

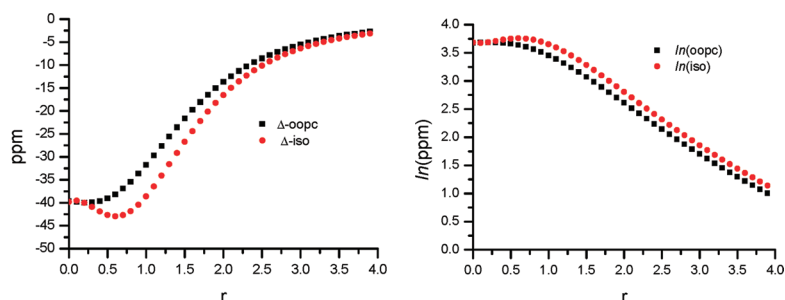
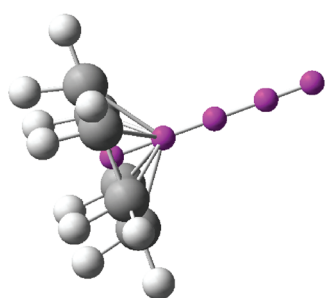
Obtaining Relative Induced Ring Currents Quantitatively from NICS[†]

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A model for obtaining the σ -only effect on the nucleus-independent chemical shift (NICS) is introduced. By subtracting the values obtained for the “ σ -only” model from the respective values of the conjugated system it is possible to obtain the NICS values that originate from the π system only. This procedure allows obtaining a quantitative measure of the relative intensities of diatropic and paratropic ring currents in different systems with a built-in measure of their accuracy. The scope and limitations of the model are discussed.

Introduction

Nucleus independent chemical shift (NICS) in its different variations¹ has been used frequently as a convenient tool for obtaining information about induced dia- and paratropic ring currents, mainly for the purpose of assigning aromaticity and antiaromaticity to molecules.² Recently we introduced a one-dimensional scan of the out-of-plane component (oopc) of the NICS values as a function of distance³

and showed that it is much safer to use than any of the single NICS values.^{4,5} The NICS-scan shape (of the oopc) shows an indicative minimum for induced diatropic ring current and a steady decay for induced paratropic ring current (Figure 1). As an analytical tool (i.e., identifying dia- and paratropic ring currents) the NICS-scan procedure performs well. However, the reason for different shapes of the curves is not immediately clear. Thus, if these shapes would represent only induced magnetic field resulting solely from induced π ring currents they should look like mirror images of each other. Furthermore, there is no physical reason why a magnetic field that results from a diatropic ring current should show a maximum (which is manifested by a minimum of the NICS-scan oopc curve) and not a steady decay with the distance (i.e., qualitatively looking like a mirror image of the picture for planar cyclooctatetraene, Figure 1b). One possibility is that the shape of the oopc as a function of distance for benzene (and other systems that produce diatropic ring current) is a result of a sum of a decaying diatropic field and a fast decaying paratropic contribution. If this is indeed the case, the only available sources for paratropic contribution to the oopc of systems that show induced diatropic ring currents are the σ electrons. If, indeed, this is true the σ electrons must contribute also to the oopc of systems that show paratropic

[†] Dedicated to Yitzhak Apeloig on the occasion of his 65th birthday.

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(1) (a) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842–3888. (b) Schleyer, P. v. R.; Manoharan, M.; Jiao, H.; Stahl, F. *Org. Lett.* **2001**, *3*, 3643–3646. (c) Kleinpeter, E.; Klod, S.; Koch, A. *THEOCHEM* **2007**, *811*, 45–60. and references cited therein. (d) Fallah-Bagher-Shaidaei, H.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 863–866. For the original NICS paper see: (e) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.

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(5) A similar method was introduced by Cossio and his collaborators. See: (a) Moreo, I.; Lecea, B.; Cossio, F. P. *J. Org. Chem.* **1997**, *62*, 7033–7036. (b) Moreo, I.; Cossio, F. P. *J. Org. Chem.* **1999**, *64*, 1868–1874.

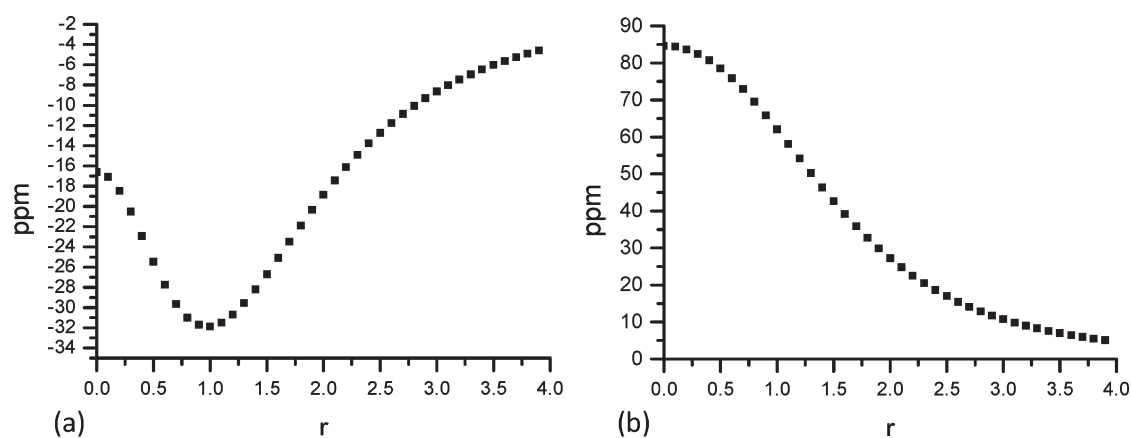


FIGURE 1. The oopc of (a, left) benzene and (b, right) D_{4h} -cyclooctatetraene at HF/6-311+G*.

ring current.⁶ To test this hypothesis and (if correct) to allow a comparison of induced ring currents between different systems, one must be able to zero the contribution of the σ electrons to the NICS.

