The Relation Between Ring Currents and Aromatic Stabilization Energies for Assessing the Degree of Aromaticity

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Abstract

Magnetically induced ring-current strength susceptibilities and nucleus independent chemical shifts (NICS) have been studied for 15 single-ring aromatic, antiaromatic and nonaromatic molecules. The current densities have been calculated at the density functional theory (DFT), Hartree-Fock (HF), and second-order Møller-Plesset perturbation theory (MP2) levels using the gauge-including magnetically induced current method (GIMIC). The ring-current strength susceptibilities have been obtained by numerical integration of the current density flowing around the molecular ring. The calculated ring-current strength susceptibilities are almost independent of the level of theory. The relative degree of aromaticity deduced from the magnetic properties has been compared with the ones deduced from hydrogenation enthalpies that are considered to be proportional to aromatic stabilization energies (ASE). For the studied single-ring molecules, GIMIC, NICS and ASE calculations yield similar trends. The study shows that there is a linear correlation between the magnetic and energetic criteria of aromaticity. The largest uncertainty originates from the accuracy of the energy data, because they are much more dependent on the employed computational level than the calculated magnetic properties. Thus, ring-current strength susceptibilities can be used for assessing the degree of aromaticity.

1 Introduction

Even though aromaticity is an important concept in chemistry, it is still not understood how to unambiguously determine the degree of aromaticity from electronic structure calculations and therefore it is continuously under debate.[1–8] Experimentally, aromaticity is known to lead to energy stabilizations, equalizations of bond lengths, preferred substitution reactions, and magnetic properties that differ from those of nonaromatic molecules.[9–21] Based on calculations, it has been suggested that molecular structures, electron sharing, and bond energies

belong to the same class of properties as aromaticity implying that the degree of aromaticity can be estimated by using them as indicators.[8] The magnetic criterion obtained in calculations and experimental proton nuclear magnetic resonance (^{1}H NMR) chemical shifts predict concordant degrees of aromaticity.[22–27]

The underlying reason for the aromaticity of organic molecules is electron delocalization in conjugated chemical bonds that form closed two- and three-dimensional electronic pathways sustaining ring currents when the molecule is exposed to an external magnetic field. The closed electron delocalization pathway of aromatic molecules leads to a stabilization of the molecule that influences its molecular structure, dissociation energy and spectroscopic properties. ^{1}H NMR chemical shifts are a particularly important indicator of aromaticity, since the ^{1}H NMR spectra show specific features such as a deshielding and downfield shift for the resonances of the protons that are attached to the exterior part of an aromatic ring.[28,29] The influence of the aromaticity on the ^{1}H NMR chemical shifts can be explained with the so called ring-current effect,[28–30] which opens the possibility for assessing the degree of aromaticity by investigating molecular magnetic properties. Calculations of magnetic properties are much simpler than estimating aromatic stabilization energies (ASE) using a series of calculations of homodesmic reaction energies.[31–33]

In the presence of an external magnetic field, aromatic molecules sustain a magnetically induced ring current that generates an induced magnetic field in the opposite direction to the applied one, whereas molecules that strengthen the applied magnetic field are said to be antiaromatic. In aromatic molecules, the electrons circle in the classical (diatropic) direction, whereas antiaromatic molecules are dominated by ring currents in the nonclassical (paratropic) direction.[34] Magnetically induced current densities have not yet been measured directly, but they are indirectly accessible through measurements of ^{1}H NMR chemical shifts and magnetizabilities. By investigating the pattern of magnetically induced current densities, one can obtain a deeper understanding of aromatic properties and more detailed interpretations of experimental ^{1}H NMR spectra.[35–38]

Magnetically induced current densities can be obtained by using quantum chemical calculations.[30,34,39–45] Integration over the current flow passing selected bonds yields a very reliable aromaticity index as first shown by Sundholm and coworkers, which has later been confirmed by others.[40,41,43,44,46–49] Magnetic properties such as magnetic susceptibility anisotropy, magnetic susceptibility exaltation, bond magnetizabilities and nucleus independent chemical shifts (NICS) have also been studied in order to estimate the degree of aromaticity according to the magnetic criterion.[30,50,51]

Recently, Frenking *et. al.* published a study of seven molecules consisting of six-membered rings of which two structures were transition states and concluded that there is no correlation between magnetic and energetic aromaticity criteria.[52] They recommended the use of the Giambiagi electron delocalization index[53] that is based on the electron density for determining the degree of aromaticity.[52] This is somewhat surprising, since a study by Cioslowski *et al.* showed already ten years ago that the Giambiagi index should be used with caution to assess aromaticity because of its strong sensitivity to the quality of the employed wave function and its inability to distinguish between anti- and nonaromatic systems.[54] In contrast, the magnetic criterion is rather insensitive to the employed theoretical level as shown in the present work.

