

Discrepancy between common local aromaticity measures in a series of carbazole derivatives†

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Received 19th August 2003, Accepted 21st November 2003

First published as an Advance Article on the web 16th December 2003

The aromaticity of a series of carbazole derivatives has been analyzed by means of different local aromaticity criteria. In particular, the evaluation of the local aromaticity has been carried out through the use of structurally (HOMA) and magnetically (NICS) based measures, as well as by using a new electronically based indicator of aromaticity, the *para*-delocalization index (PDI), which is defined as the average of all Bader delocalization indices between *para*-related carbon atoms in a six-membered ring. For a series of carbazole derivatives, the three measures of local aromaticity vary in a rather narrow range. In addition, a clear divergence is achieved between the three aromaticity criteria. This makes it very difficult to reach a definite classification of the series of compounds with respect to their local aromaticity.

Introduction

In a recent paper,¹ the local aromaticity of a series of carbazole derivatives was studied with the idea of achieving quantitative predictions about the reactivity of these molecules as a function of their substituents and their possible role in the mechanisms of asphaltene aggregation; a very serious problem in the oil industry with a huge economic impact. The local aromaticity of this series of compounds was obtained using the widely employed nucleus independent chemical shift (NICS) indicator of aromaticity.² This index, which was proposed by Schleyer *et al.*,^{2,3} is a magnetic descriptor of aromaticity based on the electron ring current that is induced when the system is exposed to external magnetic fields. The NICS index 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 values, the more aromatic the rings are.

Unfortunately, the evaluation of aromaticity is not unique and different measures are possible based on structural, magnetic, or energetic-based indices.^{4,5} Principal component analysis has revealed that, because of the multidimensional character of aromaticity, aromatic compounds cannot be normally well-characterized by using a unique index.^{5–7} Consequently, to make reliable comparisons restricted to some regions or groups of relatively similar compounds it is usually recommended to employ several aromaticity descriptors.⁸ Moreover, despite the fact that most authors consider that magnetic measures are the most reliable indicators of aromaticity, the NICS values suffer from the following series of problems:⁵ (a) NICS values are size and basis set dependent; (b) the size of the NICS does not provide an absolute measure

of aromaticity; and (c) polycyclic rings also show anomalous behavior of NICS, exaggerating or reducing the aromaticity of fused cycles due to a synergic effect (for instance, according to NICS the inner ring of anthracene has a larger aromaticity than benzene). To take into account the multidimensional character of aromaticity and to check the validity of the local aromaticity results obtained using the NICS indexes in the series of carbazole derivatives previously analyzed,¹ we have considered in this paper two additional probes of local aromaticity, namely, an aromaticity index based on the structural properties of the molecules and another one that takes into account the degree of electron delocalization in the aromatic rings.

As a structural-based measure, we have made use of the harmonic oscillator model of aromaticity (HOMA) index, defined by Kruszewski and Krygowski as:^{9,10}

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

where n is the number of bonds considered, and α is an empirical constant chosen in such a way that $\text{HOMA} = 0$ for a model nonaromatic system, and $\text{HOMA} = 1$ for a system with all bonds equal to an optimal value R_{opt} , assumed to be achieved for fully aromatic systems. R_i stands for a running bond length. This index has been found to be amongst the most effective structural indicators of aromaticity.^{6,11} Finally, as an aromaticity criterion based on electron delocalization, we have used the recently reported *para*-delocalization index (PDI),^{12,13} which is obtained employing the delocalization index (DI)^{14,15} as defined in the framework of the Atoms in Molecules (AIM) theory of Bader.^{16–18} The PDI is an average of all DI of *para*-related carbon atoms in a given six-membered ring (6-MR). The DI value between atoms A and B, $\delta(A,B)$, is obtained by double integration of the exchange-correlation density over the basins of atoms A and B, which are defined from the condition of zero-flux

† Presented at the ESF Exploratory Workshop: New Perspectives on Aromaticity, Exeter, UK, July 5–9, 2003.