There are currently two computational procedures that allow calculating the quantitative contribution of the σ and π electrons to the NICS. One is canonic molecular orbitals (CMO)-NICS, which is based on the IGLO method for chemical shifts calculations,⁷ and the second is NCS⁸ within NBO 5.G⁹ that allows separating GIAO¹⁰ calculated chemical shifts as contributions from localized NBO orbitals (also called LMO-NICS) or from canonical MOs. Both methods are based on mathematical approximations that are not always physical. The IGLO method is a gauge-dependent method, and as such it is less reliable. For calculating individual contributions of orbitals only part of the orbitals are transformed under magnetic field, which is, of course, an approximation that may be valid for some systems and not for others.¹¹ The NCS procedure uses the GIAO method, which is a gauge-independent method, and the NBO procedure which produce localized orbitals and the individual contribution of each is recalculated. Also, this approach assumes that the unoccupied MOs to which the electrons are being excited are free of the magnetic field, again, an assumption that may work in some cases and not in others. Working with localized bonds representations and canonic MOs have their own deficiencies which will be discussed later. Both methods (i.e., CMO-NICS and LMO-NICS)

do not include any measure for the goodness of the results.

Another principle way to obtain the effect of the π system is to calculate the effects of the σ frame on the NICS and subtract these values from the NICS values of the complete system. For this purpose a chemical model that is based on using the delocalized electron for binding hydrogen atoms is proposed here. Providing that the σ skeleton is unchanged and the effect of the added hydrogen atoms on the NICS values is minimal (ideally zero) such a system could serve as a σ -only model.

Theoretical Background. In cases of induced ring currents, the induced magnetic field is perpendicular to the molecular plane. Since NICS senses the induced magnetic field (and reports it by chemical shifts units) the oopc is the main reporter of the induced field. If the molecular plane is XY the oopc is χ_Z , which can be divided into σ electron contribution and π electron contribution, namely:

$$\chi_Z = \chi_Z(\sigma) + \chi_Z(\pi) \quad (1)$$

A perfect model for the σ electrons should yield the same $\chi_Z(\sigma)$ as the delocalized system and $\chi(\pi) = 0$. Thus, denoting d and m for delocalized and model systems, respectively, a perfect model should yield

$$\Delta\chi_Z = \chi_Z^d(\sigma) + \chi_Z^d(\pi) - [\chi_Z^m(\sigma) + \chi_Z^m(\pi)] = \chi_Z^d(\pi) \quad (2)$$

In other words, for a perfect model of the σ electrons contribution to the oopc of NICS, the difference between the oopc of the delocalized system and the model should yield the π contribution to the oopc of the NICS of the delocalized system.

How can the model be evaluated? There are two principal ways for this. Under the assumption that the π contribution to the ipc (which is the average of the in-plane tensors, i.e., $\text{ipc} = \frac{1}{2}(\chi_Y + \chi_X)$) of the NICS is minimal (zero in the best case) the differences between the ipc of the delocalized system and the model should be zero. One can therefore look at the plot of $\Delta(\text{ipc}) = \text{ipc}^d - \text{ipc}^m$ as a function of distance and qualitatively obtain a measure for the performance of the model.

The other way is quantitative and rests on the comparison between the isotropic shifts. Thus, the isotropic chemical shift is given by

$$\chi_{\text{iso}} = \frac{1}{3}(\chi_Z + \chi_Y + \chi_X) \quad (3)$$

(6) It has been shown the σ electrons have both dia- and paratropic contributions, however, not necessarily in equal amounts. See: Gomes, J. A. N. F.; Mallion, R. B. *Chem. Rev.* **2001**, *101*, 1349–1383.

(7) (a) Steinmann, S. N.; Jana, D. F.; Wu, J. I.-C.; Schleyer, P. v. R.; Mo, Y.; Corminboeuf, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 9828–9833. (b) Heine, T.; Islas, R.; Merino, G. *J. Comput. Chem.* **2007**, *28*, 302–309. (c) Schleyer, P. v. R.; Jiao, H. J.; van Eikema Hommes, N. J. R.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1977**, *119*, 12669–12670. (d) Schleyer, P. v. R.; Manoharan, M.; Wang, Z. X.; Kiran, B.; Jiao, H.; Puchta, J.; van Eikema Hommes, N. J. R. *Org. Lett.* **2001**, *3*, 2465–2468.

(8) Bohmann, J. A.; Weinhold, F.; Farrar, T. C. Natural Chemical Shielding. *J. Chem. Phys.* **1997**, *107*, 1173–1184.

(9) Glendening, E. D.; Badenhop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. <http://www.cdchem.wisc.edu/~nbo5>.

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(11) Never-the-less, this method has shown successes (see ref 1a and 1d) and agreement with current density analyses. For example, see the study of cyclopropane; for current density see: Pelloni, S.; Lazzarotti, P.; Zanasi, R. *J. Phys. Chem. A* **2007**, *111*, 8163–8169. For CMO-NICS see: Wu, W.; Ma, B.; Wu, J. I.-C.; Schleyer, P. v. R.; Mo, Y. *Chem.—Eur. J.* **2009**, *15*, 9730–9736.

where χ_i are the eigenvalues of the nine principle tensors of the chemical shift, and each is composed of σ and π contributions. If the ipc of the delocalized and model systems are equal and the model does not have π electrons ($[\chi_Z^m(\pi) = 0]$) then

$$\Delta\chi_{\text{iso}} = \frac{1}{3}[\chi_Z^d(\pi) + \chi_Z^d(\sigma) + \chi_Y^d + \chi_X^d] - \frac{1}{3}[\chi_Z^m(\pi) + \chi_Z^m(\sigma) + \chi_Y^m + \chi_X^m] = \frac{1}{3}\Delta\chi_Z \quad (4)$$

In other words, plotting $3\Delta\chi_{\text{iso}}$ and $\Delta\chi_Z$ as a function of distance should yield overlapping lines for a perfect model. The difference between these two lines gives a quantitative estimate for the goodness of the model.