The HF trimer was used by Frenking *et al.* to criticize the magnetic criterion for determining the degree of aromaticity, because $(HF)_3$ is a case where NICS calculations fail to predict the correct aromatic character.[55] However, current density calculations indicate that the NICS approach is unreliable for that system, since integration of the ring-current strength susceptibility shows that $(HF)_3$ sustains a very weak ring current and must be considered nonaromatic.[56] In their article, Frenking *et al.* did not discuss results obtained by explicit current-density calculations on $(HF)_3$. They also concluded that Sc_3^- based on NICS calculations sustains a paratropic ring current, citing a study by Badri *et al.*,[8] where Sc_3^- is not at all discussed. This is somewhat surprising, especially when they present their criticism of the magnetic aromaticity criterion by stating: "triatomic Sc_3^- that in spite of

sustaining paramagnetic current is a global minimum on its potential energy surface", which is a statement that has nothing in common with the magnetic aromaticity criterion. In fact, NICS calculations suggest that Sc_3^- is aromatic, whereas according to current density calculations at the complete active space self-consistent-field (CASSCF) level, Sc_3^- is practically nonaromatic,[48] showing that explicit integration of ring-current strength susceptibilities is a more reliable approach than NICS values to determine the degree of aromaticity according to the magnetic criterion.

It is a common misconception that NICS and current density calculations are identical approaches by referring to the Biot-Savart relation. A number of studies have shown that current strength susceptibilities obtained from magnetic shielding data depend on the assumed current-pathway model. This is the reason why shielding based approaches results in significant uncertainties in current strength susceptibilities, current pathways, and the degree of aromaticity, in particular when complicated molecules are under consideration. This has been pointed out by several research groups.[34,48,57–64,81] Thus, explicit current density calculations are more reliable as compared to NICS values. The calculated current density provides deep insights in particular for complicated ring systems. This is a reason why general conclusions concerning the magnetic aromaticity criterion should not be based on NICS studies only.

In the present work, we investigate whether the magnetic criterion can be used for assessing the degree of aromaticity and whether the magnetic aromaticity criterion is related to the aromatic stabilization energies or not. Mucsi *et al.* estimated the degree of aromaticity for a number of molecules using hydrogenation enthalpies, which is basically another means to estimate the degree of aromaticity through calculations of aromatic stabilization energies (ASE).[65] Here, we study the degree of aromaticity for the Mucsi set of 15 molecules consisting of one molecular ring. The degree of aromaticity has been estimated by calculating and analyzing the magnetically induced current density and nucleus independent chemical shifts. The results are compared to the degree of aromaticity calculated by Mucsi *et al.* using

hydrogenation enthalpies.[65]

The paper is organized in the following manner. We present the computational details in section 2. In section 3, the calculated ring-current strength susceptibilies and NICS values are discussed and the relative aromaticities are compared with the ones deduced from ASE energies. The final conclusions are drawn in section 4.

2 Computational details

The molecular structures were optimized at the density functional theory (DFT) level employing Becke's three-parameter functional in combination with the Lee-Yang-Parr correlation functional (B3LYP).[66,67] We used the Gaussian 09 program[68] and the 6-31G(d) basis set[69] in the structure optimization in order to obtain the same molecular structures as used in Ref. 65. Vibrational frequencies were calculated to ensure that the obtained molecular structures are minima on the potential energy surfaces.

The studied molecules shown in Figure 1 are benzene C_6H_6 (**1**), cyclobutadiene C_4H_4 (**2**), cyclohexadiene C_6H_8 (**3**), pyridine C_5H_5N (**8**), pyrimidine $C_4H_4N_2$ (**9**), furan C_4H_4O (**10**), pyrrole C_4H_5N (**11**), thiophene C_4H_4S (**12**), phosphole C_4H_5P (**13**), azete C_3H_3N (**18**), 3-methylene-2-oxiranone $C_3H_2O_2$ (**19**), 1H-acet-2-one C_3H_3NO (**20**), 2H-thiet-2-one C_3H_2OS (**21**), 1H-phosphet-2-one C_3H_3OP (**22**), and cyclooctatriene C_8H_{10} (**26**). The molecular structures are visualized using VMD.[70] We use the same numbering of the molecules as introduced by Mucsi *et al.*[65]

Nuclear magnetic shieldings were calculated for the optimized structures at the B3LYP level using the def2-TZVP basis sets.[71,72] The magnetic shieldings were calculated with Turbomole.[73–75] The magnetic shieldings were also calculated at the Hartree-Fock (HF) and second-order Møller-Plesset perturbation theory (MP2) level using Turbomole.[73,76,77] Magnetically induced current density susceptibilities were calculated at the same levels of theory with the GIMIC program.[40] GIMIC is an open-source program that uses the one-electron

density matrix and the magnetically perturbed one-electron matrices as well as basis-set information as input data.[40,42–44] GIMIC is a free software that is available online.[78] Ring-current strength susceptibilities were obtained by integrating the current density susceptibility that passes a plane perpendicularly to the molecular ring. The integration domain starts in the middle of the ring and extends 5 bohr outside the molecule. The integration plane extends 5 bohr above and below the molecular ring.