gradient in $\rho(\mathbf{r})$:¹⁴

$$\begin{aligned} \delta(\mathbf{A}, \mathbf{B}) &= - \int_A \int_B \Gamma_{XC}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 - \int_B \int_A \Gamma_{XC}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 \\ &= -2 \int_A \int_B \Gamma_{XC}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2. \end{aligned} \quad (2)$$

δ provides a quantitative idea of the number of electrons delocalized or shared between atoms A and B.^{14,15,19} Therefore, the PDI is clearly related to the idea of electron delocalization so often found in textbook definitions of aromaticity. Previous work^{12,13} indicates that for a series of planar and curved polycyclic aromatic hydrocarbons (PAHs) there is a satisfactory correlation between NICS, HOMA and PDI. In general, larger PDIs go with larger absolute values of NICS and larger HOMA values. In this work we investigate whether this correlation between the three aromaticity indexes also applies to a series of similar compounds including heterocycles. We will show that, unfortunately, for a series of carbazole derivatives there is no agreement between the three indexes of aromaticity and, therefore, the conclusions extracted from these measures have to be handled with extreme care.

Computational details

Molecular geometries for all carbazole derivatives analyzed in the present work have been taken from ref. 1 where their structures were optimized at the B3LYP/6-31++G** level of theory.^{20,21} The wave functions and electron densities required to carry out the AIM topological analysis to compute the corresponding aromaticity index have been obtained by means of the Gaussian 98 program²² using the B3LYP/6-31++G** approach. Delocalization indices have also been calculated at the same level of theory by means of the AIM-PAC package.²³ It is important to remark that within density functional theory (DFT), the calculation of DIs cannot be performed exactly, because the electron-pair density is not available at the DFT level.²⁴ As an approximation, we have used the Kohn–Sham orbitals obtained from the DFT calculation to compute Hartree–Fock-like DIs using the following expression:²⁴

$$\delta(\mathbf{A}, \mathbf{B}) = 4 \sum_{i,j}^{N/2} S_{ij}(\mathbf{A}) S_{ij}(\mathbf{B}). \quad (3)$$

In eqn. (3), the summations run over all the occupied molecular orbitals; $S_{ij}(\mathbf{A})$ is the overlap integral between molecular orbitals i and j within the basin of atom A. Eqn. (3) does not account for electron correlation effects, which generally leads to a decrease of interatomic delocalization between covalently bonded atoms. In practice, the values of the DIs obtained using this approximation are generally closer to the Hartree–Fock values than to the correlated DIs obtained with a configuration interaction method.²⁴

The numerical accuracy of the AIM calculations has been assessed using two criteria: (i) the integration of the Laplacian of the electron density ($\nabla^2 \rho(\mathbf{r})$) within an atomic basin must be close to zero; (ii) the number of electrons in a molecule must be equal to the sum of all the electron populations of a molecule, and also equal to the sum of all the localization indexes^{14,15} and half of the DIs in the molecule.¹⁵ For all atomic calculations, integrated absolute values of $\nabla^2 \rho(\mathbf{r})$ were always less than 0.001. For all molecules, errors in the calculated number of electrons were always less than 0.01.

In addition, B3LYP/6-31++G** NICS values calculated at the ring centres using the continuous set of the gauge transformation method have been taken from ref. 1.

Results and discussion

A schematic representation of the series of carbazole derivatives studied in the present study is depicted in Fig. 1. These include carbazole itself (CZ) and various derivatives, such as methyl carbazole (CZ–CH₃), hydroxyl carbazole (CZ–OH), bromide carbazole (CZ–Br), nitrile carbazole (CZ–CN), acetyl carbazole (CZ–COCH₃), (N–) unprotonated carbazole and carboxyl carbazole (CZ–COOH). In addition we have considered one additional compound having two substituents with different chemical character. This is the derivative containing one acetyl and one methyl, both on the same ring, and in positions X (CH₃) and Y (COCH₃) as shown in Fig. 1. Table 1 contains the calculated PDI, HOMA and NICS values for this series, computed for the substituted and non-substituted benzene rings as well as for the central pyrrolic ring. The PDI of the latter ring has not been calculated because PDI indexes have been only defined for 6-MRs.¹²

