

# Bridging between the magnetic and molecular orbital pictures of excited-state aromaticity

Felix Plasser

Department of Chemistry, Loughborough University

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University

# Motivation

## ?) Strategies for tuning photoredox properties

### ► Delocalisation

- Larger molecule → Reduced confinement → Lower gap

### ► Electron donating/withdrawing substituents

- Donating → Increase orbital energies
- Withdrawing → Decrease orbital energies

### ► HOMO/LUMO overlap

- Singlet-triplet splitting

## (:, Is that all there is?

# Aromaticity

## (Excited-state) aromaticity<sup>1,2</sup>

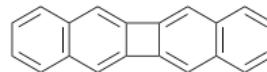
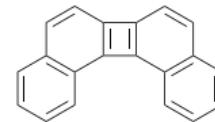
- ▶ New simple design rules
  - *Count electrons*
  - *Analysis of bonding / resonance structures / Clar sextets*
- ▶ Lowering of excitation energies
  - Low excitation energies with large singlet-triplet gaps → **singlet fission**
  - Large **Stokes shifts** (with structural flexibility)
- ▶ Altered **redox properties**
  - States with  $4n - 2$  electrons more easily accessible
  - Two-electron oxidation/reduction

<sup>1</sup>N. C. Baird, *J. Am. Chem. Soc* **1972**, 94, 4941.

<sup>2</sup>H. Ottosson, *Nat. Chem.* **2012**, 4, 969–971.

# Molecules

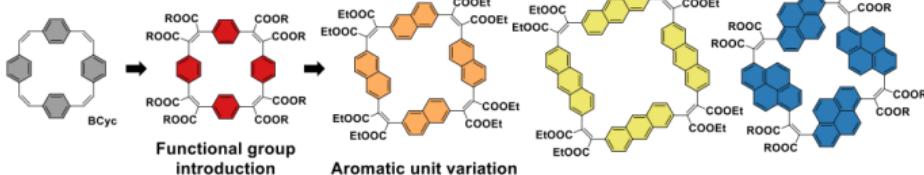
## Polycyclic hydrocarbons

Dibenzo[b,h]biphenylene (**1**)Dibenzo[a,i]biphenylene (**2**)

- ▶ Polycyclic and macrocyclic systems
  - **Excitation**
  - **Oxidation/Reduction**

- ② **Qualitative description** of these processes
- Molecular orbital picture
  - Magnetic picture

## Macrocycles



# Outline

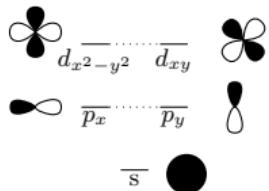
- 1 Aromaticity within the molecular orbital and magnetic pictures
- 2 Biphenylene derivatives  
→ Tuning of excitation energies
- 3 Formally antiaromatic macrocycles  
→ Redox properties and Stokes shifts
- 4 Conclusions

# Aromaticity - Molecular orbital picture

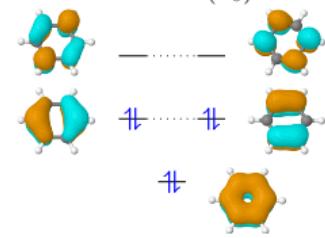
- ▶ Cyclic  $\pi$ -systems
- ▶ Orbital eigenvalues analogous to 2D **rigid rotor**
- Lowest  $\pi$ -orbital non-degenerate
- Higher  $\pi$ -orbitals come in degenerate pairs
  
- ▶ **Filled shells** for **odd** number of electron pairs ( $4n + 2$  electrons)
- ▶ **Low HOMO/LUMO gap** for **even** number of electron pairs ( $4n$  electrons)

