A new NICS-based aromaticity index; NICS-rate

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**A B S T R A C T**

The NICS-rate index is introduced as a new aromaticity indicator. The presence of a maximum/minimum in the NICS-rate curve (\(\frac{\Delta\sigma}{\Delta r}\) versus \(r\)) of a molecule indicates to aromaticity/antiaromaticity of the system. For those molecules, which show both maximum and minimum in their curves, the absolute ratio of the maximum to the minimum NICS-rates (NRR) is defined as a measure of aromaticity. Also NRR = 0.5 is found as the boundary between aromatic and nonaromatic systems. Surprisingly for those molecules in which NICS(0) cannot correctly give the aromaticities of the rings, the NICS-rate successfully predicts the aromaticities of the systems.

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1. Introduction

Aromaticity, the property resulting from cyclic conjugation [1], is an important concept in chemistry and has been subject of debate since the 19th century and is still an attracting considerable interest. Since high stability, low reactivity and sustained induced ring current imply to high aromaticity, therefore this concept is one of the features controlling the stability and reactivity of unsaturated cyclic and polycyclic compounds and has a key role in many reactions which occur in the biological systems. Theoretical investigation for the origin of this concept has gained a rapid development [2–7] and two issues of Chemical Reviews were dedicated to cover this topic [8,9]. Many efforts have been made to quantify aromaticity [10–12]; but since it is not a directly observable quantity therefore, it is usually evaluated indirectly by measuring a property that reflects the aromatic character of the molecule. Accordingly, aromaticities are evaluated on the basis of some energetic, geometric, electronic and magnetic criteria.

Several methods for the calculation of magnetic-based aromaticities are introduced [13–17]. One of the most widely used indices is the Nucleus-Independent Chemical Shift (NICS), which is defined as the negative of magnetic shielding in a given point of the molecule [18]. It is shown that negative NICS value of a ring indicates to presence of an induced diatropic ring current, which is interpreted as aromaticity; whereas positive value denotes paratropic ring current and is interpreted as antiaromaticity. This index has been used extensively to assess the aromaticity and antiaromaticity of many organic and inorganic compounds [19–26]. In some cases, however, using NICS value at the geometrical center of the ring (NICS(0)) may mislead or contradict other indices of aromaticity [27–30]. Therefore it seems that single NICS(0) value is not a very good tool for assessing whether a molecule is aromatic or not. Hence due to its conceptual imperfections, NICS has been refined considerably [31]. As shown by Lazzerezetti [27] and Aihara [32], NICS(0) values contain important spurious contributions from the in-plane tensor components that are not related to aromaticity. Therefore NICS(1) (1 Å above/below the plane of the ring), which essentially reflects \(\pi\) effects, is a better indicator of the ring current. It is recalled that, at this distance the effects of the local \(\sigma\)-bonding contributions are diminished [33,34]. It is also shown that NICS(1)zz, which is the out-of-plane zz components’ contribution of the NICS tensor 1 Å above the ring, is better correlated with the other aromaticity indices [35]. Recently Stanger [36] developed the scheme of scanning the NICS values (NICS scan) up to a certain distance from the ring center. From the scan curve it is proposed that for aromatic systems, the NICS values will pass through a minimum; while for antiaromatic species no minimum is observed. This method is also successfully applied in some inorganic systems [37,38].

The purpose of this Letter is to introduce a new method for indication of aromaticity in cyclic compounds based on the variation of NICS index at different distances from the ring center. This method, which is denoted as NICS-rate, is applied in both monocyclic and polycyclic molecular systems.