First, let us focus on the PDI values for the substituted ring, it is worth noting that they are scattered over a narrow range of values, from 0.082 e (carbazole itself) to 0.071 e (unprotonated carbazole). As a reference, the PDI value for benzene is 0.101 e at the B3LYP/6-31G* level of theory.¹² The relatively high values of the PDI indexes show that for all species considered this substituted ring is quite aromatic. However, since the PDI values of the substituted 6-MR do only suffer minor changes upon substitution, it appears that from the PDI results only it is difficult to classify this series of compounds with respect to the local aromaticity of their substituted 6-MR in a reliable way. One may expect that carbazole derivatives substituted by an electron-donor group (X = CH₃ or OH), which activates the substituted ring, would increase its aromaticity, while substitution by an electron-acceptor group (X = CN, COOH or Br), which deactivates the substituted ring, would decrease its aromaticity. Indeed this is precisely what is predicted from the NICS based aromaticity measure.¹ However, this behaviour is not seen from the present PDI measures. According to PDI values of the substituted 6-MR, the unsubstituted CZ (0.082 e) seems to have the most aromatic ring, followed by CZ–CH₃, CZ–Br, CZ–COOH and CZ–COCH₃ (0.079–0.077 e), then CZ–OH and CZ–CN (0.075 e), and finally CH₃–CZ–COCH₃ and N– (0.072 and 0.071 e , respectively). On the other hand, the PDIs for the non-substituted 6-MRs are always higher than the PDI indexes for the substituted 6-MRs. Unsurprisingly, the observed trend of almost constant PDI values for the substituted 6-MR is accentuated in the non-substituted 6-MR, with PDI measures that range from 0.083 e (CH₃–CZ–COCH₃) to 0.081 e (CZ–COCH₃), except for the carbazole anion, which again (in this case, the non-substituted 6-MR

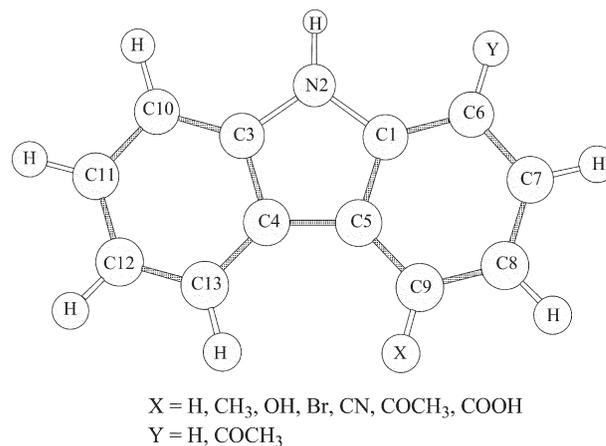


Fig. 1 Schematic representation of carbazole and the different substituted compounds analyzed in this work.

Table 1 B3LYP/6-31++G** NICS (ppm), PDI (electrons) and HOMA calculated values for the substituted (Subs), pyrrolic (Pyr) and non-substituted (N-Subs) rings of the series of carbazole derivatives studied

Molecule		NICS ^a			PDI		HOMA		
		Subs	Pyr	N-Subs	Subs	N-Subs	Subs	Pyr	N-Subs
CZ	1	-12.95	-10.24	-12.95	0.082	0.082	0.919	0.679	0.919
N-	2	-12.02	-12.02	-12.02	0.071	0.071	0.929	0.690	0.929
CZ-CH ₃	3	-13.09	-10.33	-12.81	0.079	0.082	0.904	0.648	0.912
CZ-OH	4	-13.97	-10.83	-13.35	0.075	0.082	0.920	0.653	0.912
CZ-Br	5	-13.31	-10.92	-13.85	0.078	0.082	0.915	0.654	0.919
CZ-CN	6	-12.95	-10.67	-13.32	0.075	0.082	0.903	0.694	0.916
CZ-COCH ₃	7	-12.89	-10.61	-12.92	0.077	0.081	0.797	0.400	0.891
CZ-COOH	8	-12.78	-10.66	-13.10	0.078	0.082	0.894	0.599	0.908
CH ₃ -CZ-COCH ₃	9	-12.98	-9.67	-12.07	0.072	0.083	0.859	0.636	0.928

^a Values obtained from ref. 1.

is equivalent to the substituted 6-MR) presents the lowest PDI (0.071 *e*).

