond lengths are indicated as R_i and n is the number of bonds in the ring; β is a constant such that HOMA $= 0$ for hypothetical Kekulé structures of polycyclic aromatic hydrocarbons and 1 for the system with all the bonds equal to the optimal value R_{opt}.[21,23,28] NICS are magnetic indices, the nucleus independent chemical shifts, defined as the negative of the absolute magnetic shieldings computed at the center of aromatic rings. They are such that negative and positive values indicate aromaticity and antiaromaticity, respectively. [24,25]

We wish to provide an alternative local measure of aromaticity based on the degree of alternation of the delocalization index $\delta(\text{C},\text{C}')$, taking conceptual advantage of an established empirical measure of aromaticity such as HOMA (HOMA effectively relates the loss of aromaticity in a ring to the degree of bond length alternation).[21] In this manner, we propose a reformulation of HOMA using the delocalization index instead of the distance.

II. Electron Localization and Delocalization

Electron delocalization is a consequence of the action of the Pauli exclusion principle and its quantitative description can be given in terms of the properties of the Fermi hole density.[32] The density of a spin-up electron is influenced by all other same-spin electrons, and a hole of exclusion is said to exist at its position. The same is true for a spin-down electron. The physical basis of this observation is quantitatively expressed in terms of the properties of the pair density. We have recently reviewed the theory and essential equations describing electron delocalization in an article on the spin−spin coupling in PAHs.[2] Within Hartree−Fock theory (HF), the localization $\lambda(A)$ and delocalization $\delta(A,B)$ indices, respectively, are defined as[11,33]

$$\lambda(A) = 2\sum_i\sum_j S_{ij}(A)^2 \tag{1}$$

$$\delta(A,B) = \delta(B,A) = 4\sum_i\sum_j S_{ij}(A)S_{ij}(B) \tag{2}$$

where $S_{ij}(A)$ and $S_{ij}(B)$ denote the overlap of a pair of spatial orbitals over atoms or functional groups A or B. The factors in these equations arise in order to account for the contributions of both spins in a closed-shell system and, in the case of $\delta(A,B)$, from the necessity of inclusion of both AB and BA contributions. $\lambda(A)$ and $\delta(A,B)$ are to be interpreted as the *number of electrons localized* in atom A, and as the *number of electron pairs delocalized* (shared) between atoms A and B, respectively.[11] When $\delta(A,B)$ is used to count the number of electron pairs shared between *bonded* atoms, i.e., those that share an interatomic surface and a bond path,[34] it can be interpreted as a *bond order* when no significant charge-transfer exists between A and B. For example $\delta(\text{C},\text{C}')$ values in ethane, benzene, and ethylene are 0.99, 1.39, and 1.89, respectively, indicating that approximately 1, 1.4, and 2 electron pairs are shared between these bonded atoms. $\delta(A,B)$ has a finite value between every two atoms in a molecule whether bonded or not and generally decays rapidly with their spatial separation, although not in a monotonic manner. It has been recently shown that for similar spatial separation $\delta(A,B)$ is significantly higher when the atoms in question are bonded.[35]

For a given atom *A*, the relationship $N(A) = \lambda(A) + {}^{1}/_{2} \sum_{B\neq A}\delta(A,B)$, which is always true, provides a bookkeeping for the electrons by determining the fraction of the electron population localized within *A* and the fraction delocalized onto all of the other atoms in the molecule. It also provides a rationale for the deviation of bond orders from "ideal" Lewis model values. For example, the values 0.99 and 1.89, of $\delta(C,C')$ in ethane and ethylene, respectively, deviate from 1.00 and 2.00 as consequence of the delocalization of the electrons to other atoms in the molecule.

III. Computational Methods

The delocalization and localization indices acquire physical meaning in Hartree−Fock (HF) or post-HF methods. The HF results are known to represent an upper limit for the values of the delocalization indices, as Coulomb correlation reduces electron pairing.[33] (See also the recent work by Wang and Werstiuk.[36]) It is worth noting that the delocalization indices have also been recently calculated but using the Kohn−Sham (KS) implementation of density functional theory.[37] Delocalization indices calculated using KS orbitals are slightly *larger* than those obtained using HF orbitals, thus exhibiting an opposing trend to those obtained by means of other correlated post-HF methods.[37] This numerically minor but still nonphysical aberration is probably due to the N-representability problem associated to current exchange-correlation density functionals.[38] For these reasons, we have chosen HF theory in this work.

In view of the relatively large size of the systems included in this study and those anticipated in the future, we selected the 6-31G** basis set for the geometry optimization as well as the calculation of the final wave functions. The HF/6-31G**// HF/6-31G** level of theory proved to be indeed adequate in previous studies. At this approximation, excellent correlation of some one electron properties with empirical aromaticity measures[19] and of delocalization indices with experimental proton NMR spin−spin coupling constants for some PAHs and other organic molecules[2] are obtained. The 6-31G** basis set has been shown to yield localization and delocalization indices which agree with those obtained using a 6-311++G(2d,2p) basis set typically up to the third decimal in PAHs (see Table 1 of ref 2). To further test the effect of the size of the basis set, the delocalization indices in anthracene were also calculated at the RHF/cc-pVTZ// RHF/cc-pVTZ level of theory. The sum of the differences of the symmetry-unique delocalization indices (cc-pVTZ minus 6-31G**) was found to be as small as 0.006, the sum of the magnitudes of the differences was 0.565, and the maximum absolute deviation was 0.032. These results confirm the basis set insensitivity of $\lambda(A)$ and $\delta(A,B)$ and provide a strong case for our chosen level of theory.