The chemical model for the σ electrons effect on NICS should have the same characteristics as the delocalized system, but without π electrons. Therefore, the model that is suggested here is simply hydrogenated aromatic systems. The geometry of the aromatic moiety in the model is kept unchanged and the hydrogens are added *syn*. The NICS-scan is calculated on the face which is *anti* to the hydrogens for minimizing their effect. For example, a side view of the σ -only model of benzene with five ghost atoms (BQs) is shown in Figure 2. The rationale behind this model is simple: using the delocalized electrons for bonding will prevent delocalization while keeping all other properties unchanged.

Computational Methods. Gaussian 03¹² was used for the calculations. All the conjugated systems were fully optimized at the B3LYP/6-311G(d) level and underwent analytical frequency calculations to ensure real minima (or the order of saddle points in specific cases such as D_{4h} -cyclooctatetraene, planar-COT). These geometries were used for calculating the σ -only models. In the models only the C–H bond distances and the H–C–ring bond angles for the “hydrogenation” hydrogens were optimized (unless otherwise noted), keeping the structure and symmetry of the conjugated systems. NICS were calculated at GIAO-HF/6-311+G(d) and at GIAO-B3LYP/6-311++G(d,p) computational levels for distances from 0.0 to 3.9 Å from the ring-plane in 0.1 Å intervals. The reasons for using these specific computational levels are 2-fold: The first has to do with the construction of the model, which should not depend on the computational level. Thus, a comparison between a basis set that include polarization functions and diffused functions on the hydrogens and a basis set that does not is desired. The second reason has to do with the inability of HF to correctly describe the NMR transitions for systems with small HOMO–LUMO gap, typically antiaromatic systems. It has been shown (see below) that B3LYP describes this well enough, and thus it is important to establish that the

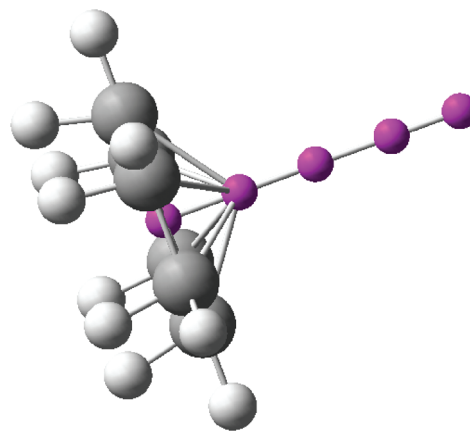


FIGURE 2. The σ -only model for benzene with five BQs for the NICS-scan calculation.

suggested model can reproduce the differences in such systems and yield similar values for systems with a large HOMO–LUMO gap (typically aromatic).

Results and Discussion

First, the model was tested qualitatively. Panels a and b of Figure 3 show the NICS-scan of the σ -only models of benzene and D_{4h} -cyclooctatetraene (planar COT). They look qualitatively as expected. The ipcs are similar for the two and to those of benzene and planar COT,³ and the oopcs look as expected: paratropic at short distances and small values at large distances. Figure 4a shows the $\Delta(\text{oopc})$ of benzene and planar COT. These indeed look as mirror images, as expected for clean induced dia- and paratropic ring currents. Figure 4b shows the $\Delta(\text{ipc})$ for benzene and planar COT, suggesting that within a few ppm the σ -only model is accurate.

For having a more quantitative estimation of the goodness of the σ -only model, a quantitative comparison between $\Delta(\text{oop})$ and $3\Delta(\text{iso})$ is needed. This is shown in Figure 5 for benzene and planar-COT. At small distances (< 1 Å) there are discrepancies between the two lines, but they converge at larger distances. A plot of $\ln(\Delta(\text{oop}))$ and $\ln(3\Delta(\text{iso}))$ as a function of distance (Figure 6) suggests that at distances larger than 1 Å these are straight lines. Indeed, for all the systems that were studied and at both computational levels linear correlations yielded correlation coefficients larger than 0.99, the smallest being 0.99 and the largest being 0.99959 for both lines. It can also be observed that between 0 and 1 Å the $\ln(\Delta(\text{oop}))$ and $\ln(3\Delta(\text{iso}))$ are almost unchanged. This is true for all the systems studied here. Thus, for comparison purposes, the chemical shifts that are going to be used are those calculated from the linear regression at a distance of 1 Å. The values that are discussed are the average of $\Delta(\text{oop})$ and $3\Delta(\text{iso})$, where the uncertainty is the measure of their reliability (or the goodness of the σ -only models). Since they represent the intensity of the ring current they will be referred to as intensities. Please note that due to the logarithmic relationships the absolute values of $\Delta(\text{oop})$ and $\Delta(\text{iso})$ are used for the correlations. For the determination of the signs (negative for diatropic ring currents, positive for paratropic ring currents) one has to look at the calculated chemical shifts.

(12) *Gaussian 03* rev. B.05, C.02 and D.02. 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, Inc., Wallingford, CT, 2004.

