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Ab initio determination of the induced ring current in aromatic molecules

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The aromatic ring current shieldings (ARCS) approach is a new method to determine the strength of the induced ring current which is related to the molecular aromaticity. In the ARCS method, the strength of the induced aromatic ring current and the size of the current ring are obtained from nuclear magnetic shieldings calculated in discrete points along a line perpendicular to the molecular plane starting at the center of the molecule. The induced ring currents are used to determine the relative degree of aromaticity for benzene, furan, pyrrole, cyclohexane, cyclohexadiene, thiophen, *p*-benzoquinone, cyclopentadienide anion, cycloheptatrienyl cation, 1,4-dihydronaphthalene, and prophin.

1. Introduction

In diamagnetic molecules an external magnetic field induces a current whose magnetic field lies in the opposite direction to the applied field. In saturated molecules, the induced currents flow in the proximity of the atoms and the chemical bonds. In cyclic unsaturated molecules where the π-electrons are delocalized around the ring, the induced current is not limited to atoms and bonds anymore. Instead, the external magnetic field creates a ring current which is much stronger than the induced current of saturated systems.[1–6] The ring current in turn induces a secondary magnetic field perpendicular to the current loop and opposite to the applied magnetic field. This characteristic property suggests that aromatic compounds can be defined as cyclic molecules with a strong induced ring current in magnetic fields.[7]

The ring current can be estimated experimentally by measuring nuclear magnetic resonance (NMR) proton shieldings.[8] However, the aromatic contribution to the proton shieldings is often relatively small and the proton shieldings also depend significantly on other factors such as the size of the current circuit, the number of electrons, and the substituents. Thus, the indirect measurement of the strength of the ring current by detecting the proton shieldings is not a general method for determining the degree of aromaticity.

Computational methods have the advantage that they can probe any point in space. Schleyer *et al.*[9,10] introduced the nucleus independent chemical shieldings (NICS) method which means that the NMR shieldings are calculated in arbitrary points such as the center of the aromatic ring. In general, the NICS values are not transferable from one molecule to another.[11] They can be used as a relative measure of the aromaticity for closely related molecules, but the NICS values do not provide any accurate information about the strength of the ring current since the shielding at the center of the molecule depends on both the size of the circuit and the current strength.

Instead of probing only one point in space, we calculate the nuclear magnetic shieldings in a set of points along a line perpendicular to the current circuit starting from the center of the molecule or from the center of the aromatic path. By using classical electrodynamics and assuming that the conductor wire is infinitely thin and circular, both the strength of the induced current and the ring size can be deduced from the long-range asymptotic behavior of the shielding function. The magnetic shieldings are obtained from quantum chemical calculations while the shieldings can be treated by classical electrodynamics. Seen from a large distance, the current circuit can be considered to be infinitely thin. The degree of aromaticity is usually assumed to be proportional to the strength of the induced ring current which is a measure of the delocalization of the π-electrons.[7] The degree of aromaticity of any molecule deduced from the calculated aromatic ring chemical shieldings (ARCS) can then be compared regardless of the size of the aromatic path. More precisely, the shieldings are proportional to the derivative of the current strength with respect to the applied magnetic field, while the ring current depends on the field strength.

The molecular aromaticity has previously been defined on the basis of energetics, geometric and magnetic criteria such as nuclear magnetic shielding tensors and magnetic susceptibilities.[6–21] However, the degree of aromaticity is even more difficult to deduce from energetic and structural data than from magnetic criteria such as magnetic susceptibility exaltations, susceptibility anisotropies, and NICS values. Kutzelnigg *et al.*[5,6] have studied the molecular aromaticity by explicitly calculating and visualizing the current density vector in discrete points around the molecule.

II. Theory

In cyclic aromatic molecules the external magnetic field (B_{ext}) creates a ring current (I_{ring}) which in turn induces a magnetic field (B_{ind}). Since the quantum mechanical system can be considered to be superconducting, the ring current, which is induced when the external field is switched on, will continue to flow in the molecular wire until the external field is turned off. By assuming that the wire carrying the ring current is circular and infinitely thin, the induced magnetic field is easily determined from classical electrodynamics using the Biot–Savart's law.[22] The expression for the magnetic field strength ($\boldsymbol{B}$) in the vicinity of a thin wire carrying a current I_{ring} is

