Aromaticity (and Conjugation)

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Aims of the Lectures

1. Discuss definitions of aromaticity
2. Present methods to estimate the degree of aromaticity
3. Present different kinds of aromaticities
4. A short presentation of our GIMIC method currents
5. Aromaticity from a ring-current point of view
6. Discuss the multidimensionality of the aromaticity
An aromatic molecule is in most cases a conjugated system having a continuous electron delocalization. They are more stable than one would expect. The bond lengths are less alternating. The chemical reactions are different. The spectroscopic properties are different. They behave differently in magnetic fields.
Detection of Aromaticity

All-Metal Aromaticity and Antiaromaticity

| Table 1. Criteria for π-Aromaticity and π-Antiaromaticity (Adapted from Reference 96) |
|---------------------------------|------------------|------------------|------------------|
| (i) electronic nature          | (4n + 2) π-electron cyclic conjugation | no cyclic conjugation | 4n π-electron cyclic conjugation |
| (ii) energy                    |                               |                   |                   |
|      cyclic conjugation        | stabilization              | standard          | destabilization   |
|      delocalization            | enhanced                   | standard          | decreased         |
|      HOMO–LUMO gap             | large                      | standard          | small             |
| (iii) geometry                 |                               |                   |                   |
|      bond lengths              | equalization               | alternation       | alternation       |
| (iv) magnetic properties       |                               |                   |                   |
|      anisotropy of diamagnetic susceptibility | enhanced |                   | small             |
|      susceptibility exaltation | high                       |                   | low               |
|      1H NMR shifts             | diatropic (low-field shift) |                   | paratropic (high-field shift) |
|      NICS (nucleus independent chemical shift) | large negative |                   | large positive    |
| (v) reactivity                 |                               |                   |                   |
|      chemical structure        | e.g., benzene              | e.g., cyclohexadiene | e.g., cyclooctatetraene |
|      retention of structure    | electrophilic substitution  | electrophilic addition | addition        |
| (vi) spectroscopy              |                               |                   |                   |
|      UV spectra                | high energy                 | standard          | low energy        |
|      IR/Raman spectra          | high symmetry               | low symmetry       | low symmetry      |
|      photoelectron spectra     | high electron detachment    | standard          | low electron detachment |
|                                  | energies                    |                   | energies          |

Detection of Aromaticity

Magnetic effects:

- The electron delocalization of the $\pi$ electrons sustains ring currents in the presence of an external magnetic field

1. $^1$H NMR spectroscopy measurements yield low-field-shifted (diatropic) signals for H outside the current path

2. The $^1$H NMR signal of the inner hydrogens of porphyrins are shifted upfield because they are inside the current path.

3. Nucleus independent chemical shifts (NICS) at the ring center of aromatic rings are generally negative

4. The magnetically induced ring current is diatropic

5. The ring current gives rise to a magnetic field opposite to the applied one (classical situation)

6. Anisotropy of the diamagnetic susceptibility
Methods for Detection of Aromaticity

Magnetic susceptibilities

The dimension-less (volume) magnetic susceptibility tensor $\chi^v$ is defined by

$$\mathbf{M} = \chi^v \mathbf{B}$$

$\mathbf{M}$ is the magnetization vector and $\mathbf{B}$ the magnetic-flux density.

The more often used molar magnetic susceptibility tensor is

$$\chi^m = (m/d)\chi^v$$

where $m$ is the molar mass and $d$ the density.
Methods for Detection of Aromaticity

Magnetic susceptibilities

The magnetic susceptibility tensor can be diagonalized yielding $\chi_{xx}^m$, $\chi_{yy}^m$, and $\chi_{zz}^m$

For planar molecules (in the xy-plane) the anisotropy of the magnetic susceptibility is

$$\Delta \chi^m = \chi_{zz}^m - \frac{1}{2} \{\chi_{xx}^m + \chi_{yy}^m\}$$

which can be used as an experimental measure of aromaticity.