In addition, to better understand the changes in the PDIs for this series, Table 2 contains, for the two 6-MRs, the three possible DIs that have been selected for each ring to compute the PDI values. As can be seen from the values in Table 2, the major changes along this series correspond to the DI of the substituted carbon atom and the related carbon atom in *para* position ($\delta(6,9)$) whereas in all other cases DIs are quite constant. Therefore, the small changes in the PDI values of the substituted ring must be attributed mainly to changes in $\delta(6,9)$. In line with previous studies,¹² we have found that *para*-DIs having one carbon atom in a bridge (for instance, $\delta(5,7)$) are always smaller than *para*-DIs linking C atoms not located in ring fusions, such as $\delta(6,9)$.

Given the small differences found in the calculated PDIs, it is our opinion that it is really difficult to guarantee that a given carbazole derivative ring in this series presents a higher or lower aromaticity than the rings of the carbazole molecule itself using the PDI values. The low differentiation found in this series of carbazole derivatives has not been observed in previous studies. For instance, we have found¹³ that planar polycyclic aromatic hydrocarbons and buckybowls, although having quite similar geometrical structures, present a much wider range of PDI values. This allows one to safely classify the different rings as a function of their PDI measure of aromaticity.

Table 1 also contains the HOMA indices calculated from eqn. (1) with $\alpha = 257.7$ and $R_{\text{opt}} = 1.388 \text{ \AA}^6$ and using the bond lengths of the B3LYP/6-31++G** optimized geometries. As a reference, the HF/6-31G* HOMA value of benzene is 0.981.¹² The HOMA values for the substituted rings reported in Table 1 expand over a wider range than the PDI values.

Remarkably, the order of aromaticity provided by the HOMA descriptor is completely changed with respect to that obtained from the PDI measures. Now, the N- species presents the most aromatic (0.929) and CZ-COCH₃ (0.797) the least aromatic substituted 6-MRs. The decreasing order of aromaticity for the substituted 6-MR as indicated by the HOMA values is: N- > CZ-OH > CZ > CZ-Br > CZ-CH₃ > CZ-CN > CZ-COOH > CH₃-CZ-COCH₃ > CZ-COCH₃. Following the same trends as the PDI values, we have found that the HOMA range of values for the non-substituted ring is reduced and that the HOMA for the non-substituted 6-MR is larger than for the substituted 6-MR, with the only exception of the CZ-OH derivative. It is also worth noting that, according to HOMA values, the aromaticity of the pyrrolic ring is clearly lower than that of the two 6-MRs in carbazole derivatives.

Finally, Table 1 also contains the NICS values calculated at the ring centre for this series of carbazole derivatives. As a reference, the benzene ring has a NICS value of -9.7 at the HF/6-31+G* level of theory. NICS values in Table 1 had been already calculated and profusely commented in ref. 1. Here we would like just to add that these values also show a rather small variation (the largest difference being of 1.95 ppm only). From the NICS results, CZ-OH (-13.97 ppm) appears to have the most aromatic substituted 6-MR, as one may expect from chemical intuition, it is simply the system with the strongest electron-donor substituent. However, a quite surprising result is that the NICS values indicate that all 6-MRs are more aromatic in carbazole derivatives than in the benzene ring itself. It is well-known that NICS overestimates the aromaticity of the central rings in polyacenes.^{5,25} Apparently, NICS is also likely overestimating the aromaticity of the 6-MRs in carbazole derivatives. In line with the PDI results, N- (-12.02 ppm) has the

Table 2 B3LYP/6-31++G** DI (electrons) and PDI (electrons) calculated values for the substituted (Subs) and non-substituted (N-Subs) rings of the series of carbazole derivatives studied. The PDI corresponds to the average of the three possible *para*-DIs in a given 6-MR