$$\mathrm{d}\boldsymbol{B} = \frac{\mu_0 I_{ring}}{4\pi} \frac{\mathrm{d}\boldsymbol{l} \times \boldsymbol{r}}{r^3} \tag{1}$$

where μ_0 is the permeability of vacuum, $\mathrm{d}\boldsymbol{l}$ is a small length element of the conductor, r is the distance from the wire, and $\boldsymbol{r}$

is the radial vector from d$\boldsymbol{l}$ to the probe. By integrating eqn. (1), the expression for the induced magnetic field strength perpendicular to the loop becomes

$$B(z)_{\text{ind}} = \frac{\mu_0 I_{\text{ring}}}{2} \frac{R^2}{(z^2 + R^2)^{3/2}} = -\sigma(z) B_{\text{ext}} \quad (2)$$

where R is the radius of the current loop, z is the perpendicular distance from the loop center, $\sigma(z)$ is the z-dependence of the isotropic nuclear magnetic shielding function, and B_{ext} is the applied magnetic field. For very large z-values, eqn. (2) yields the asymptotic behavior of z^{-3} as expected for a magnetic dipole. Recently, Bühl[11] used eqn. (2) to relate NICS values of fullerenes to the endohedral chemical shifts. By differentiating eqn. (2) with respect to the external magnetic field, one obtains the relation between the isotropic nuclear magnetic shielding and the derivative of the induced current with respect to the applied magnetic field:

$$\sigma(z) = -\frac{\mu_0}{2} \frac{\partial I_{\text{ring}}}{\partial B_{\text{ext}}} \frac{R^2}{(z^2 + R^2)^{3/2}} \quad (3)$$

The strength of the induced ring current for a given magnetic field can be obtained as:

$$I_{\text{ring}} = \frac{\partial I_{\text{ring}}}{\partial B_{\text{ext}}} B_{\text{ext}} \quad (4)$$

By calculating $\sigma(z)$ for a number of z-values in the range $z = [0, z_{\text{max}}]$ and fitting eqn. (3) to the calculated $\sigma(z)$ values, the induced current derivative ($\partial I_{\text{ring}}/\partial B_{\text{ext}}$) and the loop radius ($R$) can be deduced from the long-range part of the shielding function. Typical values for z_{max} are 30–60 a_0 depending on the loop size. Since for small z values, the shieldings do not obey the Biot–Savart's law for the circular model [eqn. (3)], the fit starts from z_{min}. Our experience is that the results are not very sensitive to the choice of z_{min} as long as it is outside the electron charge distribution. Typical z_{min} values are about 5 a_0.

III. Methods

The molecular structures have been optimized at the resolution-of-the-identity density-functional theory (RI-DFT) level[23] using the Becke–Perdew (B–P) parameterization[24–26] as implemented in Turbomole.[27] The nuclear magnetic shieldings have been calculated at the Hartree–Fock self-consistent-field (SCF) level.[28] To ensure origin-independence in the shielding calculations, the gauge-including-aromatic-orbital (GIAO) approach has been employed.[3,29–31] In the structure optimization, the Karlsruhe split-valence basis set[32] augmented with polarization functions on C, O, N and S[33] was employed, while in the shielding calculations the basis set was further augmented with polarization functions of H (SVP). The optimized auxiliary basis sets used in the RI-DFT calculations consisted of 4s2p/2s1p for H, of 8s3p3d1f/6s3p3d1f for C, N, and O, and of 12s6p5d1f1g/5s3p2d1f1g for S.[23]

In the ARCS approach, the nuclear magnetic shieldings are calculated in discrete points perpendicular to the molecular plane starting from the geometrical center of the aromatic pathway. The current derivative and its radius are obtained by fitting the long-range part of the shielding function to eqn. (3). The loop radius is determined by fitting $\log[\sigma(z)]$ as a function of $\log[R^2/(z^2 + R^2)]$. This was done by adjusting the loop radius R until the angular coefficient became 3/2. The current derivative was deduced from the intercept at $3/2\{\log[R^2/(z^2 + R^2)]\} = 0$.