Methods for Detection of Aromaticity

Magnetic susceptibility exaltation

is the difference in a calculated and measured mean magnetic susceptibilities

\[ \Lambda^m = \chi_m - \chi_{calc} \]

The calculated one is obtained by adding fragment contributions

The difference is then due to electron delocalization effects such as ring currents and aromaticity.

\[ \Lambda^m = \frac{1}{3} \Delta \chi_{London} \]
Methods for Detection of Aromaticity

$^1$H NMR chemical shifts

According to Biot-Savart’s law, the $^1$H NMR shieldings of hydrogens outside (inside) a diatropic ring current is shifted to smaller (larger) ppm values i.e. down field (up-field)

The experimental $^1$H NMR chemical shifts are therefore used as an experimental measure of aromaticity.

![Molecular structures of porphins](image)

Fig. 1 The molecular structures of the porphins, their $^1$H NMR shieldings (in ppm) and current susceptibilities (in nA T$^{-1}$).

Methods for Detection of Aromaticity

$^1$H NMR chemical shifts

![Molecular structures and chemical shifts](image)

Fig. 2 The molecular structures of the chlorins, their $^1$H NMR shieldings (in ppm) and current susceptibilities (in nA T$^{-1}$).

Methods for Detection of Aromaticity

$^1$H NMR chemical shifts of homoaromatic molecules
Methods for Detection of Aromaticity

$^1$H NMR chemical shifts

Table 4
The $^1$H-NMR magnetic shieldings (in ppm) calculated at the SCF SVP/BP SV(P) level

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$H_n$(endo)</th>
<th>$H_n$(exo)</th>
<th>H1</th>
<th>H2</th>
<th>H3</th>
<th>H4</th>
<th>H5</th>
<th>H6</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_4$H$_9$$^+$</td>
<td>26.6</td>
<td>27.7</td>
<td>23.9</td>
<td>21.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_5$H$_8$$^+$</td>
<td>24.7</td>
<td>25.2</td>
<td>19.0</td>
<td>20.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_5$H$_8$$^+$ MP2</td>
<td>24.1</td>
<td>25.2</td>
<td>19.1</td>
<td>20.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_6$H$_7$$^-$</td>
<td>28.0</td>
<td>28.8</td>
<td>29.5</td>
<td>26.3</td>
<td>29.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_7$H$_8$</td>
<td>30.3</td>
<td>29.0</td>
<td>26.4</td>
<td>25.5</td>
<td>25.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_8$H$_9$$^+$</td>
<td>32.9</td>
<td>26.6</td>
<td>25.2</td>
<td>23.4</td>
<td>22.7</td>
<td>23.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_9$H$_9$$^+$</td>
<td>32.7</td>
<td>25.2</td>
<td>23.3</td>
<td>21.7</td>
<td>21.3</td>
<td>21.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$<em>{10}$H$</em>{11}$$^+$</td>
<td>33.9</td>
<td>31.1</td>
<td>26.8</td>
<td>26.5</td>
<td>27.6</td>
<td>25.4</td>
<td>27.6</td>
<td></td>
</tr>
<tr>
<td>C$<em>{11}$H$</em>{12}$</td>
<td>29.1</td>
<td>29.5</td>
<td>26.4</td>
<td>26.3</td>
<td>26.0</td>
<td>25.8</td>
<td>25.5</td>
<td></td>
</tr>
<tr>
<td>C$<em>{11}$H$</em>{12}$ a</td>
<td></td>
<td></td>
<td>26.5</td>
<td>25.6</td>
<td>25.5</td>
<td>26.2</td>
<td>25.7</td>
<td></td>
</tr>
<tr>
<td>C$<em>{12}$H$</em>{13}$$^+$ b</td>
<td>34.1</td>
<td>30.7</td>
<td>24.1</td>
<td>24.3</td>
<td>24.8</td>
<td>23.7</td>
<td>23.5</td>
<td>24.2</td>
</tr>
<tr>
<td>C$<em>{15}$H$</em>{14}$$^+$ c</td>
<td>31.2</td>
<td>27.5</td>
<td>26.2</td>
<td>27.3</td>
<td>27.3</td>
<td>24.1</td>
<td>23.8</td>
<td>23.8</td>
</tr>
<tr>
<td>C$<em>{15}$H$</em>{14}$$^+$ d</td>
<td>28.4</td>
<td>28.2</td>
<td>27.9</td>
<td>20.9</td>
<td>23.5</td>
<td>20.8</td>
<td>27.3</td>
<td>25.2</td>
</tr>
</tbody>
</table>

