

Multicenter Bond Indices As a New Means for the Quantitative Characterization of Homoaromaticity

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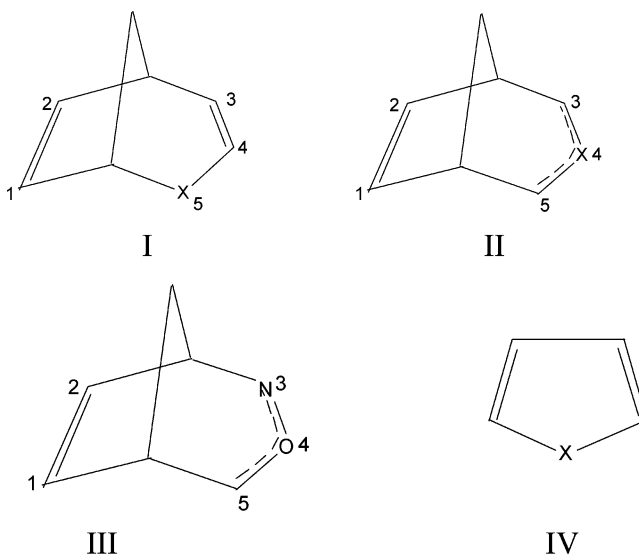
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This study reports the use of multicenter bond indices as a new tool for the quantitative characterization of homoaromaticity. The approach was applied to the series bicyclic systems whose homoaromaticity was recently discussed in terms of traditional aromaticity index, namely, NICS. In this study we found that the multicenter bond indices are indeed able to quantify the degree of homoaromaticity of the studied systems as reflected in the classification of these molecules into classes of homoaromatic, non-homoaromatic, and anti-homoaromatic systems suggested on the basis of NICS values.

Introduction

The concept of homoaromaticity was introduced by Winstein et al.¹ to denote the fact, first observed by Applequist and Roberts,² that the insertion of short insulating chains into the cyclic array of orbitals responsible for the specific properties of aromatic systems does not completely destroy the conjugative interactions between the separated subunits so that the corresponding molecules still display, albeit to a reduced extent, the properties typical for the aromatic systems. Because of its importance, the phenomenon of homoaromaticity has been the subject of a wealth of experimental and theoretical studies aiming both at the evaluation of various manifestations of this phenomenon^{3–17} and, also, to the design of new tools and procedures allowing estimating the extent of the effects responsible for its existence. An example can be, e.g., the early studies^{10–13} in which qualitative molecular orbital (MO) diagrams and perturbational MO (PMO) theory were used to estimate the energetic impact of homoaromatic stabilization. Aromatic and homoaromatic systems also both exhibit special magnetic features, and in fact the combination of both these criteria (stabilization energies and magnetic aromaticity descriptors) is widely used also in a variety of recent studies in which the phenomenon of homoaromaticity is addressed.^{18–22} The main issue of the contemporary studies of homoaromaticity is to demonstrate whether the phenomenon is restricted only to cationic structures, on which it was originally discovered, or whether it also applies to neutral or even anionic systems.^{17,23,24} Our aim in this study is to follow up with the results of our previous study of the aromaticity of polycyclic benzenoid

CHART 1



hydrocarbons²⁵ and to demonstrate that the multicenter bond indices, which were proposed as a new quantitative measure of aromaticity,²⁶ can also be used to characterize the extent of the homoaromaticity. For this purpose we report in the following part the results of the application of this new tool to the series of neutral homoaromatic molecules scrutinized in the recent study by Freeman.²⁰ The studied systems involve the three sets of molecules I, II, and III depicted in Chart 1, and as it will be shown, the 5-center bond indices involving the appropriate subsystems of the corresponding molecules do indeed correlate with the calculated NICS values,²⁷ which were shown to reflect the degree of homoaromaticity in these systems.²⁰ In addition

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to these data, we have also calculated the 5-center indices and NICS values for the set of aromatic heterocyclic molecules IV as hypothetical "precursors" of the homoaromatic systems I–III.