IV. Results

The molecular structure of benzene, furan, pyrrole, cyclohexane, cyclohexadiene, thiophen, *p*-benzoquinone, cyclopentadienide anion, cycloheptatrienyl cation, 1,4-dihydronaphthalene, and prophin have been optimized at RI-DFT level using SV(P) basis sets. All molecules except cyclohexane are planar. The optimized molecular structures can be downloaded from our world-wide-web (www) server.[34]

The ARCS have been calculated at the SCF level. The ring currents and the radii have been deduced from the ARCS as described in Section III. For most cyclic molecules there is no unique center of the ring. For pyrrole, we checked how the obtained ring current and its radius depend on the position of the ARCS center. With the ARCS center at the geometrical center we obtained a current derivative term $[(\mu_0/2R)(\partial I/\partial B)]$ of 76.40 ppm and a current radius of 1.61 a_0. By shifting the ARCS center by 0.1 a_0 away from the nitrogen atom (in the y-direction), the current derivative term and the radius became 76.28 ppm and 1.61 a_0, respectively. A similar shift of the ARCS center in the x-direction yielded a current derivative term and a radius of 76.32 ppm and 1.61 a_0, respectively. These results show that the ring current and its radius are not very dependent on the exact position of the chosen ARCS center.

To first order, the induced ring current is proportional to the strength of the applied external magnetic field. Since the magnetic field strength in a typical NMR spectrometer is 2–8 T, we chose a magnetic field of 4 T in the explicit determi-

Table 1 The geometrical radii of the molecular rings (in a_0), the effective sizes of the ring current loop (in a_0), the current derivatives with respect to the external magnetic field $[(\mu_0/2R)(\partial I/\partial B)$ in ppm], and the induced ring currents (I_{ring} in nA) calculated for the studied molecules

Molecule	Geometrical radius	Current radius	$\frac{\mu_0}{2R}\frac{\partial I}{\partial B}$	I_{ring}[a]
Benzene	2.66	2.30	41.4	32.1
Furan	2.02–2.12	1.77	52.1	31.1
Pyrrole	2.00–2.15	1.61	76.4	41.4
Thiophen	2.21–2.35	1.96	48.6	32.1
Cyclopentadienide anion	2.07–2.18	1.28	167.4	72.2
Cycloheptatrienyl cation	2.92	3.02	25.7	26.1
1,4-Dihydronaphthalene[b]	2.63–2.67	2.74	24.7	22.8
Porphin	6.54	6.83	18.1	41.6
Cyclohexane	2.81	—	6.10	2.1[c]
Cyclohexadiene	2.70–2.85	3.92	1.27	1.7
1,4-Dihydronaphthalene[d]	2.73–2.85	7.22	1.39	3.4
p-Benzoquinone	2.59–2.89	2.60[e]	19.3	7.9[c]

[a] The external magnetic field is assumed to be 4 T. [b] For the benzene-like ring. [c] Estimated from the shieldings at $z = 20$ a_0. [d] For the cyclohexadiene-like ring. [e] The angular coefficient is 1.66.

nation of the strength of the induced ring currents. The results are summarized in Table 1.

A. Aromatic systems

As seen in Table 1, the ring currents in benzene, furan, and thiophen are about 30 nA. For pyrrole, porphin, and the cyclopentadienide anion the ring currents are somewhat larger *i.e.* 41.4, 41.6 and 72.2 nA, respectively. For the seven-member ring, the cycloheptatrienyl cation, the ring current is 26.1 nA which is about 6 nA smaller than for benzene. The ring current in the benzene-like ring of 1,4-dihydronaphthalene is 22.8 nA. For comparison, Bird[13] obtained aromaticity indices of 43, 59, and 66 for furan, pyrrole and thiophen, while according to this study pyrrole is more aromatic than thiophen. In Fig. 1, the ARCS for benzene, furan, pyrrole, and thiophen are shown as a function of the perpendicular distance from the center of the current circuit. The logarithmic fits of the ARCS to eqn. (3) are also shown in Fig. 1. All these molecules are typical aromatic molecules which is also reflected in the ring currents. The geometrical radii are deduced from the distances between the heavy atoms across the ring. For molecules with no obvious geometrical radius an upper and lower bound for the geometrical radii are given. As seen in Table 1, the current radii and the geometrical radii agree well for these molecules. The ring current radii are in most cases somewhat smaller than the corresponding geometrical radii.

For benzene, the ARCS were also calculated at second-order Møller–Plesset (MP2) level.[35,36] At MP2 level the strength of the ring current and its radius are 28.2 nA, and 2.39 a_0, respectively. These values are in close agreement with the corresponding SCF results of 32.1 nA and 2.30 a_0, respectively. The agreement shows that for these molecules the ARCS can be calculated relatively accurately at the SCF level.

