Möbius Annulenes
—— Another Type of Aromatic System

CONTENTS

• Introduction of Hückel aromaticity.
• What is Möbius type conformation.
• The energy level scheme of Hückel and Möbius type conformation.
• Some types of Möbius system
Hückel aromatic annulenes are well known!

Wave functions of Hückel formulas:

\[ \chi_J = \frac{1}{\sqrt{n}} \sum_{f=0}^{n-1} \epsilon_n^f \psi_f \]

\[ \epsilon_n = e^{2\pi J / n} \]

Energy levels of Hückel formulas:

\[ \epsilon_J = \alpha + 2\beta \cos \frac{2\pi J}{n} \]

\[ J = 0, \pm 1, \pm 2 \ldots \]

\( \pm \frac{n-1}{2} \) for \( n \) odd

\( \pm \frac{n}{2} \) for \( n \) even.


Scheme for construction of energy level diagram of ring compounds. Resonance energies, unit: -\( \beta \)

\[ \epsilon_J = \alpha + 2\beta \cos \frac{2\pi J}{n} \]

\[ J = 0, \pm 1, \pm 2 \ldots \pm \frac{n-1}{2} \]

Scheme for construction of energy level diagram of ring compounds. Resonance energies, unit: -β

\[ \varepsilon_J = \alpha + 2\beta \cos \frac{2\pi J}{n} \]

\[ J = 0, \pm 1, \pm 2 \ldots + \frac{n}{2} \]

Lide, Jr., David, R. J. Chem. Phys. 20, 572 (1953)

**Hückel Rule of Aromaticity**

Conditions necessary to apply rule

* Monocyclic molecules (but works on some polycycles)
* Planar Rings
* Each atom in ring must be sp² hybridized

For a monocyclic planar ring system to be aromatic there must be \(4n+2\) \(\pi\) electrons where \(n=\text{integer}\) beginning with \(n=0\)
Resonance integral $\beta_{\mu\nu}$ of a twisted $\pi$-bond in Hückel molecular orbital (HMO)

\[ \beta_{\mu\nu} = \beta \cos \omega_{\mu\nu} \]

It is usually assumed that the total $\pi$-electron energy has an absolute maximum for the coplanar system (all $\omega_{\mu\nu} = 0$ or $\pi$)


The topological equivalent of a Möbius type conformation

\[ \omega = \pi / n \]
\[ \beta^M = \beta \cos(\pi / n) \]

A Möbius type conformation

The corresponding HMOs of a Möbius type conformation:

\[ \chi_J = \frac{1}{\sqrt{n}} \sum_{j=0}^{n-1} \epsilon_n \psi_j \]

\[ \epsilon_n = e^{i(2J+1)/n} \]

The orbital energies of a Möbius type conformation:

\[ \epsilon_J^M = \alpha + 2\beta^M \cos \frac{\pi(2J+1)}{n} \]

\[ J = 0, 1, 2, \ldots, n-1 \]

Compare with the orbital energies of Möbius and Hückel type conformation

The orbital energies of a Hückel type conformation:

\[ \epsilon_J^H = \alpha + 2\beta^H \cos \frac{2\pi J}{n} \]

\[ J = 0, 1, 2, \ldots, n-1 \]

The orbital energies of a Möbius type conformation:

\[ \epsilon_J^M = \alpha + 2\beta^M \cos \frac{\pi(2J+1)}{n} \]

\[ J = 0, 1, 2, \ldots, n-1 \]

The energy level scheme for Möbius and Hückel type perimeters

The occupancy of Möbius and Hückel type perimeters
Transformation of Hückel and Möbius type perimeters

Changing of π-electron energy:

**Step 1:**

$4\beta$

**Step 2:** each level energy

$\epsilon_j^H - \epsilon_j^M = -2\beta[\sin \pi / n][\sin \pi (2J + 1) / n]$

summing over all

$4 \sum_{j=0}^{j=1} (\epsilon_j^H - \epsilon_j^M) = -4\beta$

Mnemonics of Möbius type perimeters

$$\epsilon_j^M = \alpha + 2\beta^M \cos \frac{2\pi J}{n}$$

• Large-ring polyenes might be twisted once to give Möbius-type annulenes

• For a Möbius-type annulenes to be aromatic there must be $4n \pi$ electrons

But what is “aromaticity”??