## Cyclic $\pi$ -systems

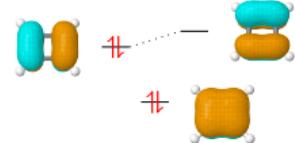
### 2D rigid rotor



### Benzene ( $S_0$ )



### CBD ( $S_0$ )

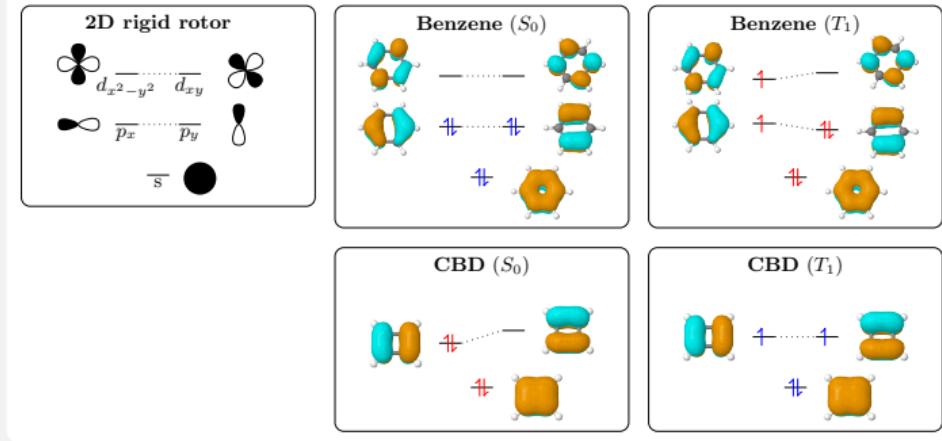


<sup>1</sup>FP, *Chemistry* 2021, 3, 532.

# Excited States

- ▶ Triplet: rules reversed
- **Baird aromaticity<sup>1</sup>**
  
- ▶ Singlet excited states: analogous orbital energetics
- **Similar aromaticity rules** apply<sup>2</sup>

## Cyclic $\pi$ -systems



<sup>1</sup>N. C. Baird, *J. Am. Chem. Soc* **1972**, 94, 4941.

<sup>2</sup>B. J. Lampkin, Y. H. Nguyen, P. B. Karadakov, B. Vanveller, *PCCP* **2019**, 21, 11608.

# Excited States

## ► Assignment

- *Initial vs final* orbital involved in the excitation

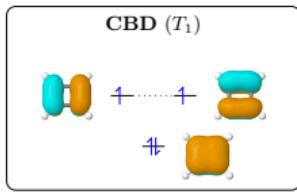
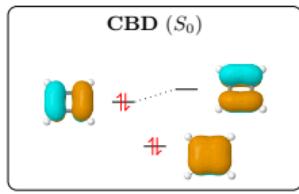
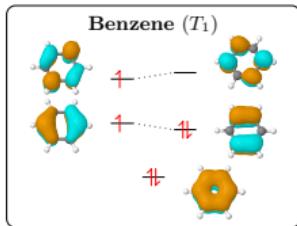
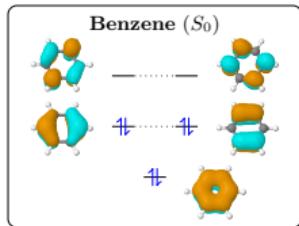
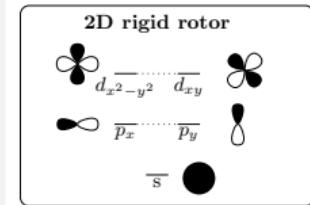
## ► Excited-state **aromaticity**

- Angular momentum / nodal planes **the same**

## ► Excited-state **antiaromaticity**

- Angular momentum / nodal planes **increase**

## Cyclic $\pi$ -systems



# Magnetic picture

- ▶ Nucleus independent chemical shift<sup>1</sup>
  - Perform **virtual NMR experiment**
  - **Shielding** for **aromatic** systems
  - **Deshielding** for **antiaromatic** systems
  
- ② How do we visualise a tensor
  - $3 \times 3$  matrix at every point in 3D space

Chemical shielding tensor

$$\mathbf{B}_{\text{ind}}(\mathbf{R}) = -\underline{\sigma}(\mathbf{R})\mathbf{B}_{\text{ext}}$$

$\mathbf{B}_{\text{ext}}$  External magnetic field

$\mathbf{B}_{\text{ind}}$  Induced magnetic field

$\underline{\sigma}$  Shielding tensor

<sup>1</sup>P. von R. Schleyer, et al., *J. Am. Chem. Soc.* **1996**, 118, 6317–6318.