The ARCS for the cyclopentadienide anion, cycloheptatrienyl cation, porphin, and for the benzene-like ring in 1,4-dihydronaphthalene as well as the corresponding fits to eqn. (3) are shown in Fig. 2. The fits show that these four molecules are also aromatic, as expected. For the cyclopentadienide anion, the effective size of the aromatic pathway is significantly smaller than its geometrical radius. Since for

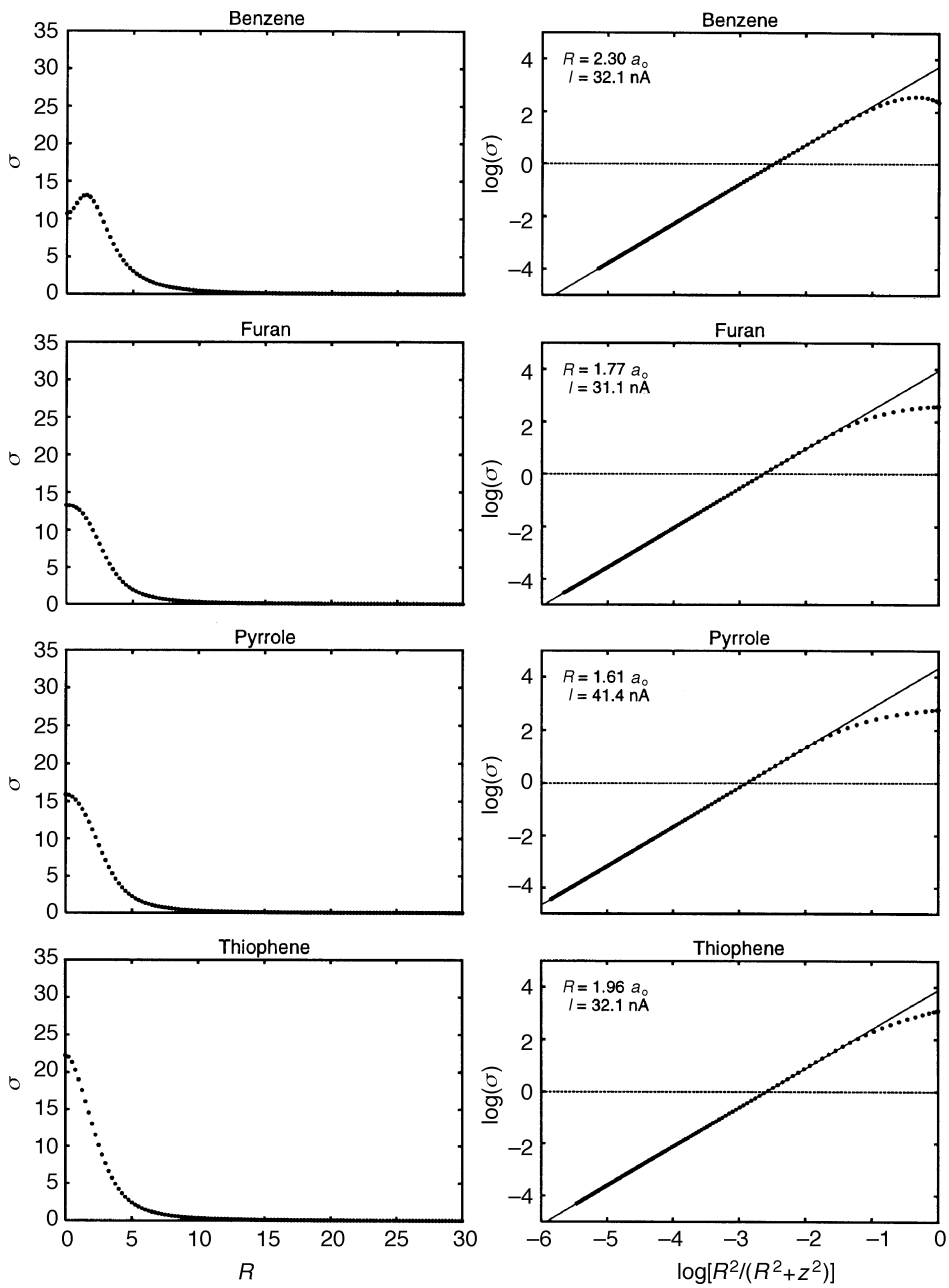

Fig. 1 The calculated ARCS (in ppm) for benzene, furan, pyrrole, and thiophen as well as the logarithmic fits of the ARCS to eqn. (3).