The relative degree of aromaticity was obtained by using benzene and cyclobutadiene as reference molecules for typical aromatic and antiaromatic compounds, respectively. The obtained ring-current strength susceptibilities for benzene and cyclobutadiene at the B3LYP/def2-TZVP level are 11.99 nAT^{-1} and -19.91 nAT^{-1}, respectively, which we here assign to 100% aromaticity and -100% aromaticity (100% anti-aromaticity), respectively. The corresponding MP2 values are 12.32 (13.03) nAT^{-1} and -19.68 (-20.53) nAT^{-1} with the HF values given in parenthesis.

NICS values were calculated for comparison at the B3LYP/def2-TZVP level,[51,79] even though NICS values have been questioned as aromaticity index by a large number of researchers.[34,35,48,57–64,80,81] NICS(0) values are the negative isotropic shielding constant calculated in the center of the molecular ring and NICS(1) values are calculated 1 Å above the ring plane. The $\mathrm{NICS}_{zz}(0)$ and $\mathrm{NICS}_{zz}(1)$ values are obtained analogously by using the zz component of the nuclear magnetic shielding tensor in the ring center and 1 Å above it, respectively.

3 Results

The ring-current strength susceptibilities and NICS values calculated at the B3LYP level are summarized in Table 1 and Table 2. In Table 1, the degree of aromaticity (in %) relative to benzene and cyclobutadiene obtained from the ring-current strength susceptibility is compared to the aromaticity scale based on enthalpies of hydrogenation reactions calculated

by Mucsi *et al.*[65] They found that the degree of aromaticity deduced from the hydrogenation enthalpies are strongly basis-set dependent with up to 20% changes in both directions when increasing the basis-set size from 6-31G(d) to 6-311++G(2d,2p).[65] Current densities do not depend much on the basis-set quality when gauge-including atomic orbitals (GIAO) are employed.[82]

The current-density calculations at the DFT, HF and MP2 levels also show that practically the same ring-current strength susceptibilities are obtained for the studied molecules at these levels of theory. The linear regression coefficients for the fit of the ring-current strength susceptibilities calculated at the B3LYP and HF levels are $a = 0.991$ and $b = -0.433$ nAT^{-1} with an R^2 value of 0.994. a is the slope and b is the intercept. The corresponding coefficients for the linear fit of the B3LYP and MP2 data are $a = 0.968$ and $b = -0.288$ nAT^{-1} with an R^2 value of 0.999. The corresponding coefficients for the linear fit of the MP2 and HF data are $a = 1.023$ and $b = -0.147$ nAT^{-1} with an R^2 value of 0.993. The plots of the fits are given as supporting information.

The ring-current strength susceptibility as well as all NICS flavors used in this study suggest that pyrrole is more aromatic than thiophene, which was also obtained in the ASE calculations and experimentally.[65] The same conclusion was drawn in a previous study.[51] In contrast, the Giambiagi index suggests that thiophene is more aromatic than pyrrole,[54] which agrees with the results of a recent shielding based study.[83] Thus, the aromaticity order of pyrrole and thiophene is not settled. However, in contrast to the Giambiagi index the calculated ring-current strength susceptibilities are not sensitive to the level of electron correlation treatment, since HF, MP2 and DFT calculations yield almost the same ring-current strength susceptibilities.

A comparison of the relative degree of aromaticity (in %) obtained from ring-current strength susceptibilities calculated at the B3LYP level and hydrogenation enthalpies taken from Ref. 65 is given in Figure 2. The black dashed line indicates the perfect agreement, whereas the red line is a linear regression fit to the calculated data. The individual data

points for each molecule are shown in red. The slope of the fitted curve is 1.035, which is very close to the ideal one of 1. The intercept is 14.6%. The correlation coefficient R^2 is 0.945. At the MP2 level, we obtained a slope of 1.060 and an intercept of 15.7% with an R^2 value of 0.939 for the fit. At the HF level, the corresponding data are 0.990, 14.7%, and 0.957.

Thus, the relative degree of aromaticity based on the ring-current strength susceptibility and on the aromatic stabilization energies agrees well. There is a clear correlation between the aromaticity indices of ring-current strength susceptibility and the energetic criterion. The largest uncertainty originates from the calculated enthalpies, which depend on the employed basis sets and level of theory. Ring-current strength susceptibilities are in general not sensitive to the employed computational level.[40]

Comparisons of the relative degrees of aromaticity (in %) obtained from NICS calculations and calculated hydrogenation enthalpies are shown in Figure 3. The correlation coefficients R^2 for NICS(1), NICS(1)$_{zz}$, NICS(0) and NICS(0)$_{zz}$ are 0.937, 0.927, 0.776 and 0.962, respectively. Thus, NICS(0)$_{zz}$ performs best for the studied molecules, whereas the NICS(0) values has the worst correlation with energy data. The NICS(1)$_{zz}$ index is generally considered as the best choice when contributions from all electrons are taken into account.[21] In the present NICS fits, the angular coefficients of 1.023, 1.043, 1.164, and 1.050 are very close to the perfect fit value of 1. In the corresponding study of Fallah-Bagher-Shaidaei *et al.*, the relation between ASE and NICS values were -1.730, -0.604, -1.213, and -0.506 kcal mol^{-1} ppm^{-1} for NICS(1), NICS(1)$_{zz}$, NICS(0) and NICS(0)$_{zz}$ calculations, respectively.[21] They did not report any relative degree of aromaticity that could be directly compared with the present results.