Care was taken to ascertain a maximum acceptable numerical integration error, which is reflected in the differences between atomic sums and the corresponding SCF values. Thus, the total energies obtained from the atomic contributions differ on the average by 0.27±1.36 kcal/mol from the SCF values, and the total charge deviates on the average by 0.005±0.005 e from electroneutrality. The average deviation of the magnitude of the sum of $\lambda+({}^{1}/_{2})\delta$ from the total number of electrons in the molecule is −0.009±0.011 e.

All electronic structure calculations were performed using Gaussian 94,[39] electron densities were analyzed using the AIMPAC[40] and AIMALL97[41] sets of programs, and the delocalization indices were calculated using AIMDELOC.[42]

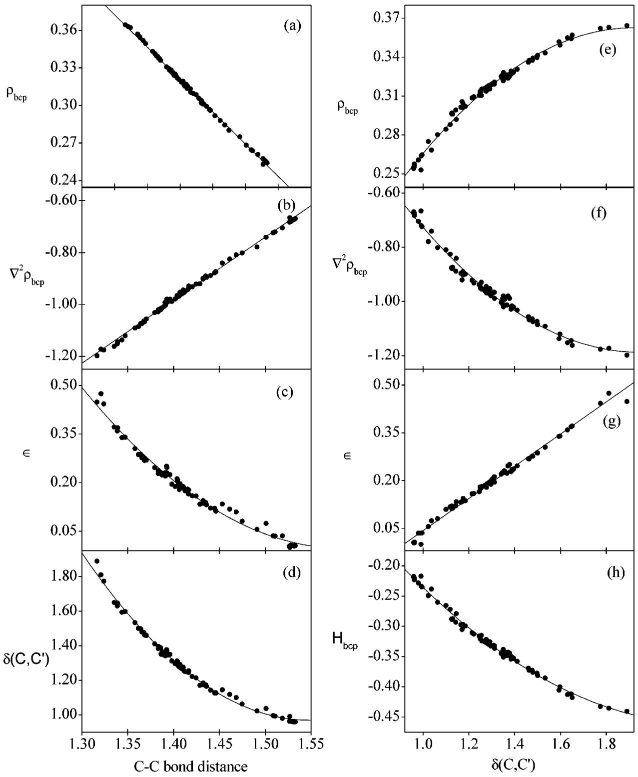


Figure 1. Plots displaying the relationships between different one-electron properties and bond length (plots a−c); between delocalization index and bond length (BL) (d); and between one-electron properties and delocalization index δ(A,B) (plots e−g). The one-electron properties analyzed are the electron density (ρ_{bcp}), its Laplacian ($\nabla^2\rho_{bcp}$), and the ellipticity (ϵ). A correlation between $\delta(C,C')$ and the electronic energy density, H_{bcp}, is also displayed (plot h). The regression equations (linear or quadratic), the correlation coefficients (*r*), and the standard deviations (*S*) for each case are (a) $\rho_{bcp} = 1.0444 - 0.5168$ BL ($r = -0.9991$, $S = 0.0012$); (b) $\nabla\,^2\rho_{bcp} = -4.3885 + 2.4319$ BL ($r = 0.9981$, $S = 0.0084$); (c) $\epsilon = 15.3202 - 19.3299$ BL $+ 6.0960$ BL^2 ($r = 0.9836$, $S = 0.0139$); (d) $\delta(A,B) = 38.5693 - 48.5658$ BL $+ 15.6821$ BL^2 ($r = 0.9934$, $S = 0.0174$); (e) $\rho_{bcp} = -0.0582 + 0.4379\,\delta(A,B) - 0.1139\,\delta(A,B)^2$ ($r = 0.9898$, $S = 0.0030$); (f) $\nabla^2\rho_{bcp} = 0.7658 - 2.0080\,\delta(A,B) + 0.5160\,\delta(A,B)^2$ ($r = 0.9849$, $S = 0.0171$); (g) $\epsilon = -0.4626 + 0.5056\,\delta(A,B)$ ($r = 0.9941$, $S = 0.0117$); (h) $H_{bcp} = 0.2750 - 0.6574\,\delta(A,B) + 0.1466\,\delta(A,B)^2$ ($r = 0.9931$, $S = 0.0048$). Included in the statistical analysis are all of the 75 symmetry-unique carbon−carbon bonds of ethane, ethylene, cyclohexane, cyclohexene, cyclohexadiene, benzene, naphthalene, tetralene, anthracene, phenanthrene, chrysene, dibenz[*a*,*j*]-anthracene, pyrene, and biphenyl (equilibrium and planar geometries). ρ_{bcp}, $\nabla^2\rho_{bcp}$, and H_{bcp} are given in atomic units, ϵ is dimensionless, and bond lengths are given in angstroms.

IV. Results and Discussion

IV.1. Global Trends in Bond Properties and Electron Delocalization in PAHs. Figure 1a−d shows the relationship between the carbon−carbon bond length and: the electron density at the bond critical point (ρ_{bcp}), the Laplacian of the electron density at the bond critical point ($\nabla^2\rho_{bcp}$), the bond ellipticity (ϵ), and the carbon−carbon delocalization index $\delta(C,C')$. Figure 1e−h display the correlations between $\delta(C,C')$ and: ρ_{bcp}, $\nabla^2\rho_{bcp}$, ϵ, and the electronic energy density at the bond critical point (H_{bcp}). We have used linear and quadratic models only to facilitate the comparisons among the regressions obtained. We have found that indeed all of these bonding descriptors are strongly correlated among themselves, in total

15 correlations of which we only display eight in Figure 1 (The interested reader may generate the remaining correlations from the data in the Supporting Information).