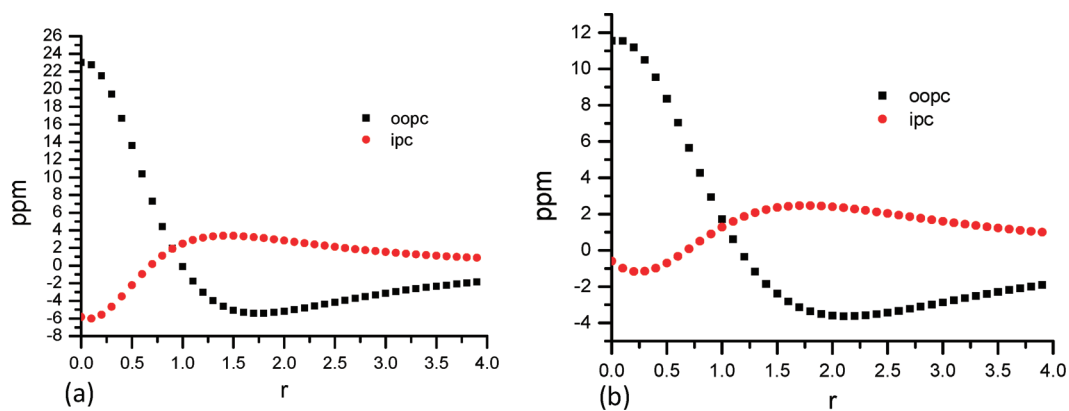


FIGURE 3. NICS-scan (at GIAO-HF/6-311+G(d)) of the σ -only models of (a, left) benzene and (b, right) planar cyclooctatetraene: black, out-of-plane component; red, in-plane component.

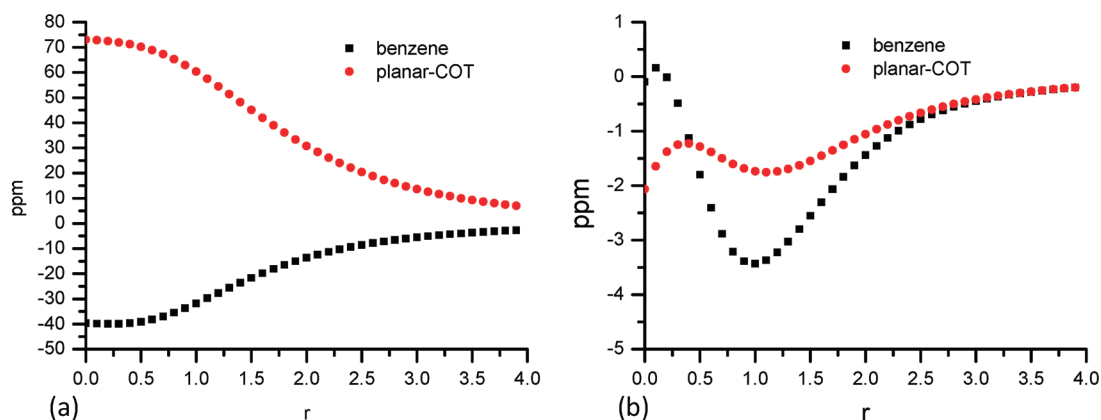


FIGURE 4. Plots of (a, left) $\Delta(\text{oopc})$ and (b, right) $\Delta(\text{ipc})$ of benzene (black) and planar cyclooctatetraene (red) at GIAO-HF/6-311+G(d).

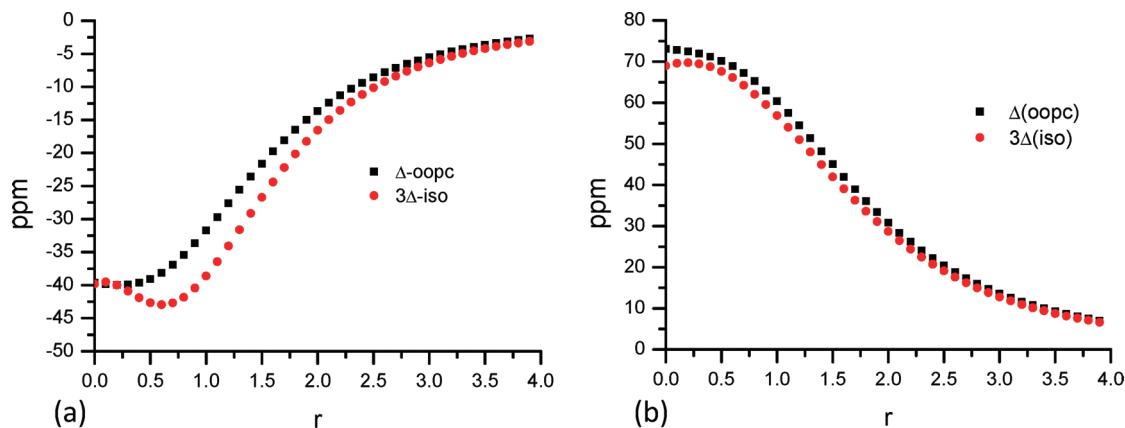


FIGURE 5. Plots of (black) $\Delta(\text{oopc})$ and (red) $3\Delta(\text{isotropic shifts})$ for (a, left) benzene and (b, right) planar cyclooctatetraene (GIAO-HF/6-311+G(d)).