4 Summary and conclusions

Magnetically induced current density susceptibilities and nucleus independent chemical shifts have been calculated for 15 single-ring aromatic, antiaromatic and nonaromatic molecules containing heteroatoms. The relative degree of aromaticity deduced from the magnetic properties has been compared with the relative aromaticity deduced from hydrogenation enthalpies reported by Mucsi *et. al.*[65] The hydrogenation enthalpies are considered to be proportional to aromatic stabilization energies (ASE).

The integrated ring-current strength susceptibilities have been calculated using the gauge including magnetically induced currents (GIMIC) approach.[40,44] The nucleus independent chemical shifts (NICS) values are the negative magnetic shieldings calculated in selected points.[51] The aromatic scales have been obtained by setting the ring-current strength susceptibilities and NICS values for benzene and cyclobutadiene to 100% and -100%, respectively. Thus, benzene and cyclobutadiene are assumed to be the archetypical aromatic and antiaromatic molecules. Linear regression shows that there is a clear correlation between the relative aromaticities obtained using the energetic and magnetic criteria. For the studied single-ring molecules, the fits of the GIMIC, NICS(1), NICS(1)$_{zz}$, NICS(0)$_{zz}$ data yield roughly concordant results. The NICS(0) index is less reliable that the other ones employed in this work. The largest uncertainty is due to the accuracy of the employed energy data, because enthalpies are much more dependent on the employed computational level and basis set than the calculated magnetic properties. Ring-current strength susceptibility calculations at B3LYP, HF and MP2 levels of theory yield qualitatively the same degree of aromaticity. Figure 4 shows an overview of the relative deviations of the GIMIC and NICS methods with respect to the hydrogenation energies.

The general applicability of the magnetic criterion for assessing the degree of aromaticity has been questioned in a recent study by Frenking *et. al.*[52] Instead of adopting the magnetic criterion Frenking and co-workers recommended to use the Giambiagi index[53] as a more reliable means for assessing the degree of aromaticity. However, it is known that the Giambiagi

index should be applied with caution to assess aromaticity because of its strong sensitivity to the quality of the employed wave function and its inability to distinguish between anti- and nonaromatic systems,[54] which is not the case for ring-current strength susceptibilities. It is important to stress that Frenking *et al.*[52] studied only 7 molecules of which 2 are higher-order transition states. Thus, it is hard to consider their conclusions of general relevance. In contrast, Fallah-Bagher-Shaidaei *et al.*[21] studied 75 molecules and found a correlation between the aromatic stabilization energy (ASE) and NICS. We have studied 15 further molecules and reached the same conclusion. The main limitation is the accuracy of the ASE data.

Our study shows that for the single-ring molecules, NICS and GIMIC yield similar trends. $\mathrm{NICS}_{zz}(0)$ is found to have the best correlation with energy data. However, for molecules consisting of several rings, the adjacent rings affects the current pathways and the induced magnetic field, rendering assessments of the degree of aromaticity using NICS values difficult.[35,36] In particular for weakly aromatic or for almost non-aromatic rings, NICS might lead to incorrect conclusions about molecular aromaticity,[56] because other currents than ring currents contribute to the magnetic shielding in selected points leading to NICS values that significantly differ from zero even though the molecule does not sustain any significant ring current as seen for example for the $(HF)_3$ trimer.[55,56] The present study shows that for common single-ring molecules, current-density and NICS calculations indeed yield the same relative aromaticity as the calculations of hydrogenation enthalpies. We obtained a linear correlation between the relative degree of aromaticity based on the magnetic and energetic criteria.

The aromatic character deduced from ring-current strength susceptibilities suggests that pyrrole is more aromatic than thiophene and furan, whereas the Giambiagi index suggests a different order.[54] The present study shows that there is clear evidence for a linear correlation between the aromatic stabilization energy and magnetic aromaticity indicators such as ring-current strength susceptibilities. Thus, the criticism of the magnetic aromaticity criterion

by Frenking *et al.* is not very well founded.[52]

Calculations of ring-current susceptibilities yield a very useful aromaticity index, because it is not sensitive to the employed level of theory and it can also be used in aromaticity studies of general molecules consisting of complex multiring structures.[84–93]

Acknowledgment

The Norwegian Research Council has supported this work through the CoE Centre for Theoretical and Computational Chemistry (Grant No. 179568/V30 and 231571/F20). The Academy of Finland has also supported this work through project 275845. We acknowledge computational resources from the Norwegian Supercomputing Program (NOTUR) grant No. NN4654K and from CSC – IT Center for Science, Finland.