The Laplacian of the electron density provides a measure of the local curvature of $\rho(\mathbf{r})$ and indicates whether the electron density is locally concentrated ($\nabla^2\rho(\mathbf{r}) < 0$) or depleted ($\nabla^2\rho(\mathbf{r}) > 0$) at a given point in space. Furthermore, the Laplacian at any point in space determines the excess of either the kinetic or the potential energy density over their virial ratio of 2:1. The latter property of the Laplacian at a point in space follows from the local statement of the virial theorem. [In atomic units: $(^1/_4)\nabla^2\rho(\mathbf{r}) = 2G(\mathbf{r}) + V(\mathbf{r})$, where $G(\mathbf{r})$ refers to the kinetic energy density, which is positive everywhere in space, and $V(\mathbf{r})$ refers to the potential energy density (the virial field), which is negative everywhere.] Cremer and Kraka[43] pointed out that chemical bonding can only be satisfactorily described if, in addition to electrostatic aspects, energetic information is also considered. They suggested the use of the electronic energy density, $H(\mathbf{r}) = G(\mathbf{r}) + V(\mathbf{r})$, as a tool for the characterization of chemical bonding. It is important to realize that the total energy density at an arbitrary point is a two-electron property because the potential energy density contribution $V(\mathbf{r})$ itself is such. When integrated over all space, $H(\mathbf{r})$ yields the total electronic energy. According to Cremer and Kraka,[43] bonding formation is associated with a gain in molecular energy resulting from the changes in the kinetic and potential energy contributions and, in the case of a covalent bond, $H(\mathbf{r})$ is always negative because the negative $V(\mathbf{r})$ contribution dominates. A greater local stabilization is associated to more negative values of both the two-electron property $H(\mathbf{r})$ and the one-electron property $\nabla^2\rho$. This is reflected in a strong linear correlation (not displayed) between the Laplacian and the energy density, both evaluated at the BCP: $\nabla^2\rho_{\mathrm{bcp}} = -0.1681 + 2.4033H_{\mathrm{bcp}}$, ($r^2 = 0.99$). Figure 1, parts h and f, shows the energetic consequence of electron delocalization: the larger the electron delocalization between two bonded carbon atoms, the more negative are both H_{bcp} as well as $\nabla^2\rho_{\mathrm{bcp}}$, indicating a dominance of potential energy and an overall stabilization at the bond critical point. The latter observation is in line with the widely accepted notion that associates electron delocalization with stabilization. This observation is also consistent with the trend of the negative values of the Laplacian of the electron density indicating a greater charge concentration at the bond critical point with respect to its surroundings with an increase of electron delocalization (Figure 1f).

Classically, the bond order may be defined as the number of formal Lewis electron pairs shared between two atoms. Instead of assigning a bond order based on such idealized electron counting, we propose to use the “actual” number of pairs shared between two bonded carbon atoms, namely, the delocalization index $\delta(\mathrm{C,C'})$ as a measure of bond order between atoms C and C′. From here on, we will use the terms bond order or delocalization index interchangeably because we only report $\delta(\mathrm{C,C'})$ values for bonded atoms, i.e., sharing an interatomic surface and linked by a bond path and a virial path. From Figure 1d we see that the bond order $\delta(\mathrm{C,C'})$ decreases nonlinearly with increasing bond length. However, because electron delocalization is associated with stabilization, the longer the bond, the less negative is the Laplacian (Figure 1b) and the energy density at the BCP (the latter correlation is not shown).

The electron density at the BCP shows strong but opposing linear and nonlinear correlations to the bond length (Figure 1a) and bond order (Figure 1e), respectively. The nonlinear correlation between the delocalization index $\delta(\mathrm{C,C'})$ and ρ_{bcp} is of particular interest. Quoting Bader (p 75 of ref 3), “...one finds that the extent of charge accumulation between the nuclei increases with the assumed number of electron pair bonds and this increase is faithfully monitored by the value of ρ at the bond critical point”. Bader goes on to define a carbon−carbon bond order n in terms of the values of ρ_{bcp} as[3,44] $n = \exp[A(\rho_{\mathrm{bcp}} - B)]$, where A and B are constants which are adjusted to yield bond orders of 1.0, 1.6, 2.0, and 3.0 for ethane, benzene, ethylene, and acetylene, respectively. To our knowledge, there is no literature relating ρ_{bcp} to the number of pairs shared between the two bonded atoms as measured by the delocalization index. We suggest to calibrate this equation using the bond orders obtained from the delocalization indices instead of arbitrarily assigned values

$$\delta(\mathrm{C,C'}) = \exp[A(\rho_{\mathrm{bcp}} - B)] \tag{3}$$

We have fitted our 75 data points to this equation and obtained for this set of molecules the following results: $A = 5.8520$, $B = 0.2711$, and $r^2 = 0.970$. Such a fitting allows the calculation of delocalization indices between bonded atoms from the more readily available ρ_{bcp} avoiding the computation of the overlap integrals needed by eqs 1 and 2 which can require significant amount of CPU time. Such a determination has the added advantage of being equally applicable to calculated as well as to experimentally determined electron densities. Experimental ρ_{bcp} values[45,46] can be fed to eq 3 to yield estimates of electron delocalization between bonded atoms of interest. Thus, the one-electron picture can be exploited to obtain certain features accessible only from a determination of the pair density, which is not routinely available from experiment. (Regular X-ray diffraction does not yield any information on the electron-pair density, which, in principle but not in common practice, can only be obtained from inelastic X-ray and electron scattering.[47−49])