“Systems of delocalized electrons in closed circuits.”

“4n rule” or “4n+2 rule” is only a RULE!
Some modern criteria of “Aromaticity”

**Geometric** (C-C bond length alternation)
- \( \Delta r \) and \( \Delta r_m \)
- \( \angle CCC \)
- Julg parameter \( A = 1 - (2/5/n) \Sigma [1 - (r_i/r)]^2 \)
- HOMA (Harmonic Oscillator Measure of Aromaticity) index

\[
\text{HOMA} = 1 - \frac{D}{n} \sum \left| R_{opt} - R_i \right|^2
\]

**Energetic** (Aromatic stabilization energies)
- Hydrogenation energy
- Isomerization methods ISE and ISE III

**Magnetic** (The effects of induced “ring currents”)
- MSE (Magnetic Susceptibility Exaltations, \( \Lambda \))
- NICS (Nucleus-Independent Chemical Shifts)
- \(^1\text{H} \) NMR chemical shifts
- Induced ring current density maps


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Some types of Möbius system

- Transition-state species
- Unstable intermediates
- **Stable Möbius-type annulenes?**
Closure of butadiene to cyclobutene

Structure of Möbius [12]annulenes

<table>
<thead>
<tr>
<th>No</th>
<th>Topol</th>
<th>Sym</th>
<th>ΔE</th>
<th>NLO</th>
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Geometry of structure 5

Structure of Möbius [16]annulenes

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Geometry of structure 11

Structure of Möbius [20]annulenes

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The first example of a Moëbius aromatic transition state that does not involve breaking or forming $\sigma$ bonds

The first example of a Moëbius aromatic transition state that does not involve breaking or forming $\sigma$ bonds
Prediction for Möbius Benzene

—the smallest conceivable antiaromatic Möbius annulene

Potential Electrocyclic Pathways for Dewar benzene

Potential energy diagram (kcal/mol) for conrotatory and disrotatory opening of Dewar benzene

MP2/6-31G* and (in parentheses) CASSCF(6,6)/3-21G optimized geometries for Mobiüs benzene

Monocyclic (CH)$_9^+$
—— An example of stable Möbius aromatic intermediate

Under ionizing conditions (liquid SO$_2$ at -66$^\circ$C), D-labeled 2 gave 3 (X=Cl) by ion-pair return, again with complete statistical distribution of the label (1/9D per C atom).


### Monocyclic (CH)$_9^+$
—— An example of Möbius aromatic system

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<th>rel E</th>
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<th>$\chi$</th>
<th>$\Lambda$</th>
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Unstable Möbius-type intermediate of pericyclic reaction

Geometry of 7 calculated at the RHF/6-31G level
Synthesis of a Möbius aromatic hydrocarbon

Relative stabilities of perimeters

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<th>$E_{\text{rel}}$</th>
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<th>$E_{\text{rel}}$</th>
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<td>$S_8$</td>
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<td>$C_1$</td>
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Strategy to stabilize the Möbius structure of annulenes

Reaction of *syn*-tricyclooctadiene with tetradehydrodianthracene
X-ray structures and photographs of the crystals of the $C_2$ Möbius and the $C_8$ Hücker isomer

Is it a real Möbius AROMATIC system?
Structure of the Möbius hydrocarbon

Comparing the geometry informations between synthesis Möbius hydrocarbon and some theoretical models

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Comparing the magnetic properties between synthesis Möbius hydrocarbon and some theoretical models

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ISEII Values (kcal/mol) for the synthesis Möbius hydrocarbon and Related Systems

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$I_{SE_{II}}$ Values (kcal/mol) for the synthesis Möbius hydrocarbon and Related Systems

Conclusion and future works

• For a Möbius-type annulenes to be aromatic there must be $4n \pi$ electrons.

• How to syntheses a real Möbius-type aromatic annulenes.

• How to validate the 40 years suppose of Heilbronner.

A example of double-twist Möbius-aromatic conformation of [14]Annulene

NICS(0) = -7.0 ppm
$\Delta r = 0.096 \text{ Å}$

NICS(0) = -18.3 ppm
$\Delta r = 0.010 \text{ Å}$

ACKNOWLEDGMENT

- Thank Prof. Yundong, Wu.
- Thank Prof. Zhixiang, Yu.
- Thank Fan, Jiang; Mingbo, Zhang; Can, Wang and all group members.