Carbocyclic Systems. Table 1 shows the chemical shifts of 1–6. Qualitatively, the data fit the chemical intuition. Thus, 3 which is bond-localized loses a part of its diatropic ring current relative to benzene (33–36%).^{4c} 4 is neither aromatic nor antiaromatic as it retains only a minimal ring current.^{4c} The magnitude of the ring currents in 2 and 5 is larger than that in benzene by 19% and 72%, respectively, at HF and by 23% and 197% at B3LYP, respectively. For 6, current

densities studies show that the main ring current is spread over the system. However, NMR chemical shifts suggest that the magnitude of ring current is stronger in the center. This is well-reflected in the magnitude of the local induced magnetic fields in anthracene. The terminal ring shows a ring current that is 83–84% of that in benzene, whereas the central ring shows a diatropic ring current that is 104–111% of that of benzene. Please note that the average ring current in anthracene

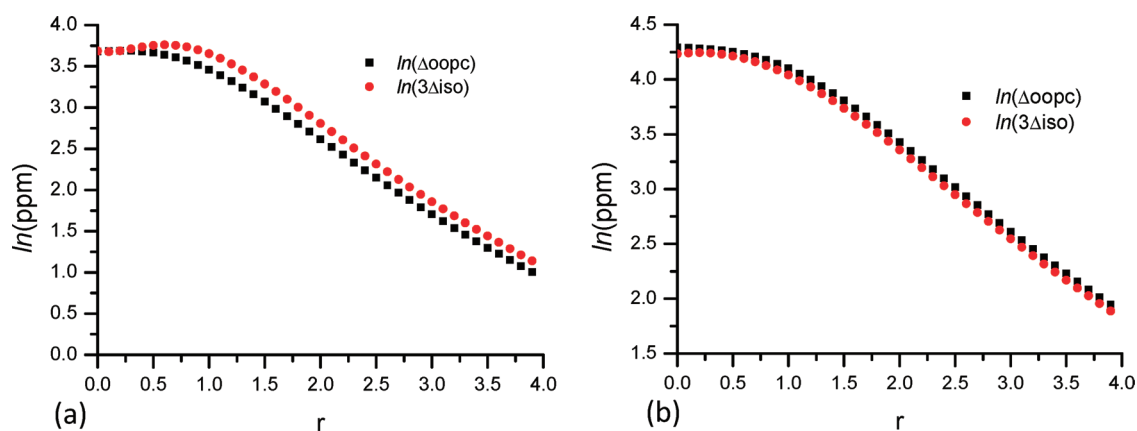


FIGURE 6. A plot of (black) $\ln(\Delta(\text{oopc}))$ and (red) $\ln(3\Delta(\text{isotropic shifts}))$ for (a, left) benzene and (b, right) planar-cyclooctatetraene (GIAO-HF/6-311+G(d)).

TABLE 1. Average Ring Current Values and Their Relative Intensity to Benzene for 1–6

compd	intensity (ppm)		relative intensity (%)	
	HF	B3LYP	HF	B3LYP
1	-36.8 ± 4.0	-34.0 ± 4.2	100	100
2	44.0 ± 3.3	42.0 ± 3.7	119	123
3	-24.5 ± 2.4	-21.8 ± 2.8	67	64
4	-2.1 ± 1.4	-5.4 ± 1.3	6	16
5	63.4 ± 2.3	101.0 ± 2.5	172	297
6-terminal	-30.4 ± 2.5	-28.6 ± 1.1	83	84
6-central	-41.0 ± 1.4	-35.3 ± 1.2	111	104

is 91–92% of that of benzene, in accordance with other methods (e.g., resonance energy per electron, REPE).¹³

The natural comparison of these results is to current density analysis. However, the two methods yield different measures. NICS reports magnetic fields that result (here) from induced ring currents. Thus, at a given distance there is a magnetic field of certain intensity that may be viewed as an integral property of the total ring current. The current density is not homogeneous and therefore cannot be directly compared to a single value of a magnetic field. For the comparisons below the maximum current is used. Unfortunately not all the data are available in the literature, and those available are not always reported in a way that allows comparisons. In anthracene, the current density is discussed over the whole system.¹⁴ Nevertheless, Anusoota et al.¹⁵ assign ring currents to the specific rings, the naphthalene

substructure, and the whole system of anthracene. A summation of these suggests that the central ring of anthracene has a ring current that is 205% of benzene and the terminal ring that is 138% of benzene. Although the absolute numbers are different considerably than the numbers we obtain here,¹⁶ the ratio between the ring currents of the two anthraceneic rings is 1.49, whereas our analysis suggests a very close ratio of 1.24–1.33 (for B3LYP and HF, respectively). Cyclobutadiene is reported in magnetic exaltation units¹⁷ and thus cannot be compared to our results. The only direct comparison that can be made is between **1** and **5**. The ratio of the ring current (COT/benzene) is reported by Soncini et al. to be 2.20 at the HF level, 4.00–4.41 at two different DFT levels, and 3.61 at CCSD.¹⁸ Havenith and Fowler report a ratio of 3.48 and 3.94 at B3LYP and PBE, and 1.65 at HF.¹⁹ Soncini and Fowler report two methods that yield a ratio of 1.56 and 1.59.²⁰ In a different paper these

(13) See, for example: (a) Herndon, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 2404–2406. (b) Herndon, W. C.; Ellzey, M. L., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 6631–6642.

(14) See, for example: (a) Fowler, P. W.; Steiner, E. *Chem. Phys. Lett.* **2002**, *264*, 259–266. (b) Steiner, E.; Fowler, P. W.; Havenith, R. W. A. *J. Phys. Chem. A* **2002**, *106*, 7048–7056. (c) Steiner, E.; Fowler, P. W. *Int. J. Quantum Chem.* **1996**, *60*, 609–616.

(15) Anusooya, Y.; Chakrabarti, A.; Pati, S. K.; Ramasesha, S. *Int. J. Quantum Chem.* **1998**, *70*, 503–513.

(16) Also, these large ring currents are not consistent with common knowledge, for example, NMR chemical shifts and REPE.