Table 1: The ring-current strength susceptibility I (in nAT^{-1}) calculated at B3LYP/def2-TZVP level and the relative aromatic character (GIMIC in %) based on the calculated ring-current strength susceptibilities are compared with the relative aromatic character deduced from the zz component of the nucleus independent chemical shift calculated 1 Å above the ring and from the hydrogenation energies ($\Delta\Delta H_{H_2}$) calculated at the B3LYP/6-311++G(2d,2p) level of theory. The $\Delta\Delta H_{H_2}$ values are taken from Ref. 65. Benzene and cyclobutadiene are used as reference aromatic and antiaromatic molecules.

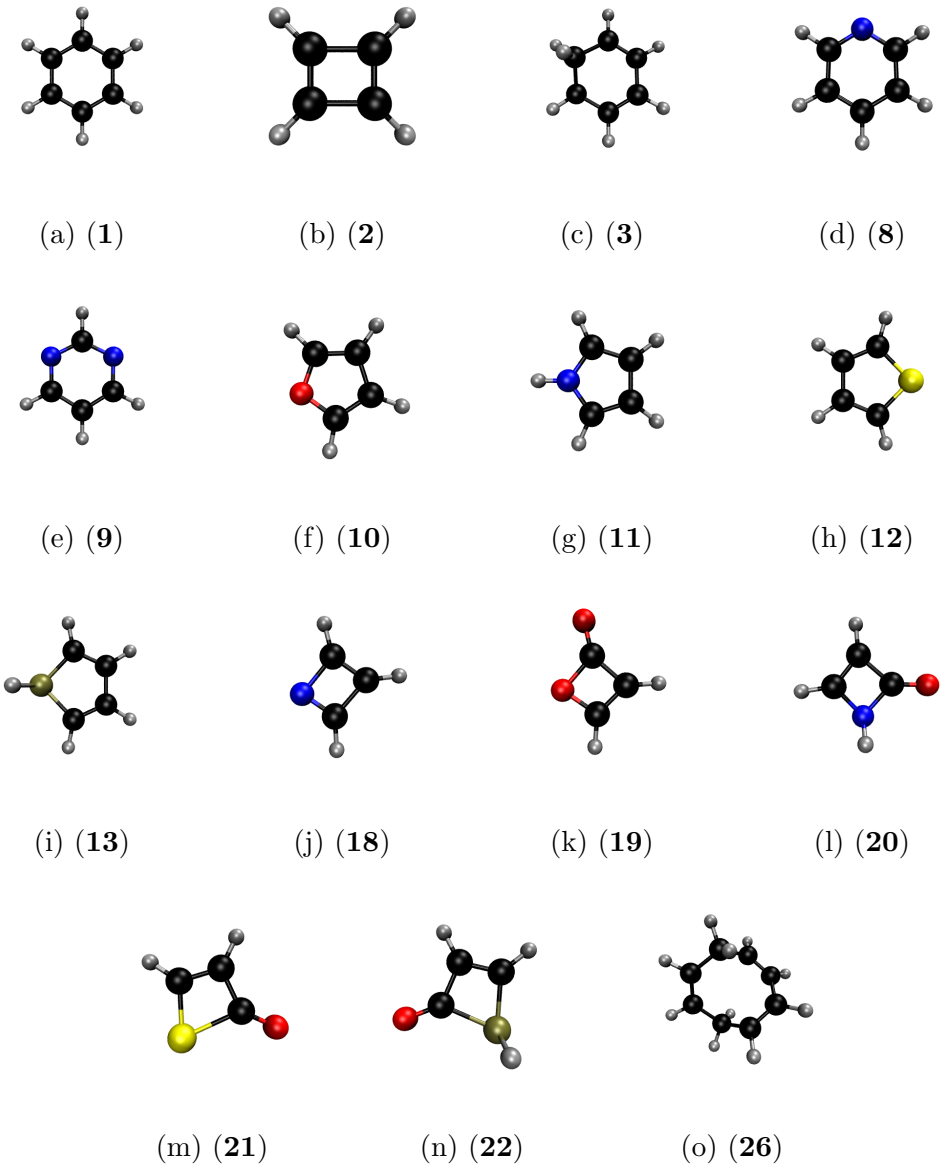
Molecule	Number	I	GIMIC %	$NICS_{zz}(1)$ %	$\Delta\Delta H_{H_2}$ %
C_6H_6	1	11.99	100	100	100
C_4H_4	2	-19.91	-100	-100	-100
C_6H_8	3	-0.39	-1.95	-7.4	2.35
C_5H_5N	8	11.47	95.66	97.9	97.25
$C_4H_4N_2$	9	10.62	88.57	93.8	76.45
C_4H_4O	10	10.21	85.15	94.3	57.42
C_4H_5N	11	11.67	97.33	107.1	64.53
C_4H_4S	12	11.41	95.16	98.1	51.94
C_4H_5P	13	6.59	54.96	52.6	14.38
C_3H_3N	18	-18.43	-92.56	-87.5	-103.20
$C_3H_2O_2$	19	-3.31	-16.62	-15.2	-36.03
C_3H_3NO	20	-3.00	-15.06	-13.5	-43.49
C_3H_2OS	21	-5.50	-27.62	-27.4	-27.71
C_3H_3OP	22	-1.71	-8.58	-11.2	-9.39
C_8H_{10}	26	2.59	21.6	-0.14	7.38

Table 2: Calculated B3LYP/def2-TZVP nucleus independent chemical shifts (NICS) values in ppm.