Theoretical

The multicenter bond indices represent a useful theoretical tool to transform the abstract picture of the molecular structure provided by quantum chemical wave functions into the language close to classical chemical concepts of bonds, bond orders, etc.^{28–32} The quantification of these concepts is based on the scrutiny of the powers of the product between the charge density and overlap matrixes (P and S respectively) of a given molecule, respectively.

$$\frac{1}{2^{k-1}} \text{Tr}(PS)^k = N =$$

$$\sum_A \Delta_A^{(k)} + \sum_{A < B} \Delta_{AB}^{(k)} + \dots + \sum_{A < B < \dots < K} \Delta_{AB\dots K}^{(k)} \quad (1)$$

The partitioning of the identity (1), valid at Hartree–Fock and formally also Kohn–Sham level of the theory, for a given value of k then gives mono-, di-, tri-, and generally k -atomic contributions which can be attributed a certain chemical or physical meaning.

Thus, for example, the monatomic terms $\Delta_A^{(1)}$ resulting from the partitioning of the identity for $k = 1$ represent the Mulliken gross electron density on the atom A.³³ Similarly, the diatomic terms $\Delta_{AB}^{(2)}$ resulting from the analogous partitioning of the identity (1) for $k = 2$ are identical with the well-known Wiberg–Mayer indices,^{34,35} which are widely used to characterize the bond order (multiplicity) of localized 2-center 2-electron bonds. The straightforward extension of the partitioning of the identity (1) to higher values of k then opens the possibility to detect similarly the nonclassical multicenter bonding and, for example, the terms $\Delta_{ABC}^{(3)}$, resulting from the partitioning of the identity (1) for $k = 3$, are widely used, as the so-called 3-center bond indices, for the detection and localization of 3-center bonding in many systems.^{36–39} Stimulated by the success of the previous applications of the bond indices, we have recently used the same approach for the description of delocalized multicenter bonding extended over even more centers.²⁵ It was shown that the 6-center bond indices could indeed be used as a new general and universal tool for the characterization of the extent of aromaticity of individual benzene rings in polycyclic aromatic hydrocarbons. Our aim in this study is to show that multicenter bond indices can also be used as a tool to characterize the extent of homoaromaticity.

Computational Details. The geometries of all the studied molecules in the present study were completely optimized at the B3LYP/6-31G* level of the theory,^{40–42} and the resulting optimized structures were shown by frequency analysis to correspond to true minima on the potential-energy hypersurface. The calculations were performed using the Gaussian03 program.⁴³ NICS values were computed at the same level of the theory using GIAO-B3LYP/6-31G* calculations. The NICS values were calculated at the center of the ring formed by the atoms involved in the homoaromatic system.

After the geometry optimization of the studied molecules, calculation of 5-center bond indices was performed using our own program GMA. The program is available upon request from PB as a Linux executable for calculation of bond indices from RHF and restricted DFT wave functions.

TABLE 1: Calculated 5-Center Bond Indices and NICS Values for the Series of Homoaromatic Systems I–IV Shown in Chart 1

series	X	5-center index $\times 10^2$	NICS
I	BH	−0.277	3.50
	AlH	−0.546	0.58
	Be	−0.308	1.49
	Mg	−0.249	1.51
	O	0.548	−1.33
	S	0.512	−2.48
	PH	0.200	−1.05
II	NH	0.816	−2.01
	PH	2.310	−6.75
	S	3.216	−7.76
	NH	3.876	−9.66
III	O	4.762	−13.52
		3.253	−8.69
IV	O	5.737	−13.18
	S	5.846	−13.51
	NH	7.663	−15.64
	PH	8.032	−16.60

Results and Discussion

The calculated values of 5-center bond indices together with the corresponding NICS values are summarized in Table 1.