# Visualisation of chemical shielding tensors (VIST)

## Eigenvalue decomposition

$$\underline{\sigma} \mathbf{q}^{(i)} = t^{(i)} \mathbf{q}^{(i)}$$

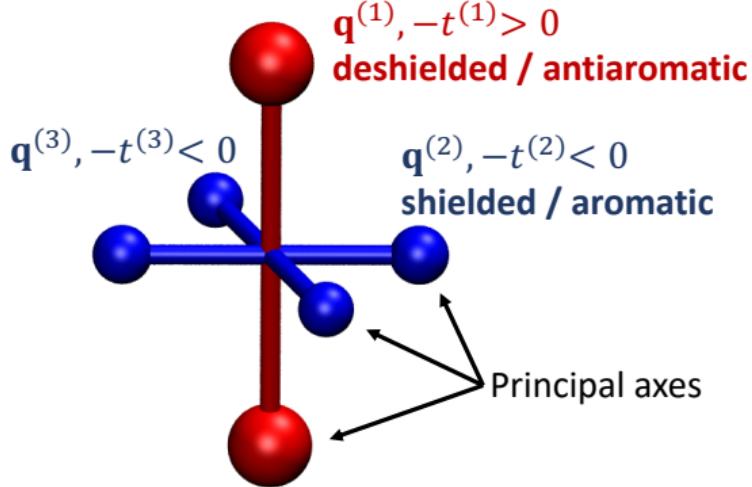
$\mathbf{q}^{(i)}$  Eigenvectors – principal axes

→  $\mathbf{B}_{\text{ext}}$  parallel to  $\mathbf{B}_{\text{ind}}$

$t^{(i)}$  Eigenvalues

- 😊 **Full information** from local shielding tensor encoded graphically
- No a priori choice of a magnetisation axis
- Suitable even for **non-planar systems**

## Visualisation of chemical shielding tensors (VIST)



<sup>1</sup>FP, F. Glöcklhofer, European J. Org. Chem. 2021, 2021, 2529.

## Visualization of shielding tensors

- 😊 Intuitive visualization of qualitative changes in magnetic properties with electronic state
- 😊 Applicable to non-planar systems → anisotropy
- 😊 Lightweight method
  
- 🙁 Same problems as original NICS<sup>1</sup>
- 🙁 Reduced spatial information compared to current density plots or isotropic shielding surfaces

<sup>1</sup>A. Stanger, *EJOC* **2020**, 2020, 3120.

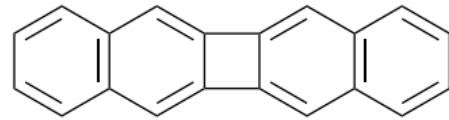
# Triplet energies

- ▶ Two isomeric polycyclic hydrocarbons
  - Built around cyclobutadiene
- ?(?) Which one has higher **excitation energies**

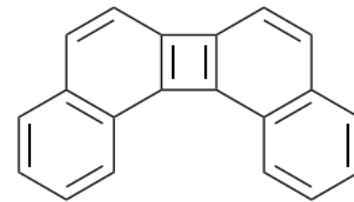
Vertical excitation energy (eV) – TDDFT/CAM-B3LYP

	<b>1</b>	<b>2</b>
$T_1$	2.74	1.56
$S_1$	3.71	2.63

- !(!) Energies shifted by **more than 1 eV**
- ?(?) Why



Dibenzo[b,h]biphenylene (1)



Dibenzo[a,i]biphenylene (2)

<sup>1</sup>FP, *Chemistry* **2021**, 3, 532.