Molecule	Number	NICS(1)$_{zz}$	NICS(0)$_{zz}$	NICS(1)	NICS(0)
C_6H_6	1	-29.60	-16.05	-9.99	-8.12
C_4H_4	2	55.81	112.27	17.46	27.40
C_6H_8	3	4.14	24.14	0.07	-2.60
C_5H_5N	8	-28.97	-14.80	-9.95	-6.78
$C_4H_4N_2$	9	-27.77	-12.62	-9.70	-5.47
C_4H_4O	10	-27.91	-10.29	-9.34	-11.78
C_4H_5N	11	-31.71	-14.11	-10.25	-13.77
C_4H_4S	12	-29.04	-11.28	-10.19	-12.90
C_4H_5P	13	-15.58	4.33	-5.55	-5.44
C_3H_3N	18	48.84	114.62	14.38	29.07
$C_3H_2O_2$	19	8.46	44.39	1.23	1.56
C_3H_3NO	20	7.52	43.31	1.14	4.14
C_3H_2OS	21	15.31	48.15	3.04	3.83
C_3H_3OP	22	6.18	35.91	0.15	6.76
C_8H_{10}	26	0.08	5.94	-2.40	-1.13

Table 3: The ring-current strength susceptibility I (in nAT^{-1}) calculated at Hartree-Fock (HF) and second-order Møller-Plesset perturbation theory (MP2) level. The relative aromatic character (GIMIC in %) based on the calculated ring-current strength susceptibilities are also given.

Molecule	Number	I(HF)	%	I(MP2)	%
C_6H_6	1	13.03	100	12.32	100
C_4H_4	2	-20.53	-100	-19.68	-100
C_6H_8	3	-0.21	-1.02	-0.39	-1.98
C_5H_5N	8	12.46	95.62	11.97	97.15
$C_4H_4N_2$	9	11.29	86.64	11.42	92.69
C_4H_4O	10	9.95	76.36	11.05	89.69
C_4H_5N	11	12.16	93.32	12.52	101.62
C_4H_4S	12	11.36	87.18	12.33	100.08
C_4H_5P	13	5.82	44.66	7.19	58,36
C_3H_3N	18	-18.21	-88.69	-19.29	-98.01
$C_3H_2O_2$	19	-2.06	-10.03	-3.11	-15.80
C_3H_3NO	20	-1.89	-9.20	-2.57	-13.05
C_3H_2OS	21	-3.51	-17.09	-5.15	-26.16
C_3H_3OP	22	-0.92	-4.48	-1.70	-8.63
C_8H_{10}	26	2.32	17.80	2.66	21.59



(a) (**1**) (b) (**2**) (c) (**3**) (d) (**8**)

(e) (**9**) (f) (**10**) (g) (**11**) (h) (**12**)

(i) (**13**) (j) (**18**) (k) (**19**) (l) (**20**)

(m) (**21**) (n) (**22**) (o) (**26**)

Figure 1: Overview of investigated molecular structures. (**1**) benzene C_6H_6, (**2**) cyclobutadiene C_4H_4, (**3**) cyclohexadiene C_6H_8, (**8**) pyridine C_5H_5N, (**9**) pyrimidine $C_4H_4N_2$, (**10**) furan C_4H_4O, (**11**) pyrrole C_4H_5N, (**12**) thiophene C_4H_4S, (**13**) phosphole C_4H_5P, (**18**) azete C_3H_3N, (**19**) 3-methylene-2-oxiranone $C_3H_2O_2$, (**20**) 1H-azete-2-one C_3H_3NO, (**21**) 2H-thiet-2-one C_3H_2OS, (**22**) 1H-phosphet-2-one C_3H_3OP, and (**26**) cyclooctatriene C_8H_{10}. The numbering of the molecules is the same as employed in Ref. 65.