Finally, the correlations involving the bond ellipticity (ϵ) also convey valuable information. We first recap the definition of the ellipticity: $\epsilon = (\lambda_1/\lambda_2) - 1$, where λ_1 and λ_2 are the two negative eigenvalues of the Hessian of the electron density evaluated at the bond critical point. These negative curvatures correspond to the eigenvectors perpendicular to the bond path, such that $|\lambda_1|$ is the largest of the two, $|\lambda_1| > |\lambda_2|$.[44] The ellipticity provides a measure of the extent to which the charge is preferentially accumulated in a given plane perpendicular to the bond path, and for this reason, it measures the π-character of a bond. The ellipticity of the carbon−carbon bond in both ethane and acetylene is zero because both are cylindrically symmetric, but it assumes the values of 0.231 in benzene and 0.449 in ethylene. Figure 1c shows that the ellipticity decreases nonlinearly and follows closely the decrease of the bond order (Figure 1d) with increasing bond length. On the other hand, Figure 1g shows a linear increase of the ellipticity with an increase in electron delocalization. These two observations indicate that the bulk of the increase in the delocalization with a decrease in the bond length comes from π contributions. A possible objection to the use of ρ_{bcp} as a measure of bond order is the incorrect argument that, because the BCP lies on the nodal plane of the π orbital, the value of ρ_{bcp} will not reflect the π occupancy which is primordial in this set of molecules. To address this concern, Bader et al.[44] emphasize a point stressed by Mulliken about the self-consistency of electronic structure: in a self-consistent field calculation, the density distributions derived from σ and π orbitals are not independent from one another. The strong coupling between σ and π orbital contributions to ρ_{bcp} was clearly demonstrated numerically by Bader et al.[44] Therefore, one cannot uncouple the σ from the π contribu-

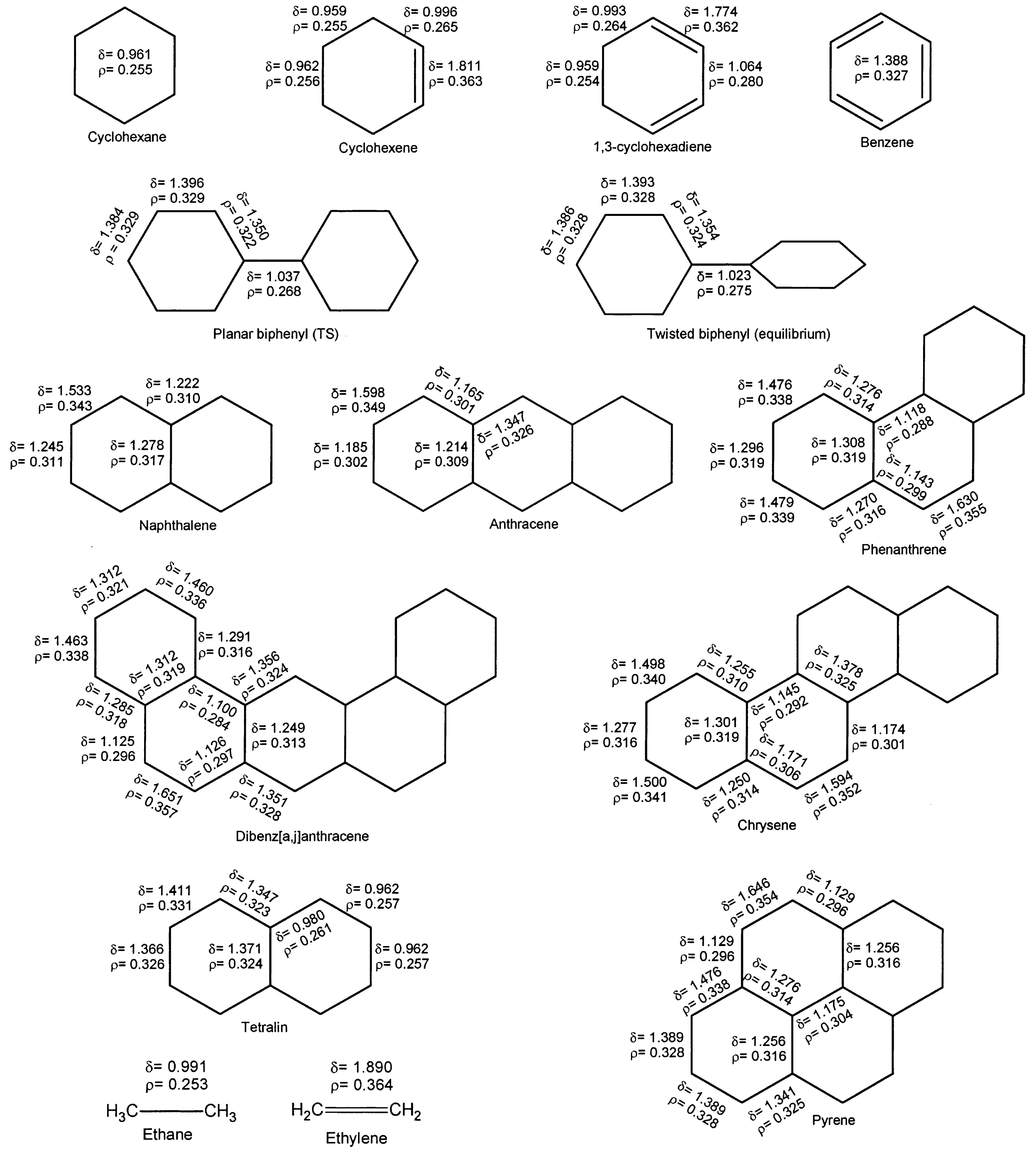
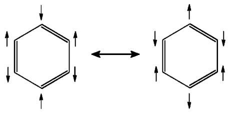


Figure 2. Carbon−carbon bond orders identified as the delocalization indices δ(C,C′) between bonded carbon atoms (top number) and electron densities at the bond critical point ρ_{bcp} (bottom number) of some hydrocarbons. Only the carbon skeleton is displayed for all molecules (except aliphatic and monocyclic molecules) because no bond order is assumed before hand.

tions at the BCP. Thus, ρ_{bcp} reflects the total electron distribution with contributions from the σ as well as the π electrons. (See also ref 50.) Further evidence from our data for this $\sigma-\pi$ coupling is the strong correlation between the ellipticity (a direct reflection of π contributions, which in turn is in itself influenced by the σ contribution) and ρ_{bcp}. This correlation (not shown in Figure 1) is $\epsilon = 0.8682 - 8.3332\rho_{\text{bcp}} + 19.5622\rho_{\text{bcp}}{}^2$ ($r^2 = 0.983$, $S = 0.0141$, $n = 75$).