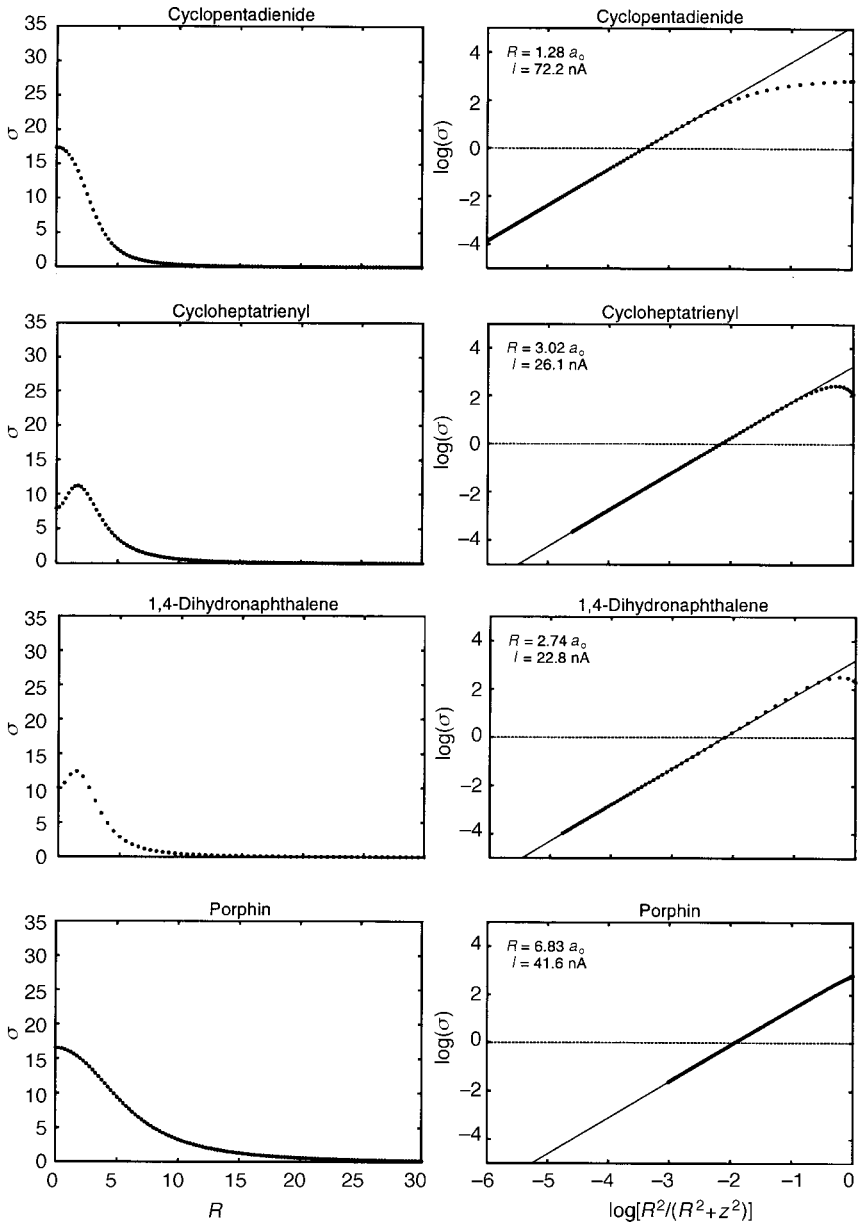

Fig. 2 The calculated ARCS (in ppm) for the cyclopentadienide anion, cycloheptatrienyl cation, porphin, and for the benzene-like ring in 1,4-dihydronaphthalene as well as the logarithmic fits of the ARCS to eqn. (3).

porphin the geometrical radius is assumed to be the distance from the molecular center to the *meso* carbons, it is not unexpected that the effective current radius is larger than the geometrical radius. In porphin, the pyrroles are part of the aromatic pathway and the distance from the center of the molecule to the β carbons is significantly larger than the distance to the *meso* carbons.

B. Nonaromatic systems

For cyclohexane, we were not able to find any radius which would give an angular coefficient of 3/2. For cyclohexadiene, the optimal radius of 3.92 a_0 is somewhat larger than one would expect since the geometrical radius of the cyclohexadiene ring is 2.70–2.85 a_0 depending on how it is defined. Since the induced current for cyclohexadiene is 20 times smaller than for benzene and its geometrical radius is 1 a_0 smaller than the obtained effective ring current radius, one may conclude that cyclohexadiene is nonaromatic.