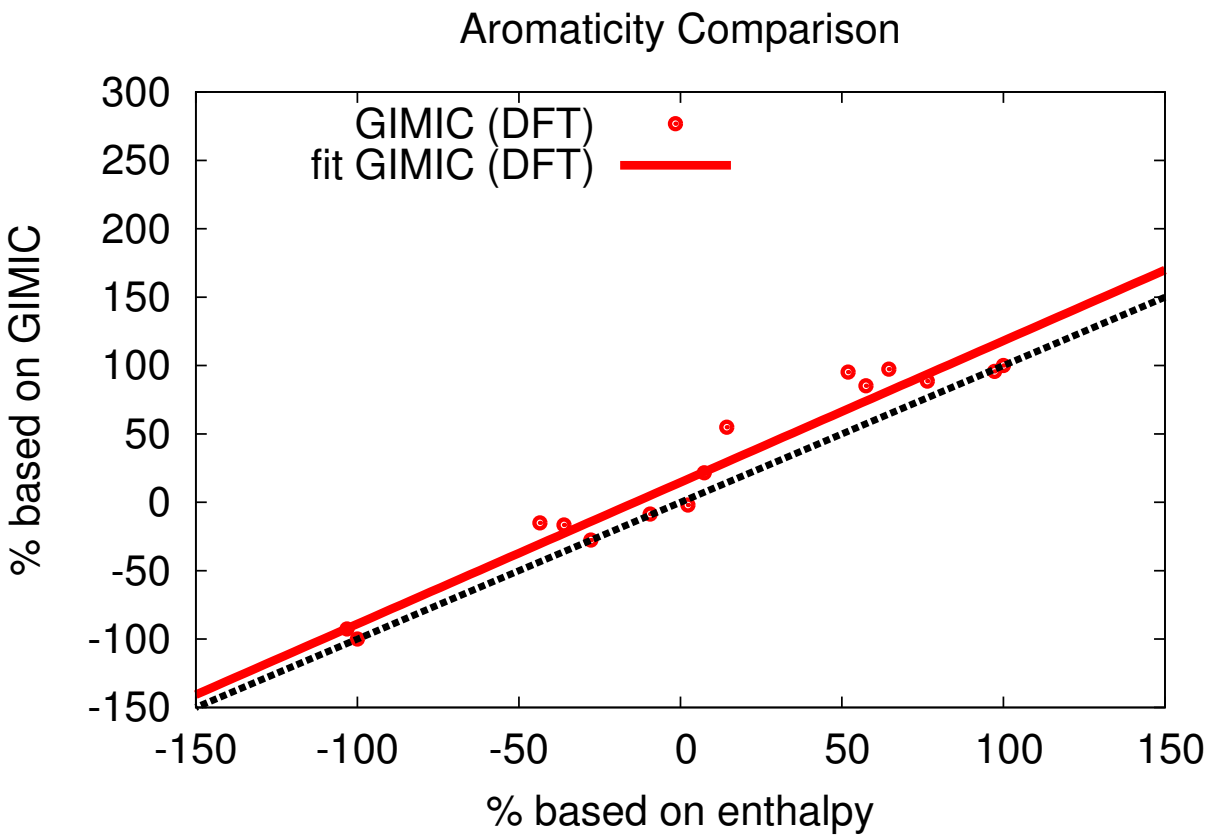


Figure 2: The linear regression fit of % of aromaticity based on GIMIC calculations at the DFT level. The fitting coefficients of $Y = aX + b$ are $a = 1.035$ and $b = 14.584\%$. The R^2 value for the correlations is 0.945. Perfect correlation is indicated with the dashed line. Errors in the coefficients are reported as supporting information.