Molecule	Substituted ring				Non-substituted ring			
	$\delta(1,8)$	$\delta(5,7)$	$\delta(6,9)$	PDI	$\delta(3,12)$	$\delta(4,11)$	$\delta(10,13)$	PDI
CZ	0.073	0.078	0.096	0.082	0.073	0.078	0.096	0.082
N-	0.058	0.066	0.088	0.071	0.058	0.066	0.088	0.071
CZ-CH ₃	0.071	0.076	0.091	0.079	0.073	0.077	0.095	0.082
CZ-OH	0.070	0.071	0.082	0.075	0.074	0.077	0.095	0.082
CZ-Br	0.072	0.073	0.090	0.078	0.073	0.077	0.096	0.082
CZ-CN	0.071	0.071	0.084	0.075	0.072	0.076	0.097	0.082
CZ-COCH ₃	0.072	0.072	0.089	0.077	0.071	0.075	0.096	0.081
CZ-COOH	0.072	0.074	0.090	0.078	0.072	0.076	0.097	0.082
CH ₃ -CZ-COCH ₃	0.063	0.075	0.078	0.072	0.074	0.077	0.096	0.083

smallest aromatic 6-MRs. Hence, the order for the substituted 6-MR is: CZ-OH > CZ-Br > CZ-CH₃ > CH₃-CZ-COCH₃ > CZ = CZ-CN > CZ-COCH₃ > CZ-COOH > N-, which again clearly differs from the classification given by the PDI index (CZ > CZ-CH₃ > CZ-Br = CZ-COOH > CZ-COCH₃ > CZ-OH = CZ-CN > CH₃-CZ-COCH₃ > N-) and HOMA (N- > CZ-OH > CZ > CZ-Br > CZ-CH₃ > CZ-CN > CZ-COOH > CH₃-CZ-COCH₃ > CZ-COCH₃) values. Unlike the PDI and HOMA results and, somewhat unexpectedly, the NICS values for the substituted 6-MR are larger than those of the non-substituted rings for three derivatives (CZ-CH₃, CZ-OH and CH₃-CZ-COCH₃). As found with the HOMA results, the aromaticity of the pyrrolic ring is smaller than or equal to the aromaticity of the 6-MRs.

To visualize the divergence in the results predicted by these three aromaticity criteria, we have represented in Figs. 2–4 the PDI *vs.* NICS, HOMA *vs.* NICS and HOMA *vs.* PDI, respectively, together with Fig. 5 which contains an overall comparison between all three aromaticity criteria. In all cases the absence of any correlation is clear enough.

Because of NICS, HOMA and PDI values are based on different properties that are related to the aromatic character of the molecules, the fact that one does not find a good correlation among them is not totally surprising.⁷ However, despite being based on different physical manifestations of aromaticity, the NICS, HOMA and PDI parameters yield similar

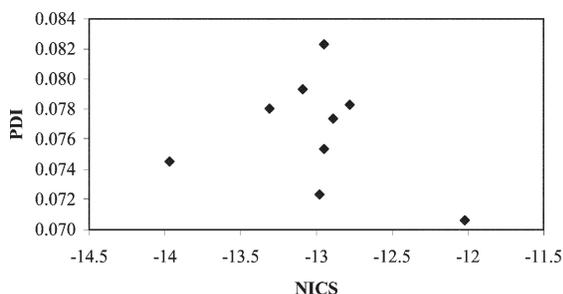


Fig. 2 Plot of PDI *versus* NICS for the series of carbazole derivatives studied.

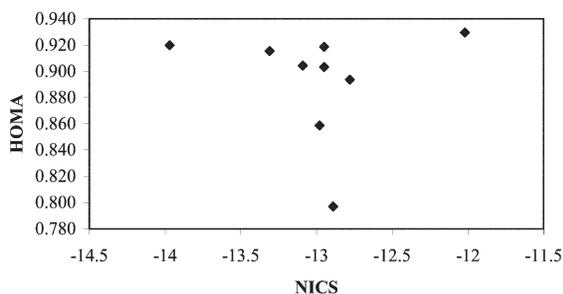


Fig. 3 Plot of HOMA *versus* NICS for the series of carbazole derivatives studied.