(17) Pelloni, S.; Ligabue, A.; Lazzeretti, P. *Org. Lett.* **2004**, *6*, 4451–4454.

(18) Soncini, A.; Teale, A. M.; Helgaker, T.; De Proft, F.; Tozer, D. J. *J. Chem. Phys.* **2008**, *129*, 074101–1–15.

(19) Havenith, R. W. A.; Fowler, P. W. *Chem. Phys. Lett.* **2007**, *449*, 347–353.

(20) Soncini, A.; Fowler, P. W. *Chem. Phys. Lett.* **2004**, *396*, 174–181.

authors report a ratio of 1.66.²¹ Both HF (1.72) and B3LYP (2.97) ratios obtained from the model presented here are within the current density results and reproduce well the difference between HF and B3LYP that was observed in the current densities studies. Another qualitative comparison that can be made is for **4**, where both current density analyses and the method that is presented here agree that the diamagnetic ring current vanishes.^{20–22}

Charged Systems. Cations and anions present an important group within aromatic and antiaromatic molecules. Devising a σ -only model for these systems poses a problem. For a charged cyclo-*n* system a model may be an *n*-1 hydrogenated system (in the same fashion as described earlier) or an *n*-hydrogenated system without a charge. On the basis of comparison to the NCS method (see below) it was decided to use the second alternative (i.e., *n*-hydrogenated, no charge) as the σ -only model. Table 2 shows the average chemical shifts at 1 Å above the molecular plane for **7–9** and the relative values to benzene. Comparison with available data of current density analysis suggests that, compared to benzene, cyclopentadienyl has a slightly reduced ring current (89.5–90.0%) and the tropylium cation is about the same as benzene (103.8–103.9%).²¹ Although the agreement between the current density and the results presented here is good, the NCS analysis (see below) suggests that the current density analyses overestimate the ring currents (relative to benzene). Please also note the similarity between the HF and B3LYP results for the aromatic **7** and **9** and the big respective difference for **8** which has a small HOMO–LUMO gap, supporting the model presented here.

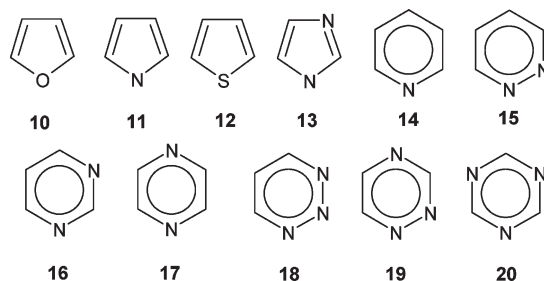
TABLE 2. Average Ring Current Values and Their Relative Intensity to Benzene for **7–9** at GIAO-HF/6-311G* and B3LYP/6-311++G**



compd	intensity (ppm)		relative intensity (%)	
	HF	B3LYP	HF	B3LYP
7	-28.0 ± 0.4	-26.2 ± 0.3	76	77
8	97.5 ± 5.4	188.5 ± 5.3	265	554
9	-36.1 ± 4.3	-33.6 ± 4.4	98	99

Heterocycles. Devising a proper σ -only model for heterocyclic systems is not trivial. In a five-membered ring (e.g., pyrrole), the possibilities are tetrahydrogenated systems or pentahydrogenated with a positive charge (i.e., protonated tetrahydrogenated). In addition, when optimizing the hydrogenated models the proton on the heteroatom tends to open the H–X–ring angle (e.g., in hexahydropyridine to approach the stable NR₃ geometry), which leaves active π electrons in the reference systems. The procedure for building a reference system for heterocyclic compounds is the

TABLE 3. Average Ring Current Values and Their Relative Intensity to Benzene for **10–20**



compd	intensity (ppm)		relative intensity (%)	
	HF	B3LYP	HF	B3LYP
10	-20.0 ± 3.0	-21.4 ± 3.1	54	63
11	-25.3 ± 2.2	-27.5 ± 2.9	69	81
12	-21.5 ± 2.8	-22.1 ± 2.1	59	65
13	-24.2 ± 2.6	-24.2 ± 2.7	66	71
14	-31.3 ± 3.0	-28.6 ± 3.6	85	84
15	-34.8 ± 5.2	-32.5 ± 5.3	95	96
16	-28.5 ± 3.6	-24.2 ± 2.9	78	71
17	-34.7 ± 4.7	-28.9 ± 4.2	94	85
18	-30.1 ± 4.8	-22.6 ± 3.7	82	66
19	-26.5 ± 3.5	-19.8 ± 3.2	72	58
20	-19.8 ± 1.9	-15.5 ± 1.4	54	46

following: (a) All the atoms in the ring have to be hydrogenated. A positive charge should be used where applicable. (b) The hydrogen atom(s) connected to the heteroatom(s) should not be optimized. The H–heteroatom–ring angle should be 95–102° and the X–H should be a typical X–H bond length. The results have a very small sensitivity to the above-mentioned geometrical parameters.

Table 3 shows the chemical shifts for **10–20**. The five-membered heterocycles show considerable reduction (19–34%) of ring current relative to benzene. This fits the organic chemical intuition since the five-membered-ring heterocycles undergo relatively easy reactions which are typical to 1,4-dienes. The six-membered rings can be divided into three groups: **14** with one nitrogen, **15–17** with two nitrogen atoms, and **18–20** with three nitrogen atoms.

Pyridine has a 15% reduced ring current relative to benzene. Among the group that contains two nitrogen atoms, the pyridazine (**15**) has the largest ring current and the smallest one belongs to pyrazine (**17**). Among the triazines a similar trend is observed: The closer the nitrogen atoms are, the stronger is the ring current. Generally, the triazines (**18–20**) show reduced ring current compared to diazines (**15–17**).