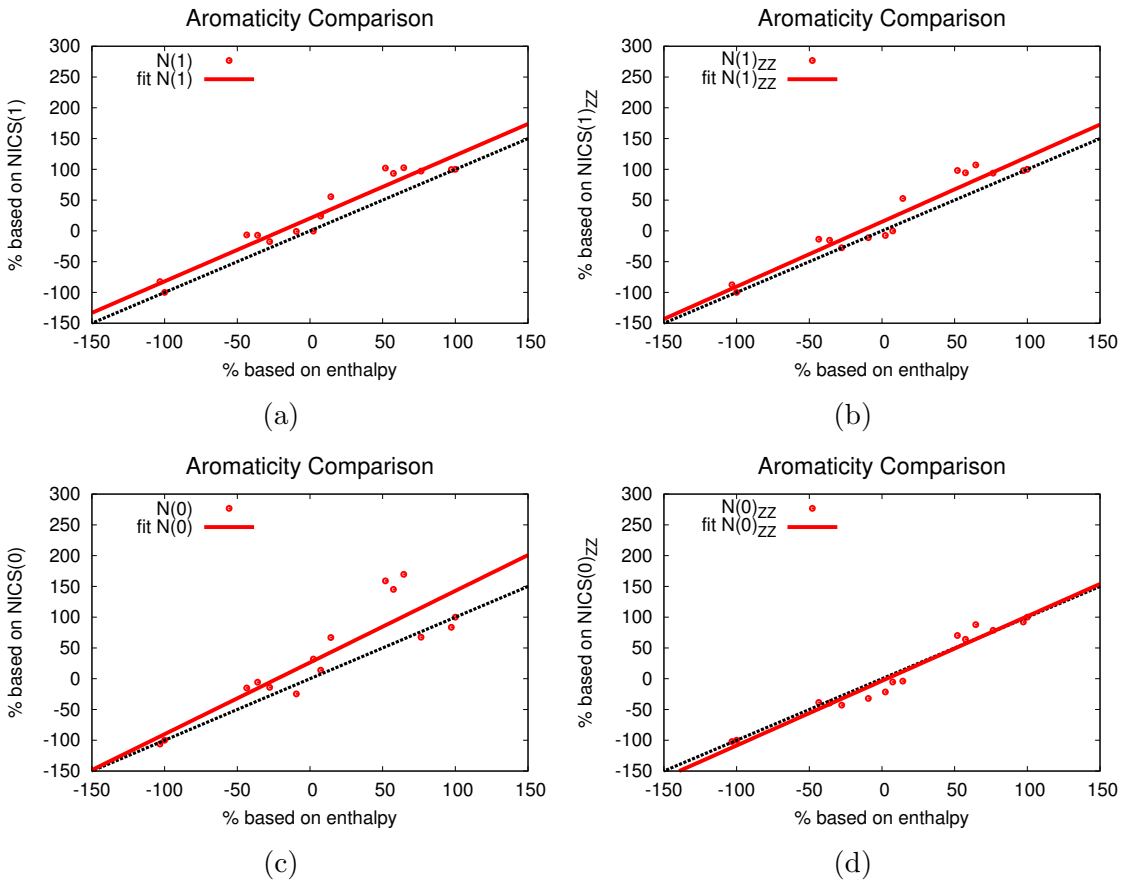


Figure 3: The linear regression fits for the NICS calculations at the DFT level. The fitting coefficients of $Y = ax + b$ are $a = 1.023$, $b = 20.294\%$, R^2=0.937 for (a), $a = 1.053$, $b = 14.792\%$, R^2=0.927 for (b), $a = 1.164$, $b = 26.326\%$, R^2=0.776 for (c), and $a = 1.050$, $b = -3.486\%$, R^2=0.962 for (d). Perfect correlation is indicated with the dashed lines. Errors in the coefficients are reported as supporting information.

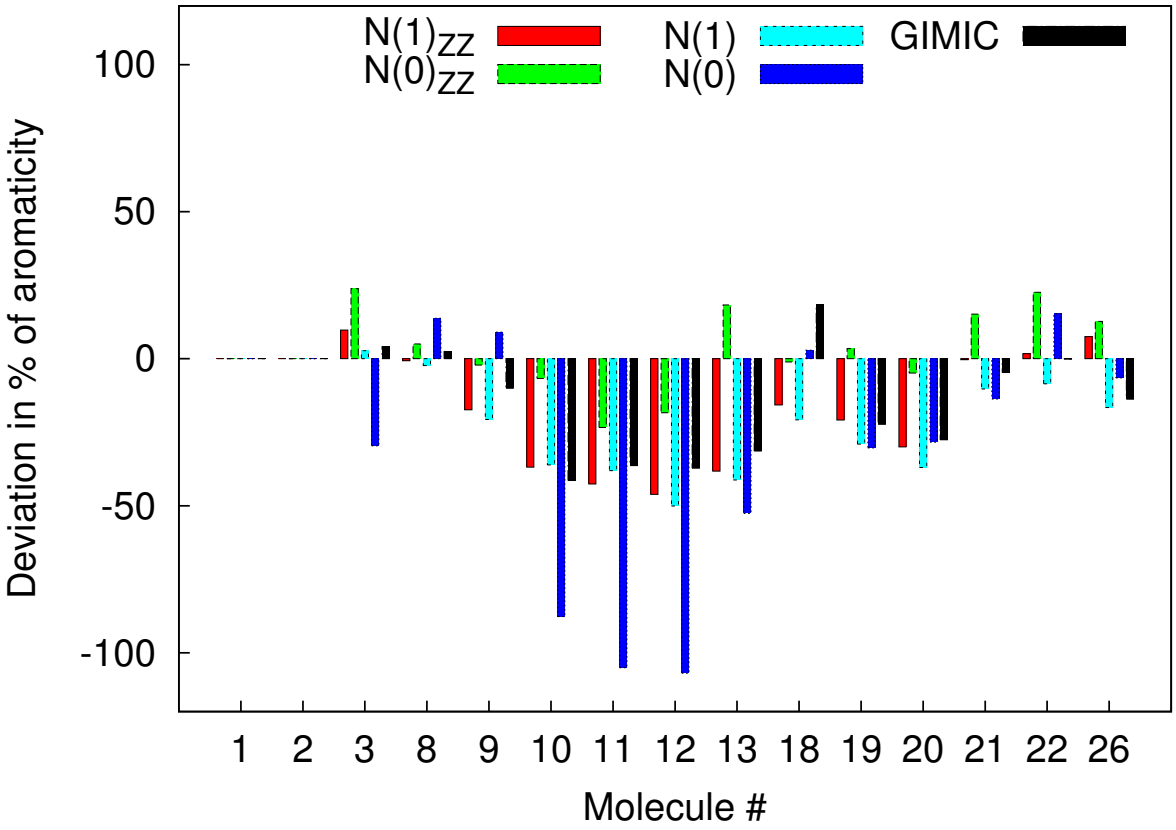


Figure 4: Overview of the deviations of the different methods as compared to the % of aromaticity based on the enthalpy, which has been taken as reference value. The present calculations have been performed at the B3LYP/def2-TZVP level.

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Supporting Information Available

Electronic supplementary information (ESI) available: Electronic energies, standard deviations of the fitting coefficients, and plots of the GIMIC fits are given in the supporting information. The Cartesian coordinates and isotropic NMR shielding constants of the investigated molecules are also reported as supporting information.

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Graphical TOC Entry