IV.2. Specifics of Bonding and Electron Delocalization in PAHs. Going beyond the global aspects concerning the trends observed between the properties of the electron density among themselves and with the delocalization index in Figure 1, it is also enlightening to analyze the values of these properties for individual bonded pairs of atoms. Figure 2 displays the values of the carbon−carbon delocalization indices and the corresponding electron densities at the carbon−carbon bond critical points for several saturated and unsaturated hydrocarbons considered in the present study. From Figure 2, the delocalization indices in ethane have the values δ(C,C′) = 1.0 and δ(C,H) = 1.0, indicating that there is one electron pair shared between

SCHEME 1



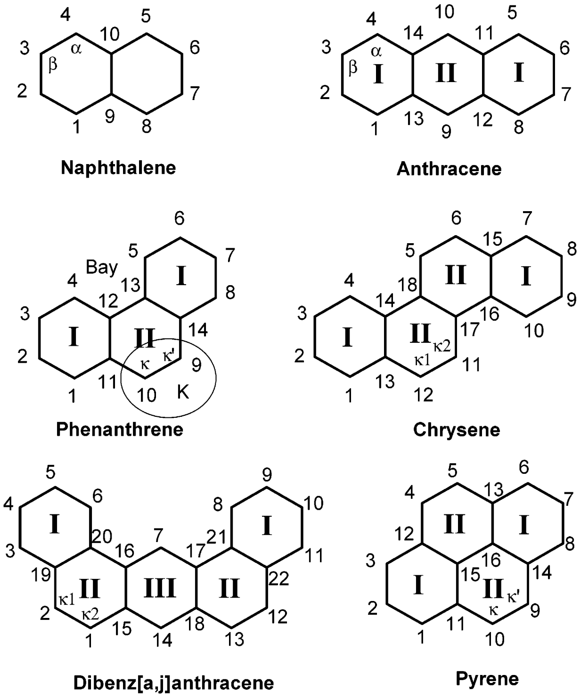
the two carbon atoms as well as between each carbon atom and its bonded hydrogen atom, consistent with the presence of only single bonds in this saturated molecule. For ethylene, $\delta(\mathrm{C,H}) = 1.0$ still corresponds to one electron pair shared between the bonded carbon and hydrogen atoms. $\delta(\mathrm{C,C'}) = 1.9$ indicates two electron pairs shared between the two carbon atoms and corresponds to a double bond. 1,3-Cyclohexadiene has clearly two conjugated double bonds, each with $\delta(\mathrm{C,C'}) = 1.8$, separated by a single bond ($\delta(\mathrm{C,C'}) = 1.1$). The values of $\delta(\mathrm{C,H})$ indicate that there is always one electron pair shared between a carbon atom and its bonded hydrogen atom. For this reason, the hydrogen-to-carbon bond properties were omitted, and the following analysis focuses exclusively on the carbon−carbon interactions.

The delocalization index for bonded carbon atoms in benzene is $\delta(\mathrm{C,C'}) = 1.4$, a value that lies between those corresponding to ethane and ethylene, as expected. The magnitudes of the delocalization indices for nonbonded carbon atoms in benzene are $\delta(\mathrm{C,C_{para}}) = 0.10$ and $\delta(\mathrm{C,C_{meta}}) = 0.07$ corresponding to internuclear separations of 2.78 and 2.40 Å, respectively. The greater magnitude of $\delta(\mathrm{C,C_{para}})$ compared to $\delta(\mathrm{C,C_{meta}})$, despite that the latter corresponds to a shorter internuclear separation, is a result of favorable spin pairing. The ground state of benzene has three π electrons of α spin and three of β spin. Scheme 1 shows a cartoon of two equivalent resonance structures with appropriate spin pairing. Because the spins of π electrons on carbon atoms that are meta with respect to each other are always the same, then, according to Pauli exclusion principle, the densities of these same-spin electrons are expected to exclude each other with the result of a reduced meta delocalization. On the other hand, because the spins of π-electrons on carbon atoms para to each other are always opposite, the densities of these same-spin electrons are not expected to exclude one another with the result of an enhancement of the para delocalization with respect to meta delocalization.

On the basis of either its reactivity[51] or of a model based on bond length alternation,[28] benzene is the molecule that exhibits the greatest aromatic character in the series of benzenoid aromatic hydrocarbons. The molecules in the series of PAHs lose some aromatic character (aromatic dilution), have more localized bonds (leading to bond length alternation), and a differential reactivity at different sites of a given molecule.

The next molecule in the series, naphthalene, exhibits preferential localization of electrons at C^{α} (see Scheme 2 for atom labeling). In addition, the shortest set of bonds in naphthalene are the $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ bonds (1.36 Å), bonds exhibiting the largest bond order in this molecule [$\delta(\mathrm{C}^{\alpha},\mathrm{C}^{\beta}) = 1.5$], the largest magnitude of ρ_{bcp} (0.34 au) and ϵ (0.31). These values are intermediate between those of ethane and ethylene but are closer to the values for ethylene. (See Figure 2.) The $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ bond in naphthalene involves the delocalization of ca. 0.15 pairs in excess to the number shared between two adjacent carbon atoms in benzene. This is mirrored in a higher $\rho_{\mathrm{bcp}}(r)$ and shorter bond length than in benzene, all consistent with a higher bond order than in the latter molecule. These observations are consistent with the known faster reaction rates of the molecule toward electrophilic substitution at the α position, compared to benzene, under conditions favoring kinetic control. The saturation of one of the rings of naphthalene to yield tetralin results in significantly less bond order alternation in the aromatic ring than in naphthalene, yet the $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ still retains the highest bond order in tetralin.