a  The shieldings for the corresponding hydrogens of the second half of the molecule with a nearly $C_2$ symmetry.
b  The chair conformation (see Fig. 9).
c  The boat conformation (see Fig. 10).
d  The fused-ring structure (see Fig. 11).
Methods for Detection of Aromaticity

Geometric criteria

Aromatic molecule has a very small bond-length alternation (BLA)

The first aromaticity index based on the bond lengths is

$$A_J = 1 - \frac{225}{n} \sum \left(1 - \frac{R_r}{R}\right)^2$$

$R_r$ are the individual bond lengths and $R$ the average one. $A_J$ is a function of the variance of bond lengths.

Methods for Detection of Aromaticity

Geometric criteria

For molecular rings with heteroatoms, an aromaticity index $I$ is obtained by replacing the bond lengths by bond orders

$$I = 100 \cdot \left(1 - \frac{V}{V_k}\right)$$

where

$$V = \frac{100}{\bar{N}} \sqrt{\frac{\sum (N - \bar{N})^2}{n}}$$

and

$$N = \frac{a}{R^2} - b$$

$N$ is bond order, $\bar{N}$ is their mean. $a$ and $b$ are Bird’s constants. $V_k$ is 33.3 and 35 for 5- and 6-membered rings.

Methods for Detection of Aromaticity

Harmonic Oscillator Model of Aromaticity (HOMA)

\[
\text{HOMA} = 1 - \frac{\alpha}{n} \sum_{i=1}^{n} (R_{\text{opt}} - R_i)^2
\]

\(R_{\text{opt}}\) is the optimal bond length, defined as the C–C bond for which the energy of the compression to the length of a double bond and expansion to the length of a single bond in 1,3-butadiene is minimal.

\(\alpha\) is chosen to give HOMA=0 for \(C_6H_6\) with bond lengths taken from 1,3-butadiene.

Methods for Detection of Aromaticity

Harmonic Oscillator Model of Aromaticity (HOMA)

HOMA separates into a bond elongation (EN) and bond alternation (GEO)

\[
HOMA = 1 - \frac{\alpha}{n} \sum (R_{opt} - R_i)^2 =
\]

\[
1 - \left[ \alpha (R_{opt} - R_{av})^2 + \frac{\alpha}{n} \sum (R_{av} - R_i)^2 \right] =
\]

\[
1 - EN - GEO
\]

Detection of Aromaticity

Energetic effects:

- The electron delocalization around the ring stabilizes the molecules
  1. Leading to a blue shift of the UV-vis spectra
  2. a large HOMO-LUMO gap
  3. high electron detachment energies in the photo-electron spectra
  4. Substitution reaction rather than addition reactions are preferred because substitution preserves the aromaticity whereas addition would destroy it.
Methods for Detection of Aromaticity

Aromatic Stabilization Energies (ASE)

- Many approaches have been used to estimate the ASE
- One example is homomolecular homodesmotic reactions

\[
\text{H}_{\text{benzene}} + \text{C}_{\text{hexane}} \rightarrow 2 \text{C}_{\text{cyclohexane}} 
\]

Methods for Detection of Aromaticity

Harmonic Oscillator Stabilization Energy (HOSE)