2. Computational details

The geometries of the considered molecules in this study are optimized at the MP2 level with 6-311++G** basis set. Note that, this level of theory considers both correlation and dispersion effects in energy calculation. Vibrational frequencies are also calculated to verify that the optimized structures are local minima on the potential energy surfaces. Using the optimized structures, NICS values are calculated at the HF/6-31+G** level of theory using the GIAO method [39]. It is mentioned that the ghost atom (Bq) is a very good tool for assessing whether a molecule is aromatic or not. Hence due to its conceptual imperfections, NICS has been refined considerably [31]. As shown by Lazzerezetti [27] and Aihara [32], NICS(0) values contain important spurious contributions from the in-plane tensor components that are not related to aromaticity. Therefore NICS(1) (1 Å above/below the plane of the ring), which essentially reflects \(\pi\) effects, is a better indicator of the ring current. It is recalled that, at this distance the effects of the local \(\sigma\)-bonding contributions are diminished [33,34]. It is also shown that NICS(1)zz, which is the out-of-plane zz components’ contribution of the NICS tensor 1 Å above the ring, is better correlated with the other aromaticity indices [35]. Recently Stanger [36] developed the scheme of scanning the NICS values (NICS scan) up to a certain distance from the ring center. From the scan curve it is proposed that for aromatic systems, the NICS values will pass through a minimum; while for antiaromatic species no minimum is observed. This method is also successfully applied in some inorganic systems [37,38].

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sensor point without energy contribution only if HF calculations are applied and in some other methods the ghost atom gets its own electron density and shows some influence on the energy of the studied molecule [40,41]. The probe (ghost atom, Bq) is placed at the ring center of the considered molecule (0.0 Å) and its distance is varied (up to 4.0 Å) perpendicular to the molecular plane at an interval of 0.2 Å. To calculate the NICS-rate at a given distance \( r \) from the ring center, the following mathematical description for a derivative is used:

\[
\text{NICS-rate}(r) = \frac{d\text{NICS}}{dr} \equiv \lim_{\Delta r \to 0} \frac{\text{NICS}(r + \Delta r) - \text{NICS}(r)}{\Delta r} \tag{1}
\]

Then by using finite difference approximation, NICS-rates are simply calculated from the difference between two successive NICS values \( \text{NICS}(r) = \text{NICS}(r + \Delta r) - \text{NICS}(r) \) and \( \Delta r = 0.2 \). The Gaussian 98W program [42] was applied to perform all of these calculations. The obtained NICS-rates (\( \text{NICS(r)} \)) are finally plotted against distances \( r \).

### 3. Results and discussion

Overall 30 molecules, which are depicted in Fig. 1, are considered in this study. These molecules are included aromatic, antiaromatic and nonaromatic systems with both monocyclic (20 molecules) and polycyclic (10 molecules) structures. The evaluated NICS and NICS-rate values for these molecules are collected in Supporting information, separately.

The obtained NICS and NICS-rate values for furan, thiophene and pyrrole are given in Tables S1–S3, respectively. All of these molecules are aromatic with negative NICS values at their ring centers. Note that in these systems, an increase in \( r \) causes a decrease in the NICS value. Fig. 2 shows the NICS-rates of these systems as a function of distance. It is clear that NICS-rate values are distance-dependent and in each case, the curve passes through a maximum, which is observed nearly at 1 Å above the ring center, and then asymptotically going to zero when the distance increases. Surprisingly, the obtained trend for the maximum NICS-rates of furan (6.653), thiophene (7.481) and pyrrole (8.710) is the same as the aromaticity order which is predicted using NICS index. Hence this comes in mind that the maximum NICS-rate value for a given molecule has something to do with the aromaticity; which means that more aromaticity causes more variation in the NICS index. It is mentioned that both \( \sigma \)- and \( \pi \)-electrons can contribute in the magnetic shielding of a molecule. Although at the ring center \( (r = 0) \), this contribution for \( \sigma \)-electrons are less than \( \pi \)-ones, but in a small ring (such as four- and five-membered rings in which the bonds are close to the ring center) \( \sigma \)-contribution in the NICS is not negligible. In these cases, by an increase in \( r \) the contributions of \( \sigma \)- and \( \pi \)-electrons quickly decreases and increases, respectively. But the positive values for the NICS-rates indicate to the fact that the decrease of \( \pi \)-electrons contribution in the NICS is more than the increase of \( \pi \)-electrons contribution.