SCHEME 2



Numbering Scheme for Polycyclic Hydrocarbons

The *linear* fusion of a third ring to naphthalene (to yield anthracene) results in more bond alternation at the peripheral rings than in naphthalene, with the $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ still exhibiting the largest bond order. On the other hand, the *angular* fusion of a third ring to naphthalene (to yield phenanthrene) results in an intermediate effect on the peripheral ring, intermediate between the two extremes represented by tetralin and anthracene. The highest bond order in phenanthrene is found between C^{9} and C^{10} (in this paper, we will denote equivalent carbon atoms in the K-region as κ and κ'). The value of the delocalization index, $\delta(\mathrm{C}^{\kappa},\mathrm{C}^{\kappa'}) = 1.6$, lies between $\delta(\mathrm{C,C'})$ of benzene and ethylene and is the largest in the molecule. This observation is in agreement with the known olefinic character of the $\mathrm{C}^{\kappa}-\mathrm{C}^{\kappa'}$ bond manifested by the ability of the molecule to undergo addition as well as oxidation and reduction reactions at this bond under the proper experimental conditions. In the case of anthracene, notice the high degree of dienic character of a four carbon atom fragment in the central ring, for which the values $\delta(\mathrm{C}^{10},\mathrm{C}^{11}) = \delta(\mathrm{C}^{10},\mathrm{C}^{14}) = 1.4$ and $\delta(\mathrm{C}^{11},\mathrm{C}^{12}) = 1.2$, are in agreement with the characteristic addition reactions of the molecule to yield 9,10-disubstituted dihydroanthracenes.

Chrysene is similar to phenanthrene in its reactions because the molecule can be oxidized to the 5,6-quinone. This reactivity is also in line with the delocalization indices in Figure 2 from which the largest value is 1.6 and corresponds to the $\mathrm{C}^{\kappa 1}-\mathrm{C}^{\kappa 2}$ bonds (in this work, $\kappa 1$ and $\kappa 2$ are non equivalent carbon atoms in the K region). Chrysene, which can be regarded as two naphthalene molecules fused at a common $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ bond, has peripheral rings which are most similar (in terms of bond orders) to naphthalene when compared with tetralin, anthracene, and phenanthrene. The fusion of the fourth ring to phenanthrene (to yield chrysene) induces a decrease in the bond order of the $\mathrm{C}^{\kappa}-\mathrm{C}^{\kappa'}$ bond by 0.04 electron pair. In contrast, the fusion of a

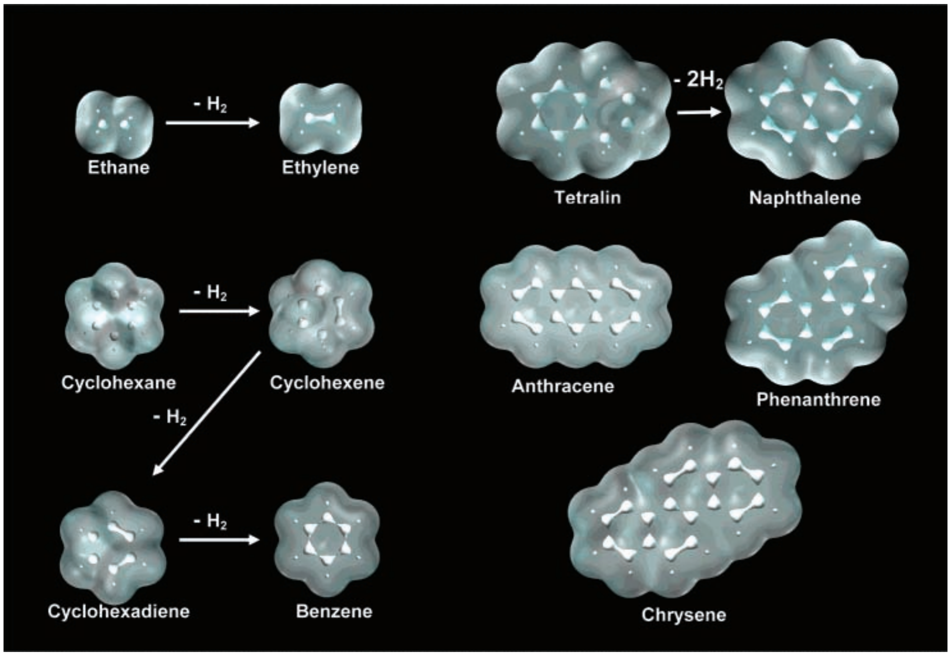


Figure 3. Three-dimensional electron isodensity envelopes of several saturated and unsaturated hydrocarbons. The outer (transparent) isodensity surface is the 0.001 au envelope which corresponds to the van der Waals envelope in gas phase and which typically contains more than 99% of the electron population of the molecule. The inner isodensity surface has the value of ρ_{bcp} for benzene (0.3274 au). The inner envelope is connected, enclosing the two nuclei of the bonded atoms, only when the density at the BCP is greater than that at the BCP between two carbon atoms in benzene.

fourth ring in the bay region of phenanthrene (to yield pyrene) results in a slight increase in the bond order of the $C^{\kappa}-C^{\kappa'}$ bonds by 0.02 electron pair. Finally, the fusion of a phenanthrene molecule at the $C^{\alpha}-C^{\beta}$ bond of naphthalene (to yield dibenz[a,j]anthracene) results in the largest $C^{\kappa1}-C^{\kappa2}$ bond order in this set of molecules ($\delta(C^{\kappa1},C^{\kappa2}) = 1.7$). In contrast, the peripheral rings of dibenz[*a*,*j*]anthracene exhibit the smallest bond order and bond length alternation in the set. A general conclusion emerges from the above considerations: in a system of fused rings, the higher the bond order of the $C^{\kappa}-C^{\kappa'}$ bond, the more pronounced the bond order alternations within the second ring (ring II), and the less the bond order alternation of the peripheral ring (ring I).