# Excited-state aromaticity

## ► Hückel's rule

- 😊 Ring with **6 electrons** → aromatic
- 😢 Ring with **4 electrons** → antiaromatic

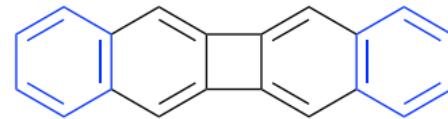
## ► Baird aromaticity

- Antiaromatic molecules become aromatic in their excited triplet state<sup>1</sup>

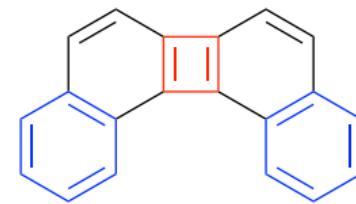
## ► Resonance structures

- **1** cannot have quartet and sextets at the same time
  - **2** has quartet + two sextets
- **Hypothesis:** **2** is more antiaromatic in its ground state and more aromatic in its excited states (see Ref. 2)

## ► Look at shielding tensors and orbitals



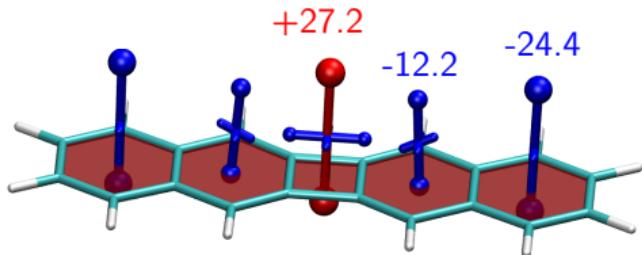
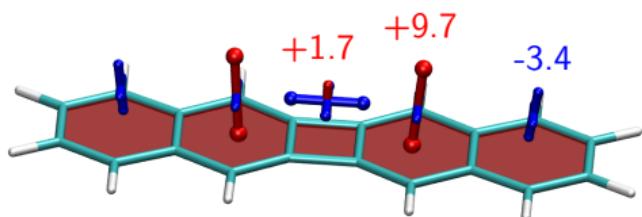
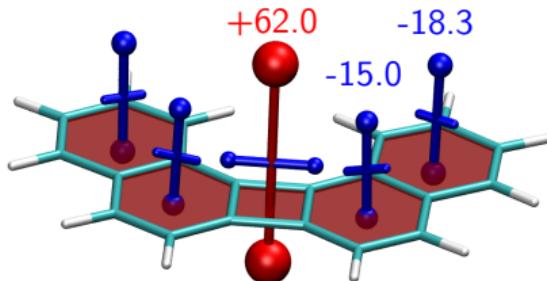
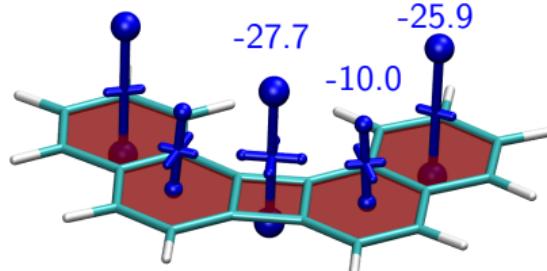
Dibenzo[b,h]biphenylene (**1**)



Dibenzo[a,i]biphenylene (**2**)

<sup>1</sup>N. C. Baird, *JACS* **1972**, 94, 4941–4948.

<sup>2</sup>R. Ayub, O. El Bakouri, K. Jorner, M. Sola, H. Ottosson, *J. Org. Chem.* **2017**, 82, 6327–6340.

Molecule 1 –  $S_0$  – RKS/TPSShMolecule 1 –  $T_1$  – UKS/TPSShMolecule 2 –  $S_0$  – RKS/TPSShMolecule 2 –  $T_1$  – UKS/TPSSh