The NICS values of cyclobutadiene, as an antiaromatic system, are given in Table S4 together with the corresponding NICS-rates. The NICS-rate curve of this molecule (see Fig. 3) shows a significant minimum (−24.536), which is observed at about 1 Å above the ring center. Again the competition between \( \sigma \)- and \( \pi \)-electrons is responsible for the shape of NICS-rate curve. Therefore it seems that a minimum should be expected in the NICS-rate curves of antiaromatic molecules. The NICS-rate curves of borol and alumol (two other antiaromatic molecules), which are shown in Fig. S1, support this claim. The related values for these systems are collected in Tables S5 and S6. Surprisingly, the observed minimum in the NICS-rate graph of borol molecule (−12.621) is nearly twice of the alumol (−6.236), and both are less than the minimum of cyclobutadiene. It is recalled that borol is more antiaromatic than alumol, which is nicely reflected in their NICS-rate minimums. Phosphole, as a weak aromatic system, shows a maximum (4.446) in its NICS-rate graph at 1.4 Å above the ring center (see Table S7 and Fig. S1); which may indicate to this fact that the \( \pi \)-electrons cloud of this system is far from the molecular plane. The NICS-rate values for cyclopentadienyl cation (antiaromatic) and cyclopentadienyl anion (aromatic) are also gathered in Tables S8 and S9, respectively. The presence of a maximum (7.474)/minimum (−38.811) in the NICS-rate curve of this anionic/cationic species is in accordance with the aromatic/antiaromatic character of the molecule (see Fig. S2) [43]. The same behaviors are observed for the ionic forms of silolyl molecule, which their calculated NICS-rate values are collected in Tables S10 and S11; the curves are also presented in Fig. S3. Therefore it seems that, the presence of a maximum/minimum in the NICS-rate curve of a molecule indicates to the aromatic/antiaromatic character of the system. General shape of the NICS-rate plots for charged species are similar to those which are obtained for the neutral systems.

Calculated NICS-rate values and the related curve for benzene, as a paradigm of aromaticity, are given in Table S12 and Fig. 4. Note that, contrary to what observed for the four- and five-membered rings, the NICS values of benzene initially increase and then asymptotically going to zero; which implies to some different competition between \( \sigma \)- and \( \pi \)-electrons in the NICS index, in comparison with the previous cases. The presence of both maximum and minimum in the NICS-rate curve also verifies this difference. It seems that in benzene, the effect of \( \pi \)-electrons in NICS is slowly diminished; whereas the \( \pi \)-electrons contribution is quickly increased till it reaches to the maximum influence (which is seen as a maximum in the NICS-rate at nearly 1.5 Å) and thereafter it decreases, which causes a rapid decrease in the NICS-rate values. It is clear that the magnitude of maximum (6.918) is more than the minimum (−4.711) and the absolute ratio of these two NICS-rates, which is symbolized with NRR (NICS-Rates Ratio) hereafter, is 1.468. Therefore a dimensionless parameter is defined as:

\[
\text{NRR} = \frac{|\text{NICS} \text{- rate(Max)}|}{|\text{NICS} \text{- rate(Min)}|}
\]

which may consider as a measure of aromaticity in this molecule. The same shape is observed for the NICS-rate curve of pyridine, which its values and the corresponding graph are shown in Table S13 and Fig. S4. The minimum (−6.240) and the maximum (7.556) NICS-rates for this aromatic system (NRR = 1.211), are observed at 0.4 and 1.6 Å, respectively. Note that since benzene is more aromatic than pyridine, it comes in mind that the extent of aromaticity may has something to do with the NRR index; i.e. more significant NRR values are observed for those molecules which are more aromatic.

The NICS-rate graph of cyclopentadiene, as a nonaromatic system, shows both minimum and maximum (see Table S14 and Fig. S2). The calculated NRR = 0.911 predicts less aromaticity for this molecule than benzene and pyridine. Note that NICS(0) = −3.185 also indicates slight aromaticity for this ring, which may arise from delocalization of sigma electrons in cyclopentadiene system (\( \sigma \)-aromaticity). The evaluated NICS-rates and related graphs for neutral and ionic forms of cycloheptatriene and cyclooctatetraene molecules are given in Tables S15–S20 and Figs. S5 and S6. The corresponding NRR values are also collected in Table 1. Again the obtained results are in agreement with the experimental evidences [43].