The main features of the unsaturation pattern deduced on the basis of the values of ρ_{bcp} and $\delta(C,C')$ depicted in Figure 2 can also be obtained from electron density isosurfaces. Two isodensity envelopes are displayed for several molecules in Figure 3. The outer envelope is the 0.001 au isodensity envelope representing the van der Waals surface of the molecule in the gas phase.[3] The inner one is the isodensity envelope with a value equal to the density at the C−C′ bond critical point in benzene ($\rho_{bcp(benzene)} = 0.327$ au). For a given molecule, this envelope will enclose without breaks any nuclei of bonded atoms with ρ_{bcp} higher than that of benzene, enclosing a larger volume the larger the value of ρ_{bcp}. On the other hand, when ρ_{bcp} is less than in benzene, the envelope will break into two separate closed regions each surrounding one nucleus of the two bonded atoms. The visual (and hence necessarily qualitative) unsaturation patterns provided by the $\rho_{bcp(benzene)}$ isodensity envelopes in Figure 3 faithfully agree with the information contained in properties of the electron density at the bond critical points and, by virtue of eqn 3, with the bond order defined on the basis of electron delocalization. The results discussed so far indicate that the information provided by $\delta(C,C')$, ρ_{bcp}, $\nabla^2\rho_{bcp}$, ϵ, and the bond length provide a clear and consistent picture of bond order in the PAHs.

IV.3. Aromaticity Index Based on the Delocalization of the Fermi Hole Density. Within the structural criteria used to define aromaticity, it is accepted that bond length alternation in PAHs leads to the definition of useful indices. According to a model based on the harmonic oscillator potential, the optimal structure for benzene is that where all of the C−C bond distances are equal to each other with an optimal value of 1.397 Å.[23] In this model, benzene is the molecule with the highest aromatic character. The bond length alternation in the rings of PAHs leads to a decrease in the aromatic character of a molecule. According to Kruszewski and Krygowski,[23] the known relation between the calculated bond orders and bond lengths allows one to define an index of aromaticity based on calculated C−C bond orders. Extensive support to the use of the delocalization indices as a measure of bond order was given in the previous subsections. Because aromaticity is a host of phenomena rooted in electron delocalization within a ring of atoms, we propose a revision of the aromaticity index using the calculated bond order alternation as a measure of aromaticity. Thus, we define the aromaticity index θ

$$\theta = 1 - \frac{c}{n}\sqrt{\sum_{i=1}^{n}(\delta_0 - \delta_i)^2} \tag{4}$$

In this expression, c is a constant such that $\theta = 0$ for cyclohexane, $n = 6$ for PAHs, δ_0 is a reference value, the total electron delocalization of a carbon atom of benzene with all other C atoms in that molecule, and δ_i is the total electron delocalization of a carbon atom with the other carbon atoms forming a ring in a given PAH. The values $c = 0.1641$ and $\delta_0 = 3.0170$ correspond to the present level of calculation. It is important to note that this index does not rely on the $\sigma-\pi$ separability assumption. Because eq 4 utilizes the bond order (instead of bond length) to define the alternation within a ring, the quantitative as well as the qualitative trends can deviate from

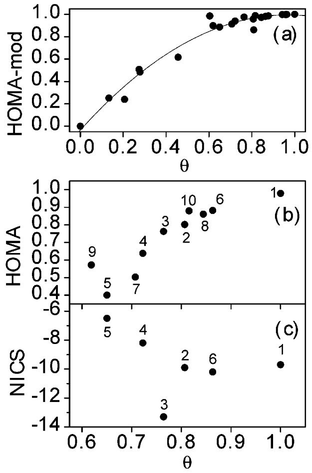


Figure 4. Comparison of the aromaticity index θ with the indices (a) HOMA-mod, (b) experimental HOMA, and (c) NICS. The θ axis in part a covers a wider range of values to properly display the trend. The NICS values of benzene, naphthalene, anthracene. and phenanthrene were taken from ref 24. The experimental HOMA values in part b were taken from ref 28 for the same molecules and for chrysene and pyrene. In the case of pyrene, the X-ray based HOMA indices were used. Labels in parts b and c are as follows (labels I and II are as in Scheme 2): benzene, 1; naphthalene, 2; anthracene II and I, 3 and 4; phenanthrene II and I, 5 and 6; chrysene II and I, 7 and 8; pyrene II and I, 9 and 10.

TABLE 1: Electron-Delocalization-Based Local Aromaticity Index θ for Rings in Some Polycyclic Hydrocarbons and Related Systems[a]

	θ		
molecule	I	II	III
benzene	1.000		
biphenyl	0.963		
9,10-dihydroanthracene	0.960	0.278	
tetralin	0.960	0.133	
biphenyl (TS)[b]	0.959		
9,10-dihydrophenanthrene	0.942	0.274	
phenanthrene	0.863	0.650	
chrysene	0.844	0.707	
pyrene	0.816	0.619	
naphthalene	0.807		
anthracene	0.722	0.764	
dibenz[*a*,*j*]anthracene	0.604	0.809	0.877
1,3-cyclohexadiene	0.456		
cyclohexene	0.206		
cyclohexane	0.000		

[a] Rings I and II of tetralin are the aromatic and saturated rings, respectively; for the other molecules, rings I, II, or III are as indicated in Scheme 2. [b] Biphenyl, transition state geometry of the phenyl−phenyl internal rotation (planar structure).