Pelloni et al. published a current density study on different five-membered rings,²³ but the data are graphic and cannot be directly compared to the results here. Anusooya et al. obtained (at the PPP level) ring current ratios which are similar to what we obtain here at the HF level: 97.0% for pyridine (**14**) and 97.6% for pyrazine (**17**).¹⁵ Jusélius and Sundholm used their own ARCS method to calculate ring current in different systems.²⁴ They obtained much stronger

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(22) (a) Soncini, A.; Havenith, R. W. A.; Fowler, P. W.; Jenneskens, L. W.; Steiner, E. *J. Org. Chem.* **2002**, *67*, 4753–4758. (b) Fowler, P. W.; Havenith, R. W. A.; Jenneskens, L. W.; Soncini, A.; Steiner, E. *Chem. Commun.* **2001**, 2386–2387.

(23) Pelloni, S.; Faglioni, F.; Zanasi, R.; Lazzeretti, P. *Phys. Rev. A* **2006**, *74*, 012506–1–8.

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ring currents for the heterocyclic systems relative to benzene: 96.9%, 129.0%, and 100.0% for **10**, **11**, and **12**, respectively. However, ARCS also assigns a ring current to cyclopentadienyl anion to be 225% relative to benzene, so it seems that this method assigns different numbers than other current density methods. Nevertheless, if the ARCS of **10–12** are compared, **10** and **12** have ring currents of 75.1% and 77.5% relative to **11**, whereas here we get the respective ratios of 75.9% and 85.2% at HF, i.e., in at least a semiquantitative agreement. It is worth noting that a study of a few aromaticity indices has found the same order for aromaticity for **15**, **17**, **16**, and **20** as the order of magnitude of the ring current that is found here.²⁵ However, pyridine (**14**) was found to be more aromatic than **15**, whereas the intensity of the ring current found here is about the same as that for **17**. It is also noted that some aromaticity indices failed to arrange this order and that the NCS analysis (see below) supports the order obtained here.

Substituted Benzenes. It is well established that electronically active substituents (e.g., OR, BR₂) reduce the ring current of benzene.²⁶ Therefore, **21–26** were calculated to see if the method that is presented here can reproduce this. The construction of the σ -only model for these systems is identical with that of the uncharged hydrocarbons **1–6**. Table 4 shows the results. To the best of our knowledge there are no current density data available for these systems, but the results fit the chemical intuition. (a) All the substituted systems have ring currents that are smaller than that in benzene. (b) The more substituted the system is, the weaker the ring current becomes. (c) Whereas OH is a π donor, BH₂ is a π acceptor. Therefore in the OH and BH₂ substituted systems the quinoid resonance structures which are responsible for the attenuation of the ring currents are impotent. The fact that both attenuate the ring current to about the same extent suggests that the π donation ability of OH is similar in magnitude to the π accepting ability of BH₂.

	R1	R2	R3
21	OH	H	H
22	OH	OH	H
23	OH	OH	OH
24	BH ₂	H	H
25	BH ₂	BH ₂	H
26	BH ₂	BH ₂	BH ₂

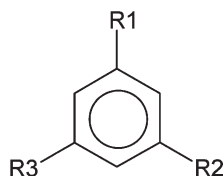


TABLE 4. Average Ring Current Values and Their Relative Intensity to Benzene for **21–26**

compd	intensity (ppm)		relative intensity (%)	
	HF	B3LYP	HF	B3LYP
21	-33.9 ± 3.1	-30.1 ± 3.0	92	88
22	-29.7 ± 2.0	-25.1 ± 1.5	81	74
23	-24.8 ± 0.9	-19.1 ± 0.4	67	56
24	-34.7 ± 3.8	-31.0 ± 3.9	95	91
25	-28.9 ± 2.2	-25.3 ± 2.5	79	74
26	-25.7 ± 1.9	-22.4 ± 1.9	70	66

Comparison with NCS. As mentioned in the Introduction, the NCS analysis, which is a part of NBO 5, can provide specific contributions to a chemical shift or to their respective

tensors. This can be done in two alternative ways: One is through the localized bonds that are calculated by NBO and the second is through canonic molecular orbitals. The first option is somewhat problematic. For example, the population of the three localized π bonds in benzene is 4.99263 electrons. The population of the π^* bonds is 0.99774 electrons. Thus, the sum of electrons in the localized π bonds is 5.99 electrons instead of 6. It does not seem to be a large difference, but when analyzing the π contribution to the oopc of, for example, NICS(0) and NICS(1) it is 33.95 and 28.74, respectively, whereas from the canonic MO it is 35.71 and 29.04, respectively. Thus, the small fraction of the electron density that occupies many of the Rydberg functions does make a difference in the quantitative analysis. Artifacts resulting from this are further discussed in the Supporting Information for **18–20**. The analysis according to canonical MOs is therefore favored, but it has its own disadvantages. Thus, in systems that contain a mixture of the substituents' orbitals into the ring's π orbitals (e.g., **3**, **21–23**, and some of the heterocycles) the respective canonic MOs are not identical to the π MOs and therefore their contributions to the chemical shifts is different. It is practically impossible to retrieve the net effect of the ring's π electrons in the NICS. However, for most of the systems discussed here the canonic π MOs are identical with the π MOs and can therefore be compared. Figure 7 shows examples of four such comparisons (all the comparisons can be found in the Supporting Information). Indeed, between 0 and 1 Å there are discrepancies between $\Delta(\text{oopc})$, $3\Delta(\text{iso})$, and the NCS curve, but at distances larger than 1 Å (which are used for the quantitative determination of the ring current) the agreement between the NCS analysis and the model presented here is remarkable. The NCS is always between $\Delta(\text{oopc})$ and $3\Delta(\text{iso})$, emphasizing the necessity for a measure of the goodness of the model used, and does not exist in NCS (or in CMO-IGLO) and is a built-in feature of the model presented here. Of course, systems like **3** and **21–23** can be easily analyzed with the σ -only model.