For the cyclohexadiene ring in 1,4-dihydronaphthalene, the radius is about 3 times larger than the geometrical radius of the molecule and furthermore, the ring current is one tenth of the value for benzene. That means that the cyclohexadiene ring is nonaromatic and the large radius probably reflects the fact that the cyclohexadiene ring is attached to an aromatic benzene ring. Whether the shieldings above the cyclohexadiene-like ring in 1,4-dihydronaphthalene ring originate from the benzene-like ring was checked by performing ARCS calculations on benzene starting with the ARCS from the point corresponding to the center of the cyclohexadiene-like ring. This calculation yielded a ring current of 2.9 nA with a radius of 7.65 a_0 which can be compared to the corresponding values for the cyclohexadiene-like ring of 3.4 nA and 7.22 a_0. The calculations on 1,4-dihydronaphthalene show that the ARCS method can also be applied to molecules consisting of several aromatic and nonaromatic rings. The contribution from an aromatic ring outside the studied ring is almost vanishingly small and can be regarded as a small perturbation, even when the two rings are close to each other.

In Fig. 3, the ARCS and the corresponding fits are shown for cyclohexane, cyclohexadiene, and the cyclohexadiene-like ring in 1,4-dihydronaphthalene which are all nonaromatic. For nonaromatic molecules, the nuclear magnetic shielding function, $\sigma(z)$, disappears with the electronic charge density

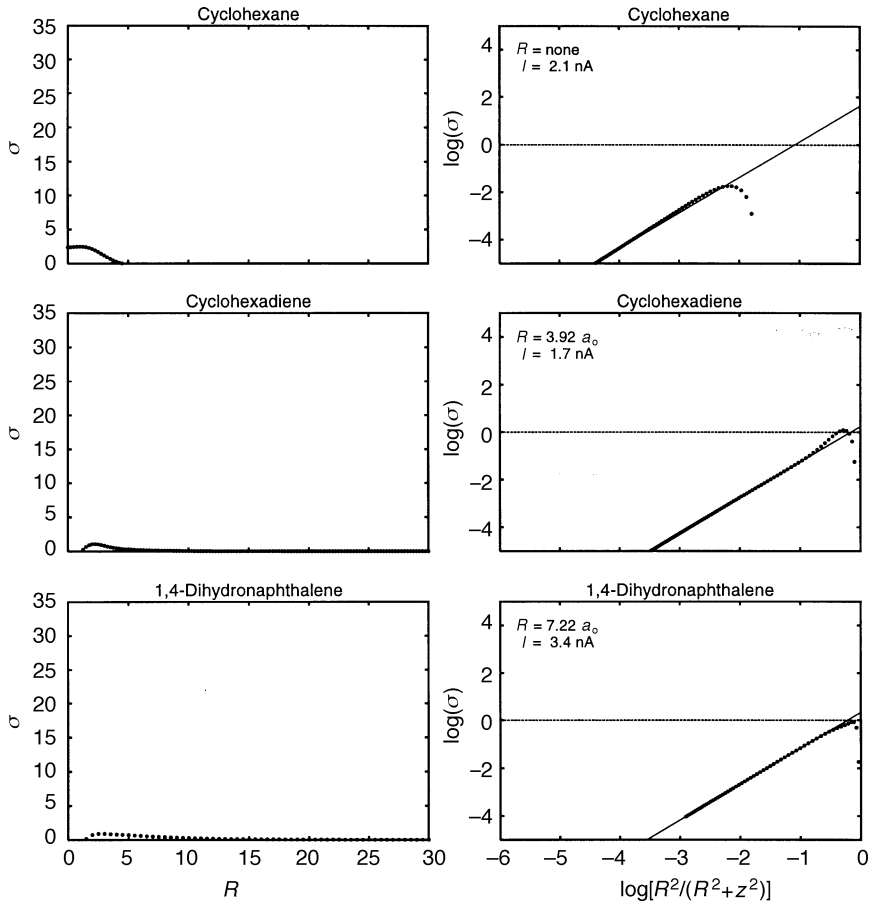

Fig. 3 The calculated ARCS (in ppm) for cyclohexane, cyclohexadiene, and the cyclohexadiene-like ring in 1,4-dihydronaphthalene as well as the logarithmic fits of the ARCS to eqn. (3).

while the aromatic ones possess long-range magnetic shieldings. A comparison of Figs. 1, 2, and 3 reveals the large difference in the magnetic properties of the aromatic and nonaromatic molecules. The molecules displayed in Figs. 1 and 2 are all aromatic molecules, while those in Fig. 3 are nonaromatic.