In contrast to well-established examples of cationic homoaromaticity, the question of the homoaromaticity of the neutral systems is a much more debated issue.¹⁷ There are numerous neutral systems that have been *calculated* to be homoaromatic; however there are only few, rather special examples that have succumbed to experimental determination of homoaromaticity. An interesting example corroborating the existence of this phenomenon was reported in the recent study²⁰ in which the authors demonstrated that there is a fairly satisfactory correlation between the stabilization energies, which reflect the energetic impact of homoaromaticity in the series of neutral molecules I–III, with the magnetic properties characterized by the NICS values. The results of the study²⁰ are very interesting since they clearly demonstrate that, while the neutral homoaromaticity can convincingly be demonstrated for bicyclo-3,2,1-octa-3,6,dien-2-yl series II and III, the situation with the series I is slightly more complex. Still according to Freeman,²⁰ part of the systems, namely, those corresponding to X = O, S, NH, PH, displays non-homoaromatic behavior, while the rest of the molecules can be classified as anti-homoaromatic. Stimulated by these results, we decided to reconsider the problem of neutral homoaromaticity in the same series of molecules using the formalism of multicenter bond indices. These indices were, namely, shown to provide a new efficient tool for the quantitative characterization of aromaticity of polycyclic aromatic hydrocarbons,²⁵ and it was of interest to see whether they would also be able to measure also subtler homoaromatic effects. The answer to this question is affirmative, and Figure 1 displays the correlation of the recognized aromaticity index NICS with the values of 5-center bond indices calculated over the subsystems involving the numbered atoms in Chart 1. Before discussing the conclusions suggested by this correlation it is, however, useful to say a few words about the interpretation of the bond indices. Such an interpretation requires taking into account both the absolute value of the indices and their sign. The situation with absolute value is quite simple; the higher this value, the better are the conditions for the existence of cyclic delocalized bonding. From this point of view, one can already see a clear difference between the molecules belonging to the series II, III, and IV, for which the values are an order of magnitude higher than for the series I. Additional insight into

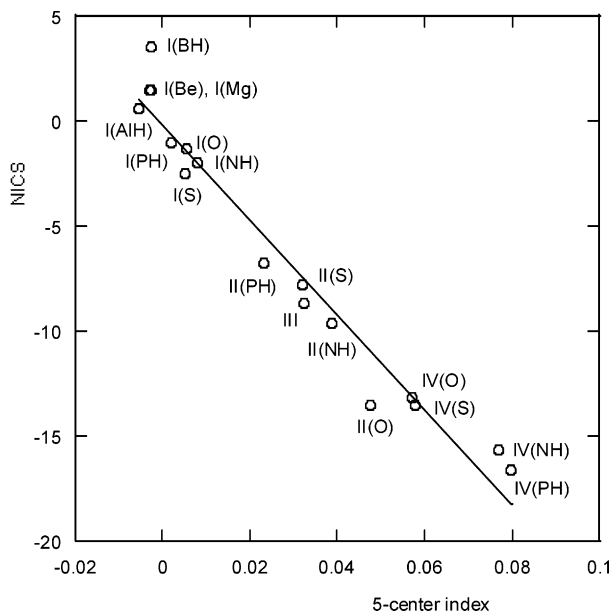


Figure 1. Dependence of the calculated values of 5-center bond indices on the aromaticity indices NICS ($N = 17$, $r^2 = 0.96$).

the interpretation of the values comes then from the sign of the indices. In previous studies it was shown, namely, that the sign of the multicenter bond indices is closely related to the number of electrons involved in cyclic delocalized bonding.^{32,44,45} Thus, for example, the positive values of 3-center bond indices were shown to correspond to 3-center 2-electron bonding, while negative indices are characteristic for 3-center 4-electron bonding. The situation is similar for the bond indices characterizing the cyclic bonding delocalized over more centers.⁴⁶ In our case of 5-center bonding, the negative values are typical for 5-center 4-electron bonding while positive values correspond to 5-center 6-electron bonding. This result is very important since the cyclic delocalized bonding involving 6 ($4n + 2$) electrons is typical for aromatic systems. Taking now into account that the difference between aromaticity and homoaromaticity is only due to partial weakening of the cyclic delocalized bonding, one can expect that bond indices for homoaromatic systems should be also positive but a bit lower than the analogous indices for aromatic systems. An example of the aromatic systems in our study are the molecules belonging to the series IV and Table 1 shows that the bond indices are indeed positive with largest absolute values of the indices. The expected weakening of delocalized cyclic bonding in homoaromatic systems is also straightforwardly evident from Table 1. The molecules belonging to the series II and III also exhibit positive indices with still fairly large absolute values but clearly smaller than the corresponding molecules in series IV. It is well worth noting that these are just the systems that were classified as homoaromatic in the study by Freeman, where magnetic criteria and stabilization energies were used.²⁰