# Excitation process

?) Why is there such a big difference

→ Comparison with MO picture

► Natural transition orbitals<sup>1</sup>

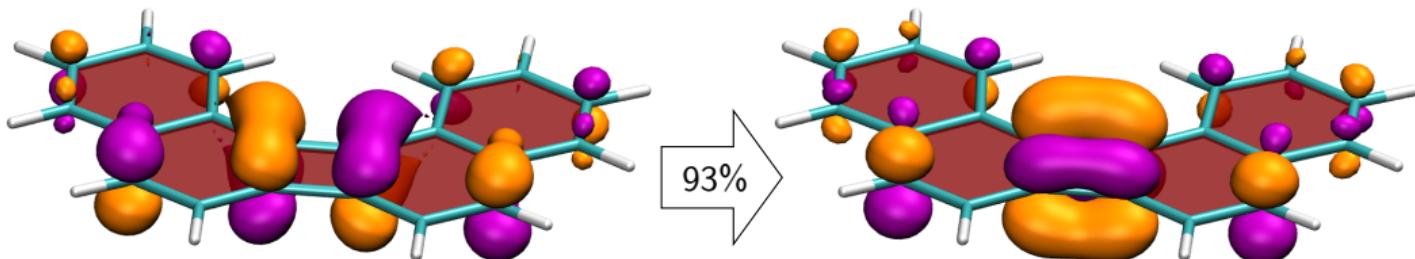
- Singular value decomposition of the *transition density matrix*<sup>2</sup>

<sup>1</sup>R. L. Martin, *JCP* **2003**, 118, 4775–4777.

<sup>2</sup>F.P. M. Wormit, A. Dreuw, *JCP* **2014**, 141, 024106.

# Excitation process

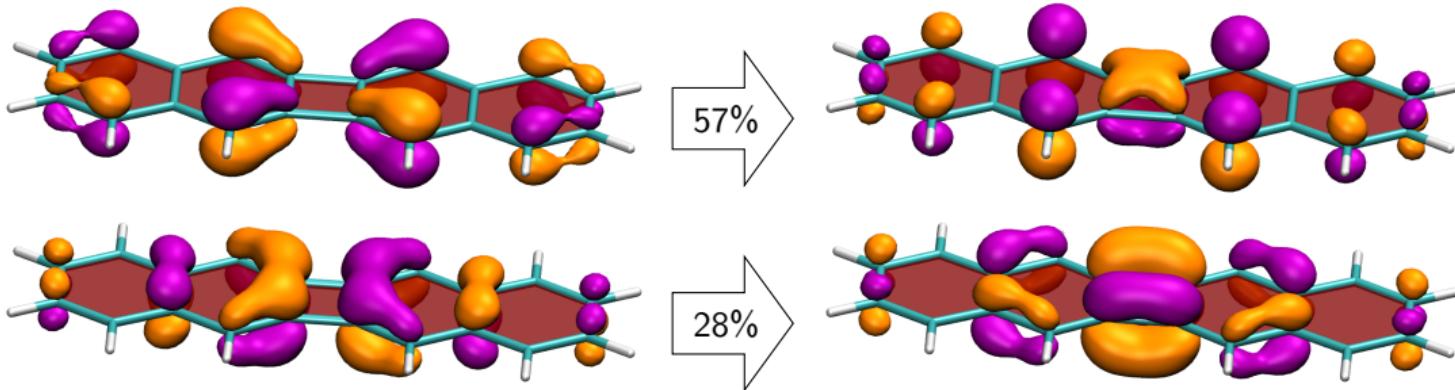
Molecule 2 – Natural transition orbitals ( $S_0 \rightarrow T_1$ )



- ▶ Dominant transition around cyclobutadiene
- ▶ Orbitals of **same angular momentum**
- Fits with previous discussion on **Baird aromaticity**

# Natural transition orbitals

Molecule 2 – Natural transition orbitals ( $S_0 \rightarrow T_1$ )



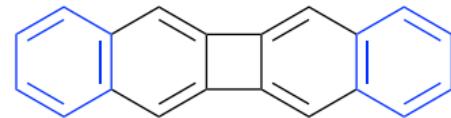
- ▶ Two interacting configurations
  - First one naphthalene HOMO/LUMO transition
  - Only second one around cyclobutadiene
- **Reduced Baird aromaticity**

# Summary

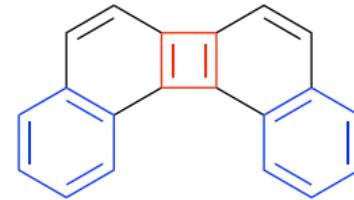
► Consistent picture

→ Baird aromaticity enhanced for 2

- Quartets/sextets
- Excitation energies
- Chemical shielding tensors
- Natural transition orbitals



Dibenzo[b,h]biphenylene (**1**)



Dibenzo[a,i]biphenylene (**2**)