Some polycyclic molecules, which are shown in Fig. 1, are selected to check the ability of this method in prediction of local aromatics. Three simple polycyclic aromatic hydrocarbons (naphthalene, anthracene and phenanthrene) are chosen to investigate the local aromaticsities in linear and angular polycyenes by
using their NICS-rates. As in the benzene, both of maximum and minimum are observed in the obtained NICS-rate curves (see Figs. S7–S9 and Tables S21–S25). The NRR = 1.452 for naphthalene implies that the six-membered rings of this molecule are nearly as aromatic as benzene. In anthracene the inner ring (NRR = 1.756) is more aromatic than the outer one (NRR = 1.242); whereas in phenanthrene the outer ring shows more aromaticity (NRR(outer) = 1.488 and NRR(inner) = 0.968). Therefore the obtained local aromaticities for the external and internal rings in linear and angular polyacenes are opposite. It is in agreement with those local aro-
In contrast with the benzocyclobutadiene, the six-membered ring of biphenylene with NRR = 1.222 is nearly high aromatic (see Tables S28 and S29 and Fig. S11); but the predicted aromaticity using NICS(0) is underestimated (NICS(0) = −4.986). In contrast with the NICS(0), the NICS-rate method successfully predicts the aromatic character of six-membered ring in biphenylene. On the other hand, the observed minimum in the NICS-rate curve of four-membered ring (NICS-rate(Min) = −17.811) implies to less antiaromatic character with respect to the same ring in benzocyclobutadiene.

Six-membered rings of acenaphthylene and pyracyclene show two different behaviors (see Tables S30–S33 and Figs. S12 and S13). Although this ring in acenaphthylene shows an aromatic character (NRR = 1.3610 that is nearly identical to that of the benzene), the six-membered ring of pyracyclene is weakly aromatic (NRR = 0.711). On the other hand, five-membered rings of these molecules show a rather normal NICS-rate picture. Although this ring in pyracyclene is predicted to be antiaromatic (see Fig. S13), the five-membered ring of acenaphthylene with NRR = 0.131 shows a nonaromatic character. These observations are supported by the corresponding NICS(0) values.

An interesting example is calicene molecule. Some theoretical evidences [36] suggest considerable contribution of dipolar aromatic form of this molecule in the character of the system. The NICS and NICS-rate values for both three- and five-membered rings of calicene are given in tables S34 and S35, respectively. The curve of three-membered ring just contains a maximum (see Fig. S14), which indicates to its aromatic character and both NICS(0) and NICS-rate values (NICS(0) = −24.340 and NICS-rate(Max) = 27.096) predict very high aromaticity for this ring, which may arise from the π-electrons contribution. On the other hand, since cyclopentadienyl anion is highly aromatic, the five-membered ring of calicene should be more aromatic than benzene. It is nicely reflected in its significant NRR value (NRR = 2.946), which indicates to high aromaticity of this system; whereas NICS(0) = −7.003 predicts an aromaticity even less than benzene for this ring, which is not in agreement with the experiment.

The obtained NICS-rate values for azulene molecule are also gathered in Tables S36 and S37. Five- and seven-membered rings of this molecule show both maximum and minimum in their graphs (see Fig. S15) with NRR = 1.989 and 1.217, respectively. It is clear that the obtained NICS(0) =−19.592 for the five-membered ring overestimates the aromaticity and is not in accordance with the obtained NRR value. NICS-rate curves for both rings of [1,2]4,5 bicyclo[2.2.2]octadieno-benzene are shown in Fig. S16 (also see Tables S38 and S39). NICS(0) index show high aromaticity for these rings and even predict more aromaticity for the four-membered ring (NICS(0) = −12.282) than the six-membered one (NICS(0) = −10.088); whereas the opposite order of aromaticity is correctly assumed by NICS-rate curves. Therefore it seems that the obtained local aromaticities predicted by NICS and some other aromaticity scales such as NICS(0), HOMA, FLU etc. [44–46].