those obtained from the geometrical version of this formula (HOMA). This difference is due to the nonlinear relationship between bond order and bond length, Figure 1d. To illustrate this behavior, the following geometric index is defined: HOMA-mod $= 1 - (\alpha/n)\sum_i(R_{\mathrm{opt}} - R_i)^2$. In this expression, $n = 6$ and $\alpha = 81.0729$ is such that HOMA-mod = 0 for cyclohexane; R_i values are the C−C bond distances in a ring of a PAH and R_{opt} is the C−C bond distance in benzene, both obtained at the present level of calculation. The results are illustrated in Figure 4a, where the values of HOMA-mod index calculated from the C−C bond distances obtained at the present level of calculation are compared with the corresponding θ values for each of the molecules in Table 1. One important feature of this figure is that most of the θ values are spread over a wider range than HOMA-mod (ca. 0.6−1.0 vs 0.8−1.0 for θ and HOMA-mod, respectively). This indicates that the θ index is a sensitive and appropriate measure of aromaticity.

Important information can be obtained from Table 1, which displays the aromaticity index θ of some PAHs and related molecules. From eq 4, the highest value of θ corresponds to benzene ($\theta = 1$). In all other cases, aromatic dilution is obtained, as indicated by θ being less than 1. In the case of the rings of biphenyl (either at the equilibrium geometry or the transition state) and of the external rings of 9,10-dihydrophenanthrene and 9,10-dihydroanthracene, the θ values are very close to 1, indicating high aromaticity. Notice that, after hydrogenation of one of the rings of naphthalene to yield tetralin, θ of that ring decreases to 0.133, a value intermediate between those of cyclohexane and cyclohexene, and the other ring becomes almost fully aromatic, $\theta = 0.960$. Also, notice that the inner ring of anthracene is predicted to be more aromatic than the outer ones and that the outer rings of phenanthrene are more aromatic than the inner one. These results are in agreement with the observed patterns obtained from the electron density contours shown in Figure 3. The same conclusion can be obtained for the molecule chrysene.

The relation of θ with the aromaticity indices NICS or HOMA (obtained from experimental data) is displayed in Figure 4, parts b and c. The exceptions in the correlation with NICS are the values for benzene and for the inner ring (II) of anthracene. According to NICS, the inner ring of anthracene is more aromatic than the one in benzene, whereas by definition, θ of a ring in a PAH cannot have a larger value than that for benzene. In the case of the comparison with HOMA, the indices HOMA and θ display the same behavior, leading to a better correlation.

Thus, the results obtained in this work allow one to introduce a new aromaticity index, θ, one that is based on the electron delocalization δ between the atoms defined by the QTAIM and that is rooted in Pauli exclusion principle. The values of θ parallel those of the HOMA index, a bond length alternation model whose foundation lies in the strong correlation between bond length and bond order, a correlation reflected in Figure 1d. The results discussed show that electron delocalization in PAHs can be quantified by means of δ which holds a relationship with the electronic energy density, as displayed in Figure 1h. The relationship between one and two electron properties, Figure 1, the pattern displayed by the electron isodensity envelopes in Figure 3 and the information contained in θ, show a consistent global picture of bonding and electronic structure in the PAHs.

V. Conclusions

The quantum theory of atoms in molecules provides a measure of electron delocalization between atoms by the double integration of the Fermi hole density over the basins of the two atoms in question. Although such a delocalization index can be calculated for any pairs of atoms in a molecule, whether bonded or not, in this paper, we identified the delocalization index between two *bonded* carbon atoms with the bond order. We have explored the correlation between the bond order, a two-electron property, and the one-electron density (ρ_{bcp}) at the bond critical point (BCP). We found a very strong exponential relationship between these two different quantities. At first sight, this result may seem surprising because the BCP in PAHs is located on the nodal plane of the π orbitals. We presented arguments supporting the nonseparability of the σ and the π contributions to the density at the BCP in self-consistent field calculations. Moreover, we have found that the ellipticity, a bond property reflecting the π character of the bond, is strongly correlated to ρ_{bcp}, a fact providing further support to the nonseparability of σ and π contributions. The strong correlation between the bond order and ρ_{bcp} can be exploited for a fast estimate of an unknown bond order, because the calculation of bond critical point properties is much faster than the atomic integrations necessary to compute the delocalization index. This correlation can also be used to obtain estimates of bond orders from X-ray diffraction experiments, because these experiments do not generally provide information derived from the pair density.

We have also studied several correlations among one-electron and two-electron bond properties. Perhaps most interestingly, we found a strong negative correlation between two-electron properties, the total energy density at the BCP (H_{bcp}) and the delocalization, index a finding in line with the expectation of increased stability with increased electron delocalization. This is also reflected in the negative correlation between the Laplacian density at the BCP and the delocalization index, because a term proportional to the Laplacian enters in the local statement of the virial theorem.

The delocalization index has also been used to define an aromaticity index similar to the geometric HOMA using the delocalization index as a measure of alternation within a ring. Thus, by re-formulating HOMA in terms of the delocalization indices, we are taking the aromaticity index one step closer to its root cause: electron delocalization. In the analysis of the effect of ring annealation on bond orders, it was found that annealation which result in a loss of aromaticity of a middle ring increases the aromatic character of the peripheral ring. Moreover, the loss of aromatic character of an inner ring in an angular PAHs is associated with an increase of the bond order of the C atoms at the K region. The aromaticity index proposed in this work has been found to display a similar trend as the independent measure of aromaticity provided by the HOMA index. The one and two-electron properties analyzed in this work provide a consistent global picture of bonding and electronic structure in polycyclic aromatic hydrocarbons.

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Supporting Information Available: Wave functions of all of the molecules presented in this study and a table of one- and two- electron bond properties along with bond length and atomic numbering corresponding to the wave functions. This material is available free of charge via the Internet at http://pubs.acs.org.

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