Series I is a slightly more complicated case. The absolute values of the bond indices are, in this case, always considerably lower compared to what is observed for aromatic and homoaromatic systems. This result can be interpreted in a sense that those molecules with small but positive values of bond indices can be regarded as non-homoaromatic and the systems with negative values, which are characteristic of 5-center 4-electron bonding, as slightly antihomoaromatic. This interpretation is consistent with the values of NICS and our results thus in fact completely corroborate the conclusions of the study by Freeman.²⁰

In addition to demonstrating the applicability of multicenter bond indices as a new tool for the characterization of homoaromaticity, Figure 1 is interesting also for another reason. It is seen that the same correlation line involves not only the homoaromatic, non-homoaromatic, and anti-homoaromatic systems I, II, and III but also the aromatic molecules belonging to the series IV. This result is very important since it straightforwardly demonstrates that there is in fact no difference between the aromaticity and homoaromaticity except in the extent of the conjugative interactions in the cyclic delocalized array of participating orbitals. In this connection it is, however, necessary to remember that the existence of the correlation similar to Figure 1 is slightly exceptional. The reason is that classical and magnetic criteria of aromaticity are generally orthogonal^{47–49} so that correlation between such aromaticity measures is unlikely unless the studied molecules form a set of closely structurally related molecules,²⁵ which is just the case of our study and the study.²⁰

It is worth noting that the correlation between the multicenter indices and the NICS values for the molecules from series I–III, is even better than the correlation between the stabilization energies and NICS values reported by Freeman.²⁰ This justifies the conclusion that the multicenter indices can indeed be used as a measure for aromaticity, including homoaromaticity. It further has the important advantage over many other measures since multicenter indices can be computed very efficiently because only the charge density and overlap matrixes from a single self-consistent field procedure are required. Computing the multicenter index requires less than one second on a personal computer for the molecules in Chart 1.

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Supporting Information Available: Computational parameters, Cartesian coordinates of all molecules, NICS and multicenter indices, total energies, and number of imaginary frequencies are available as Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- Winstein, S. *J. Am. Chem. Soc.* **1959**, *81*, 6524.
- Applequist, D. E.; Roberts, J. D. *J. Am. Chem. Soc.* **1956**, *78*, 4012.
- Rosenburg, J. L., Jr.; Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1962**, *84*, 2842.
- Winstein, S. *Quart. Rev. Chem. Soc.* **1969**, *23*, 141.
- Warner, P.; Harris, D. L.; Bradley, C. H.; Winstein, S. *Tetrahedron Lett.* **1970**, 4013.
- Winstein, S.; Kreiter, C. G.; Brauman, J. I. *J. Am. Chem. Soc.* **1966**, *88*, 2047.
- Olah, G.; Staral, J. S.; Spear, R. J.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 5489.
- Paquette, L. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 106.
- Child, R. F. *Acc. Chem. Res.* **1984**, *17*, 347.
- Hehre, W. J. *J. Am. Chem. Soc.* **1973**, *95*, 5807.
- Jorgensen, W. L. *J. Am. Chem. Soc.* **1976**, *98*, 4.
- Haddon, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 3608.
- Haddon, R. C. *J. Org. Chem.* **1979**, *44*, 3608.
- Williams, R. V.; Kurtz, H. A. *Adv. Phys. Org. Chem.* **1994**, *29*, 273.
- Goren, A. C.; Hrovat, D. A.; Seefelder, M.; Quast, H.; Borden, W. T. *J. Am. Chem. Soc.* **2002**, *124*, 3469.
- Brandt, P.; Jia, Z.; Thibblin, A. *J. Org. Chem.* **2002**, *67*, 7676.
- Williams, R. V. *Chem. Rev.* **2001**, *101*, 1185.