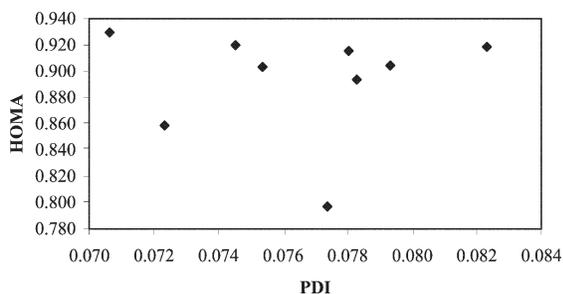


Fig. 4 Plot of HOMA *versus* PDI for the series of carbazole derivatives studied.

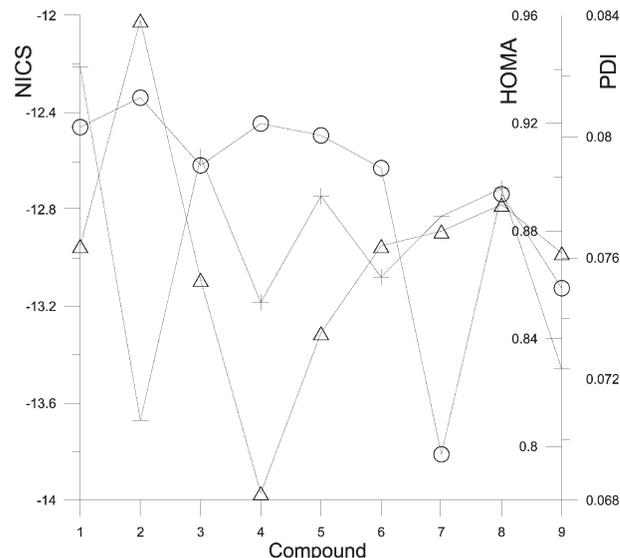


Fig. 5 Comparative plot of HOMA (+), NICS (Δ) and PDI (○) for the series of carbazole derivatives studied. The x-axis numeration can be found in Table 1.

orderings, at least for a rather large family of compounds.^{12,13} In the present case, as substituents, in general, represent only minor first-order perturbations, the several indexes measuring the change of aromaticity due to the effect of the different substituents give totally divergent results. When various aromaticity criteria provide the same answer, then one can be quite sure about the relative aromaticity of a series of rings. However, in some cases, such as the present carbazole derivative series, different indices afford conflicting answers. In this case, it is important to stress that it is unsafe to reach definite conclusions about the local aromaticity of the systems studied.

Conclusions

In the present paper we have analyzed the local aromaticity of a series of carbazole derivatives using three different aromaticity criteria. We have shown that, as far as the relative aromaticity of the different derivatives is concerned, there is a clear divergence among the three methods used to quantify the local aromaticity. This is at variance with previous studies^{12,13} and shows that when a given aromaticity criterion yields small differences in a given series, and particularly, when different methods provide different orderings, one must be very cautious with the results. In particular, no categorical conclusions on the local aromaticity of the species considered can be achieved.

Hence, it is very important to warn chemists about the limitations of the different methods to analyze aromaticity. In particular, chemists wishing to use these interpretative tools should be aware that, first, for comparisons restricted to groups of relatively similar compounds more than one aromaticity parameter must be used.⁷ And second, that 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.

Acknowledgements

Financial help has been furnished by the Spanish MCyT Projects No. BQU2002-0412-C02-02 and BQU2002-04029-CO2-01 and, in part, by Generalitat de Catalunya grant 2001SGR-00043. M. S. and F. I. are indebted to the DURSI of the Generalitat de Catalunya for financial support through the Distinció de la Generalitat de Catalunya per a la promoció

de la Recerca Universitària awarded in 2001. J. P. thanks the Departament d'Universitats, Recerca i Societat de la Informació de la Generalitat de Catalunya (DURSI) for benefiting from the doctoral fellowship no. 2000FI-00582.

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