Conclusions

A construction of model systems for producing the effect of σ electrons on the oopc of the NICS is described. Subtracting the oopc of the model from the oopc of the studied molecule enables obtaining NICS values that are induced by the π electrons only. This allows a quantitative comparison between the ring currents in different systems. The goodness of the model can be evaluated by comparing the ipc's of the system and its σ -only model, and should be zero for a perfect model. The model systems which are suggested here produce a difference in the range of ± 2 to ± 3 ppm. A comparison between the differences of the oopc and three times the differences of the isotropic NICS value of the system and its σ -only model allows a quantitative assessment of the goodness of the model. This is done through a linear correlation of the logarithm of these differences as functions of distance from the molecular planes and extrapolations to

(25) Feixas, F.; Matito, E.; Poater, J.; Solá, M. *J. Comput. Chem.* **2008**, *29*, 1543–1554.

(26) One of the ways to rationalize this is the existence of quinoid canonic structures which do not have ring currents.

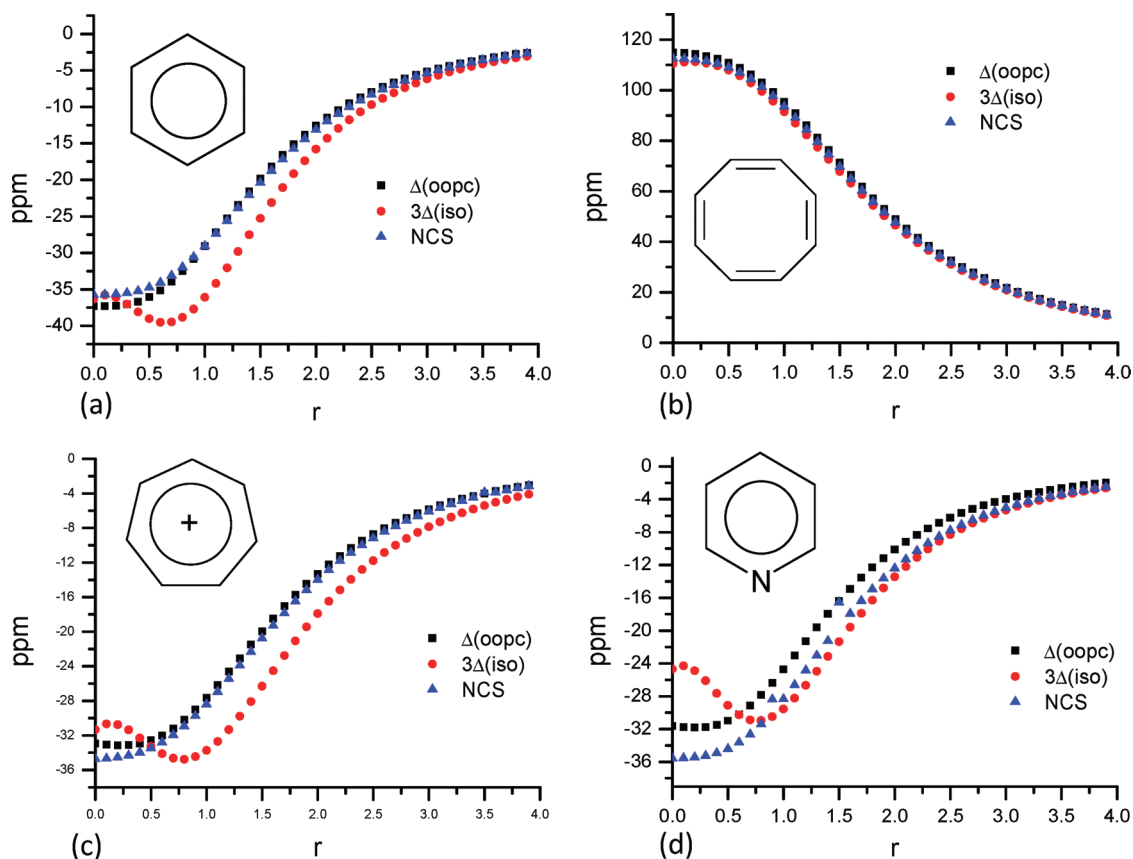


FIGURE 7. Comparisons (at B3LYP/6-311++G**) between the σ -only model (oopc, black squares; $3\Delta(\text{iso})$, red circles) and NCS analysis (blue triangles) for (a) benzene (**1**), (b) planar-cyclooctatetraene (**5**), (c) tropylium (**9**), and (d) pyridine (**14**).

the values 1 Å above the molecular planes which are about the same as the values in the molecular plane. This model has been shown to work for charged and uncharged aromatic and antiaromatic systems, heterocycles, and substituted benzene derivatives, with good agreement to available current density data and to chemical intuition. A comparison to the NCS computational model shows a remarkable agreement between the two for systems that can be compared. The σ -only model is, however, more general since it takes care only on the π electrons of the studied ring, contains a built-in measure for its goodness, and avoids

artifacts such as those found for **18–20** which result from the localized bond model. In summary, this paper introduces a chemical model as an alternative for the mathematical models for obtaining relative intensities of ring currents through NCS.

Supporting Information Available: All the geometries of the systems that are discussed in the paper and the comparisons between the σ -only model and NCS. This material is available free of charge via the Internet at <http://pubs.acs.org>.