HOSE in kJ/mol are given by

$$\text{HOSE}_i = 301.15 \left[ \sum_{r=1}^{n_1} (R^r - R_{0s}^s)^2 \cdot k_r' + \sum_{r=1}^{n_2} (R^r - R_{0d}^d)^2 \cdot k_r'' \right]$$

$k_r'$ and $k_r''$ are force constants

$R_{0s}$ and $R_{0d}$ are reference bond lengths

Methods for Detection of Aromaticity

Nucleus Independent Chemical Shifts (NICS)

- NICS (in ppm) are NMR chemical shifts calculated at the center of the aromatic ring under consideration.
- NICS($q$) (in ppm) are NMR chemical shifts calculated $q$ Å above the ring center.

Methods for Detection of Aromaticity

Nucleus Independent Chemical Shifts (NICS)

NICS(1)_{zz} values correlate well with magnetic susceptibility exaltation ($\Lambda^m$) of aromatic and antiaromatic hydrocarbons.

Nucleus Independent Chemical Shifts (NICS)

• \( \text{NICS}(1)_{zz} \) and \( \Lambda^m \) are affected by the size of the ring.

• Anions had the largest deviation from the line indicating computational difficulties

• Summation of \( \text{NICS}(1)_{zz} \) values for individual ring systems of polycyclic ring systems gives a measure of the aromaticity of the entire system.

• \( \text{NICS}(1)_{zz} \) values for individual ring systems are reliable measures of local aromaticity/antiaromaticity.

Methods for Detection of Aromaticity

Magnetic shielding functions

- Nuclear magnetic shieldings can be calculated along the symmetry axis of the molecular ring
- Nuclear magnetic shieldings can be calculated in any point in space

Magnetic shielding functions

- Nuclear magnetic shieldings can be calculated along the symmetry axis of the molecular ring.
- The strength of the magnetically induced current can be estimated from the shielding function.

The Aromatic Ring Current Shielding (ARCS) Method

Shieldings calculated along the symmetry axis of the molecular ring (left)

The strength and the radius of the ring current is obtained from the shielding function by fitting (right)

\[ -\log [\sigma(z)] = \frac{3}{2} \left( \log \left( \frac{R^2}{\varepsilon^2 + R^2} \right) \right) + \log \left( \frac{\mu I_{\text{ring}}}{2R \cdot B_{\text{ext}}} \right) \]

A first attempt to estimate the strength of the magnetically induced ring current.

Methods for Detection of Aromaticity

Ring currents:

Aromatic molecules sustain diatropic ring currents whereas all molecules sustaining ring currents are not aromatic

A uniform time-independent magnetic field with a flux $\mathbf{B}$ induces a current density $\mathbf{J}(r)$ in the electron density

$$\mathbf{J}(r) = \frac{i}{2} \int dr_2...dr_n (\psi^* \nabla \psi - \psi \nabla \psi^* + 2i\mathbf{A} \psi^* \psi).$$

$\psi$ is the wave function,

$\mathbf{A}$ is the vector potential of the external magnetic field
**Induced Currents**

- The induced current density circulates mainly around the nuclei where the electron density is high.
- These currents give rise to the largest part of the observed NMR chemical shifts.
- The current can flow along chemical bonds.
- For ring-shaped molecules the current density can form closed loops around the molecular ring.
- *Diatropic* currents result in induced magnetic fields with opposite direction to the external one.
- *Paratropic* currents strengthen the external field
Aromaticity According to Ring Currents

Ring-shaped molecules

• sustaining net diatropic ring currents are aromatic.
• sustaining net paratropic ring currents are anti-aromatic.
• can sustain simultaneously diatropic and paratropic currents of the same size; no net current.
• can sustain diatropic ring-strain currents
• can sustain no ring currents
Methods to Calculate Magnetically Induced Currents

Three approaches to compute currents:

1. Continuous Transformation of the Origin of the Current Density (CTOCD)

2. Anisotropy of the Induced Current Density (ACID)

3. Gauge-Including Magnetically Induced Currents (GIMIC)

Reviews:
Gauge-Origin Independence

GIMIC is the only one that has no reference to the gauge origin

- Gauge-origin independence is obtained in NMR shielding calculations by using Gauge-Including Atomic Orbitals (GIAO) or London orbitals.

\[ \chi_{\mu}(r) = e^{-\frac{i}{2}(\mathbf{B} \times [\mathbf{R}_\mu - \mathbf{R}_0] \cdot \mathbf{r})} \chi^{(0)}_{\mu}(r) \]

- GIAOs eliminate gauge-origin dependence in current calculations

- The currents are to some extent divergent as gauge invariance is never achieved when using finite basis sets.

- GIAOs lead to a faster basis-set convergence in the current calculations as in shielding calculations.
Expression for the Current Density

Combining

- The analytical gradient NMR shielding expression with
- the corresponding Biot-Savart’s expression yields

\[ J_{\alpha}^{B\beta}(r) = \]

\[ \sum_{\mu\nu} D_{\mu\nu} \frac{\partial \chi^*_\mu(r)}{\partial B_\beta} \frac{\partial \tilde{h}}{\partial m^l_\alpha} \chi_\nu(r) + \sum_{\mu\nu} D_{\mu\nu} \chi^*_\mu(r) \frac{\partial \tilde{h}}{\partial m^l_\alpha} \frac{\partial \chi_\nu(r)}{\partial B_\beta} + \]

\[ \sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial B_\beta} \chi^*_\mu(r) \frac{\partial \tilde{h}}{\partial m^l_\alpha} \chi_\nu(r) - \epsilon_{\alpha\beta\delta} \left[ \sum_{\mu\nu} D_{\mu\nu} \chi^*_\mu(r) \frac{\partial^2 \tilde{h}}{\partial m^l_\alpha \partial B_\delta} \chi_\nu(r) \right], \]

without any reference to the gauge origin.
The vector expression for $J_{\tau}^{B\nu,\kappa}(r)$ is then given by

$$J_{\tau}^{B\nu,\kappa} = v^T P_{\nu}^{\kappa} d_{\tau} - b_{\nu}^{T} D_{\tau}^{\kappa} d_{\tau} + v^T D_{\tau}^{\kappa} q_{\tau \nu} - \epsilon_{\tau \nu \phi} \frac{1}{2}(v^T D_{\tau}^{\kappa} v) r_{\phi}$$

with $D_{\tau}^{\kappa}$ as the AO density matrices for the $\alpha$ and $\beta$ electrons, $P_{\tau}^{\kappa}$ are the corresponding perturbed AO density matrices. The quantities $b_{\tau}, d_{\tau}, q_{\tau \nu}$ given by

$$b_{\tau} = \frac{\partial v}{\partial B_{\tau}}; \quad d_{\tau} = \frac{\partial v}{\partial r_{\tau}}; \quad q_{\tau \nu} = \frac{\partial^2 v}{\partial r_{\tau} \partial B_{\nu}}; \quad (\tau, \nu = x, y, z)$$

Here, $v$ are GIAOs, $\epsilon_{\alpha \delta \gamma}$ is the Levi-Civita tensor, and $r_{\phi}$ the Cartesian directions $x, y, z$. 

Current Density for Open- and Closed-Shell Molecules
Availability

- The current density can be calculated at any level for which $D$ and $P_\alpha$ are available.
- GIMIC is an independent program.
- It has been interfaced to CFOUR (ACESII) and TURBOMOLE.
- The current density has been calculated at the HF SCF, MP2, CCSD, CCSD(T), CCSDT, and DFT levels.
- The current density can also be calculated for open-shell systems at the HF SCF, MP2, CCSD, and CCSD(T) levels.
Calculations of Ring-Current Strengths