Calculated NICS and NICS-rate values for the rings of benzocyclobutadiene molecule are collected in Tables S26–S27. Both of these indices predict high antiaromatic and nearly aromatic characters for the four- and six-membered rings, respectively (see Fig. S10); but the fused four-membered ring in this system is less antiaromatic than a single cyclobutadiene ring. On the other hand, because of joining with an antiaromatic system, such as cyclobutadiene, the aromaticity of six-membered ring is considerably decreased (NICS(0) = −2.396 and NRR = 0.886) with respect to the benzene ring.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>NICS(0)</th>
<th>NRR</th>
<th>Molecule</th>
<th>NICS(0)</th>
<th>NRR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclopentadiene</td>
<td>−3.184</td>
<td>0.911</td>
<td>Naphthalene</td>
<td>−9.989</td>
<td>1.452</td>
</tr>
<tr>
<td>Benzene</td>
<td>−9.702</td>
<td>1.468</td>
<td>Azulene(5)</td>
<td>−19.592</td>
<td>1.968</td>
</tr>
<tr>
<td>Pyridine</td>
<td>−8.144</td>
<td>1.211</td>
<td>Azulene(7)</td>
<td>−6.953</td>
<td>1.216</td>
</tr>
<tr>
<td>Tropylium cation</td>
<td>−7.531</td>
<td>1.133</td>
<td>Benzocyclobutadiene(6)</td>
<td>−2.396</td>
<td>0.886</td>
</tr>
<tr>
<td>Cycooctatetraenyl dication</td>
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<td>1.133</td>
<td>Biphenylene(6)</td>
<td>−4.986</td>
<td>1.222</td>
</tr>
<tr>
<td>Anthracene(1)</td>
<td>−8.413</td>
<td>1.241</td>
<td>Acenaphthylene(6)</td>
<td>−8.643</td>
<td>1.361</td>
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<tr>
<td>Anthracene(2)</td>
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<td>1.756</td>
<td>Acenaphthylene(5)</td>
<td>2.981</td>
<td>0.130</td>
</tr>
<tr>
<td>Phenanthrene(1)</td>
<td>−10.224</td>
<td>1.488</td>
<td>Calicene(5)</td>
<td>−7.003</td>
<td>2.263</td>
</tr>
<tr>
<td>Phenanthrene(2)</td>
<td>−6.533</td>
<td>0.968</td>
<td>Bicyclo[2.2.2]octadieno-benzene(4)</td>
<td>−12.282</td>
<td>0.872</td>
</tr>
<tr>
<td>Bicyclo[2.2.2]octadieno-benzene(6)</td>
<td>−10.088</td>
<td>2.243</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyracyclene(6)</td>
<td>−2.662</td>
<td>0.705</td>
<td></td>
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<td></td>
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</tbody>
</table>
matics from NICS-rate method is more reliable than those which are concluded from NICS(0) index. All of the evaluated NRRs for those compounds which show both maximum and minimum in their NICS-rate curves and the related NICS(0) values are collected in Table 1. When all the considered molecules are taking into account (20 points), the correlation between these two aromaticity indices has $R^2 = 0.479$. Surprisingly, most deviations are observed for those rings that NICS(0) values are not successful in predicting their aromaticities; i.e., both rings of [1,2][4,5] bicyclo[butadienobenzene, six-membered ring of biphenylene and five-membered rings of azulene and calicene molecules. By removing these five points from the correlation curve, the regression coefficient improved to 0.934 (for 15 points). This relation is shown in Fig. 5. The obtained linear equation (NICS(0) = –10.06 NRR + 4.977) predicts NRR = 0.5 as the boundary between nonaromatic and aromatic systems. The ability of this method in predicting the aromaticities of all metal clusters and inorganic compounds is under investigation in our group.

4. Conclusion

An alternative NICS-based method, in which the NICS-rates ($D_{NICS}$) are evaluated over a distance from the molecular plane, is introduced for indication of aromaticity in cyclic compounds. The method is applied to monocyclic hydrocarbons, some linear and angular polycyclic hydrocarbons with benzenoid and non-benzenoid rings. It is shown that the presence of a maximum in NICS-rate curve of a ring indicates to aromaticity; whereas the observed minimum in a graph denotes antiaromaticity. For those molecules, which show both maximum and minimum in their curves, a dimensionless parameter (the absolute ratio of the maximum to the minimum NICS-rates or NRR) is introduced as a measure of aromaticity in these systems. NICS-rate is also shown to be quite suitable in discriminating the local aromaticities of different rings in polycyclic compounds. Surprisingly, for those molecules in which NICS(0) cannot correctly give the aromaticities of the rings (such as biphenylene, azulene, etc.), the NICS-rate method successfully predicts the aromaticities of these systems. According to the obtained linear correlation between NICS(0) and NRR values, the NRR = 0.5 is considered as the boundary between aromatic and nonaromatic systems.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2010.05.025.

References


Fig. 5. Correlation between NICS(0) and NRR values.