C. *p*-Benzoquinone

The ARCS plots for *p*-benzoquinone are shown in Fig. 4. As seen in Fig. 4, the ARCS calculated for *p*-benzoquinone differ from the ARCS obtained for the other aromatic molecules. The NICS value at the center of the molecule indicates a very strong aromaticity of the molecule. However, the form of the shielding function shows that this is not necessary the case. For *p*-benzoquinone, we were not able to find any current radius yielding an angular coefficient of 3/2. Since we had difficulties in obtaining meaningful ring currents for cyclohexane and *p*-benzoquinone using the circular model, the ring currents given for them in Table 1 are deduced from a few points at $z = 20\ a_0$ using eqn. (2). As seen in Fig. 4, the ARCS are not particularly linear in the logarithmic plot. At short distances from the molecular center the calculated ARCS function is larger than the fit, while for all the other molecules studied, the shieldings obtained from the fit are larger than the ARCS values.

Judged from the NICS values, *p*-benzoquinone would be the most aromatic molecule of the ones studied, while the strength of the induced ring current suggests that the cyclopentadienide anion is the most aromatic molecule. By using only a few ARCS values at $z = 20\ a_0$ one obtains for *p*-benzoquinone a ring current of 7.9 nA. The current strengths show that the aromaticity of *p*-benzoquinone is about one fourth of the aromaticity of the benzene molecule. The NICS value for thiophen is about a factor of two larger than for benzene, while the strength of the ring currents are almost equal. Note that the NICS value is a local minimum for the benzene rings and for the cycloheptatrienyl cation, while they

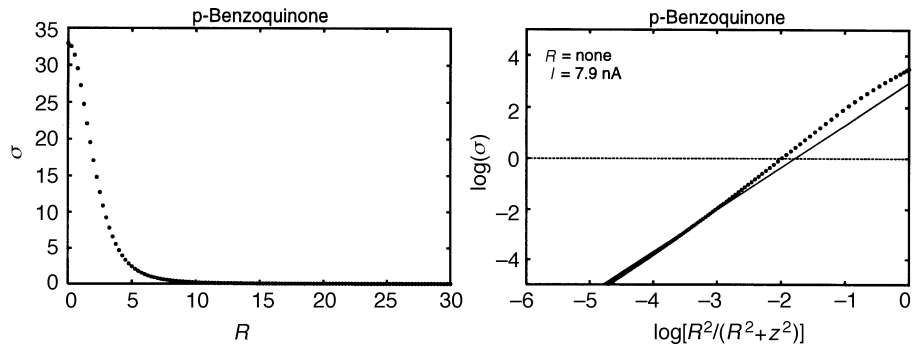

Fig. 4 The calculated ARCS (in ppm) for *p*-benzoquinone and the logarithmic fit of the ARCS to eqn. (3).

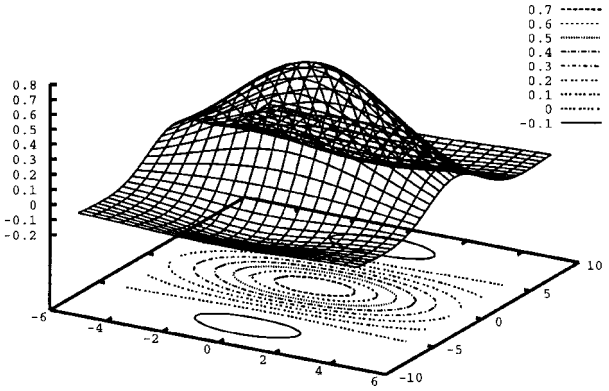

Fig. 5 The magnetic shielding (in ppm) for *p*-benzoquinone calculated in a plane parallel to the molecular plane 7 a_0 from the molecule.

are maxima for the five-member rings, for *p*-benzoquinone, and for porphin. This must affect the conclusions drawn from calculated NICS values. See Figs. 1 and 2.