- Current-density plots aid the understanding of the molecular current paths.
- They do not provide any quantifiable measures of the current strengths nor are they suitable for comparing current strengths in different molecular systems.
- Quantitative values for the ring current can be obtained by numerical integration of the current flow passing through specific bonds.
- The net current strength is one measure of aromaticity.
Integration of current strengths

FIG. 4. The integration cross section used in the calculation of the integrated current-density distributions.
Aromaticity Dialects

- Originally aromaticity was a hydrocarbon property
- The concept has been generalized to all kind of molecules
- Good old $\pi$ aromaticity, $\sigma$ aromaticity, $\delta$ or $d$ aromaticity, all-metal aromaticity, spherical aromaticity, homoaromaticity, aromaticity of open-shell systems, Hückel and Möbius aromaticity, ....
  (and antiaromaticity)
- How loud can one whisper? Where goes the borderline between aromatic and nonaromatic?

Some of these topics will be discussed in the following
Hückel Aromaticity Rule

The extended Hückel’s rules for aromaticity

- Aromatic molecules has $[4n + 2]_{\pi}$ electrons
- Anti-aromatic molecules has $[4n]_{\pi}$ electrons
- Möbius aromatic molecules has $[4n]_{\pi}$ electrons
- Möbius anti-aromatic molecules has $[4n + 2]_{\pi}$ electrons
- For triplet states, Anti-aromatic $\leftrightarrow$ Aromatic.

E. Heilbronner Tetrahedron Lett. (1964) 1923
N.C. Baird, J. Am. Chem. Soc. 94 (1972) 4941
Hückel Aromaticity Rule

The generalized Hückel’s rules for aromaticity
For twisted and multiply twisted molecular rings.

- Aromatic molecules have $[4n + 2] \pi$ electrons when twisted $2M\pi$, $M = 0, 1, 2, \ldots$ radians

- Aromatic molecules have $[4n] \pi$ electrons when twisted $(2M + 1)\pi$, $M = 0, 1, 2, \ldots$ radians

- Anti-aromatic molecules have $[4n + 2] \pi$ electrons when twisted $(2M + 1)\pi$, $M = 0, 1, 2, \ldots$ radians

- Anti-aromatic molecules have $[4n] \pi$ electrons when twisted $2M\pi$, $M = 0, 1, 2, \ldots$ radians

The ring current of benzene consists of a paratropic one inside the ring and a dominating diatropic one outside.

The diatropic current is strongest in the molecular plane.

The current is **NOT** transported by the $\pi$ electrons above and below the ring.

$\text{C}_6\text{H}_6$, current strength = 11.8 nA/T i.e. 16.7 nA/T and −4.9 nA/T
The Anti-Aromaticity of Cyclobutadiene

\[ \text{C}_4\text{H}_4, \text{ current strength} \ -19.9 \ \text{nA/T i.e. 3.5 nA/T and} \ -23.4 \ \text{nA/T} \]

For cyclobutadiene, the paratropic current inside the ring dominates.
Ring Currents in Homoaromatic Molecules

$C_7H_8$, current strength 6.1 nA/T i.e. 13.1 nA/T and –7.0 nA/T

$C_8H_9^+$, current strength 12.9 nA/T i.e. 18.1 nA/T and –5.2 nA/T
Current Pathways in Homoaromatic Molecules

- The diatropic current circles at the periphery of the ring.
- The ring current is split at the CH$_2$ moiety.
- The main fraction of the current flow passes outside the CH$_2$ at the hydrogens.
- Some current flows inside the carbon atom.
- The diatropic current does not take the through-space shortcut pathway.
- The paratropic current does take the inner route.
(HF)$_3$: a failure for NICS

The exponent is 1.88, not 1.5

Ring-current profile

Current density plot

Pyrene: a failure for NICS

The NICS(0) value in the end ring is -11.3 ppm.
The ring-current susceptibility is 16.4 nA/T

The NICS(0) value in the side ring is -4.2 ppm
The ring-current susceptibility is 10.4 nA/T