- (18) Jiao, H.; Nagelkerke, R.; Kurtz, H. A.; Williams, R. V.; Borden, W. T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1997**, *119*, 5921.
- (19) Freeman, P. K.; Pugh, J. K. *J. Org. Chem.* **2000**, *65*, 6107.
- (20) Freeman, P. K. *J. Org. Chem.* **2005**, *70*, 1998.
- (21) Freeman, P. K.; Dacres, J. E. *J. Org. Chem.* **2003**, *68*, 1386.
- (22) Freeman, P. K. *J. Am. Chem. Soc.* **1998**, *120*, 1619.
- (23) Grutzner, J. B.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 1372.
- (24) Kaufmann, E.; Mayr, H.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1375.
- (25) Bultinck, P.; Ponec, R.; Van Damme, S. *J. Phys. Org. Chem.*, accepted.
- (26) Giambiagi, M.; Giambiagi, M. S.; dos Santos, C. D.; de Figueiredo, A. P. *Phys. Chem. Chem. Phys.* **2002**, *2*, 3381.
- (27) Schleyer, P. v. R.; Mareker, C.; Dransfeld, A.; Jiao, H.; van Eikema Hommes, N. J. R. *J. Am. Chem. Soc.* **1996**, *118*, 6317.
- (28) Sannigrahi, A. B.; Kar, T. *Chem. Phys. Lett.* **1990**, *173*, 69.
- (29) Sannigrahi, A. B.; Nandi, P. K. *Chem. Phys. Lett.* **1992**, *188*, 575.
- (30) Giambiagi, M.; Giambiagi, M. S.; Mundim, K. C. *Struct. Chem.* **1990**, *1*, 123.
- (31) Mundim, K. C.; Giambiagi, M.; Giambiagi, M. S. *J. Phys. Chem.* **1994**, *98*, 6118.
- (32) Ponec, R.; Mayer, I. *J. Phys. Chem. A* **1997**, *101*, 1783.
- (33) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.
- (34) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083.
- (35) Mayer, I. *Chem. Phys. Lett.* **1982**, *97*, 270.
- (36) Ponec, R.; Yuzhakov, G.; Tantillo, D. J. *J. Org. Chem.* **2004**, *69*, 2992.
- (37) Ponec, R.; Roithová, J.; Sannigrahi, A. B.; Lain, L.; Torre, A.; Boichichio, R. *THEOCHEM* **2000**, *505*, 283.
- (38) Boichichio, R.; Ponec, R.; Torre, A.; Lain, L. *Theor. Chem. Acc.* **2001**, *105*, 292.
- (39) Ponec, R.; Cooper, D. L. *Int. J. Quantum Chem.* **2004**, *97*, 1002.
- (40) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- (41) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B: Condens. Matter* **1988**, *37*, 785.
- (42) Stephens, P. J.; Devlin, J. F.; Chabalowski, C. F. *J. Phys. Chem.* **1994**, *98*, 11623.
- (43) 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.; Kitao, 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.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, 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.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.05; Gaussian, Inc.: Wallingford CT, 2004.
- (44) Kar, T.; Sanchez-Marcos, E. *Chem. Phys. Lett.* **1992**, *192*, 14.
- (45) Giambiagi, M. S.; Giambiagi, M. Z. *Naturforsch. A* **1994**, *49*, 754.
- (46) Ponec, R.; Yuzhakov, G. *J. Org. Chem.* **2003**, *68*, 828.
- (47) Jug, K.; Koster, A. M. *J. Phys. Org. Chem.* **1991**, *4*, 163.
- (48) Katritzky, A. R.; Karelson, M.; Sild, S.; Krygowski, T. M.; Jug, K. *J. Org. Chem.* **1998**, *63*, 5228.
- (49) Katritzky, A.; Barczynski, P.; Musumarra, G.; Pisano, D.; Szafran, M. *J. Am. Chem. Soc.* **1989**, *111*, 7.