The circular approximation seems to work very well for most molecules, but for *p*-benzoquinone, we were not able to find any radius giving an angular coefficient of 3/2. Since the two oxygens in *p*-benzoquinone are part of the conjugated π-system, the current loop in *p*-benzoquinone is not necessarily circular. To be able to describe the long-range magnetic shieldings of *p*-benzoquinone, the calculated shieldings were fitted to an extended model derived for an elliptical current circuit. The elliptical approach gives a somewhat better description. However, the elliptical model was not able to completely describe the long-range magnetic shieldings of *p*-benzoquinone, either. For *p*-benzoquinone, the ARCS calculated at MP2 level are not very different from those obtained at the SCF level thus the observed different behavior is not due to electron correlation.

To resolve the problem, the magnetic shieldings were calculated in a plane parallel to the molecular plane 7 a_0 from the molecule. The shielding function in this plane is illustrated in Fig. 5. As seen in Fig. 5, there are three main contributions to the long-range magnetic shielding: the aromatic current shielding originating from the ring current and two weaker but long-range paramagnetic shieldings originating from the carbonyl lone pairs. The three contributions result in a slightly different long-range asymptotic behavior of the shielding as compared to the other aromatic molecules studied.

Table 2 Calculated nuclear magnetic proton shieldings for the molecules studied (in ppm)

Molecule	H(1)	H(2)	H(3)	H(4)
Benzene	24.28	—	—	—
Furan[a]	24.31	25.19	—	—
Pyrrole[b]	24.55	24.97	25.38	—
Thiophen[a]	24.67	24.41	—	—
Cyclopentadienide anion	26.59	—	—	—
Cycloheptatrienyl cation	22.28	—	—	—
1,4-Dihydronaphthalene[c]	24.47	24.48	—	—
Porphin[d]	39.86	20.88	21.39	21.66
Cyclohexane	30.26	—	—	—
Cyclohexadiene[e]	29.26	26.05	—	—
1,4-Dihydronaphthalene[f]	28.42	25.85	—	—
p-Benzoquinone	24.85	—	—	—

[a] For furan and thiophen, the numbering starts from the α-carbon. [b] For pyrrole, the numbering of hydrogens starts from the one connected to the nitrogen. [c] The numbering of the hydrogens of the aromatic ring starts from carbon number 6. [d] The inner hydrogens are labelled H(1). The hydrogens at the *meso* carbons are labelled H(2). The hydrogens at the β carbons of the pyrrole rings with an inner hydrogen are labelled H(3). [e] For cyclohexadiene, the numbering starts from the hydrogen connected to the saturated carbon atom. [f] The numbering of the hydrogens of the nonaromatic ring starts from carbon number 1.

D. Proton shieldings

For comparison, the calculated proton shieldings are given in Table 2. An estimated value of 31.69 ppm for the absolute shielding of tetramethylsilane (TMS) can be obtained by comparing the calculated NMR proton shielding of cyclohexane of 30.26 ppm with the experimental chemical shift of 1.43 ppm. The calculated proton shift for benzene relatively to TMS is then 7.41 ppm. The proton shielding for the cyclopentadienide anion which is the molecule with the strongest ring current is 26.59 ppm or 2.31 ppm larger than for benzene. The proton shielding of the hydrogen at the unsaturated carbon in cyclohexadiene is 26.05 ppm which shows that the proton shielding is not an accurate measure of the aromaticity.

V. Summary

The ARCS approach is a straight-forward method to detect induced ring currents and molecular aromaticities. The method works well for molecules containing typical aromatic rings such as benzene, pyrrole, furan, thiophen, and porphin. The ring aromaticity can also be obtained for molecules consisting of several aromatic or nonaromatic rings.

Judged from the strength of the induced ring currents, the cyclopentadienide anion is the most aromatic molecule of the ones studied. The degree of aromaticity of pyrrole and porphin is comparable but larger than for benzene, furan and thiophen. The cycloheptatrienyl cation is somewhat less aromatic than benzene and the benzene-like ring in 1,4-dihydronaphthalene is the least aromatic ring among the aromatic ones. Cyclohexane and the cyclohexadiene rings must be considered nonaromatic, while the degree of aromaticity for *p*-benzoquinone cannot be accurately determined from the ARCS using the simple circular model.

The ARCS calculated for nonaromatic molecules such as cyclohexane and cyclohexadiene differ completely from the ARCS obtained for the aromatic ones which means that it is relatively easy to determine whether a molecular ring is aromatic or not. The only problematic molecule among the ones studied is *p*-benzoquinone which apparently is somewhat aromatic but its degree of aromaticity cannot be accurately determined using our simple model.

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