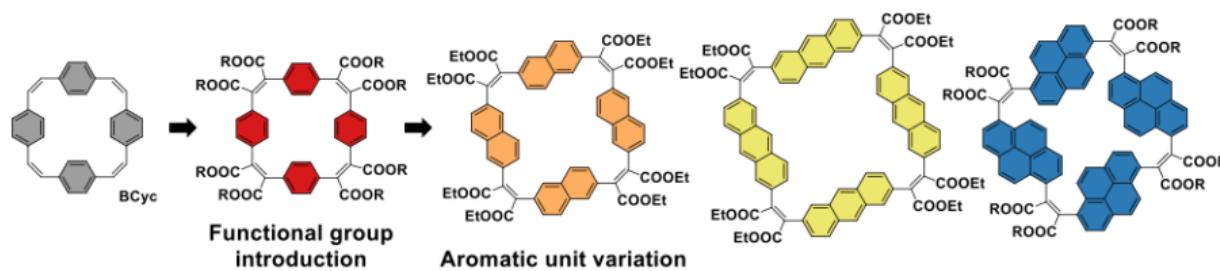
<sup>1</sup>FP, F. Glöcklhofer, *European J. Org. Chem.* **2021**, 2021, 2529.

<sup>2</sup>FP, *Chemistry* **2021**, 3, 532.

# Macrocycles

- ▶ Synthesis of different macrocycles<sup>1</sup>
  - All with a **formally antiaromatic**  $4n \pi$ -electron perimeter
- ▶ Consequences of  $4n \pi$ -electron perimeter
  - Doubly charged states become **aromatic** → Multielectron reduction → Batteries<sup>2</sup>
  - Excited states become **aromatic** → Excited-state relaxation
- ?(?) What happens along the series

## Macrocycles



<sup>1</sup>M. Rimmelle, W. Nogala, et al., *Org. Chem. Front.* **2021**, 8, 4730.

<sup>2</sup>S. Eder, et al., *Angew. Chemie - Int. Ed.* **2020**, 59, 12958.

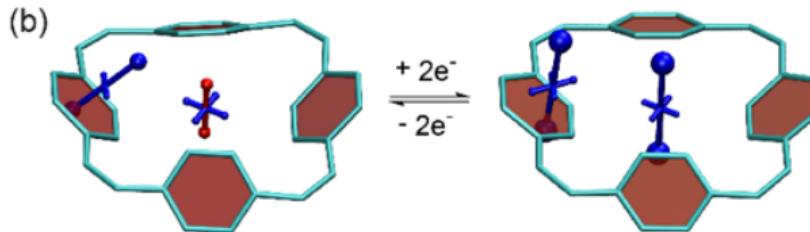
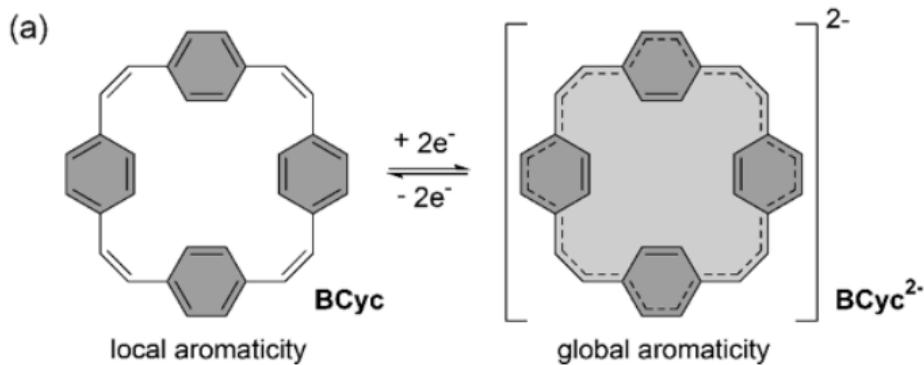
## Macrocycles

- ▶ Neutral state
    - Local **aromaticity**
    - Weak/no global **antiaromaticity**
  - ▶ Dianion
    - Global **aromaticity**

?

How about the other cycles

## Two-electron reduction

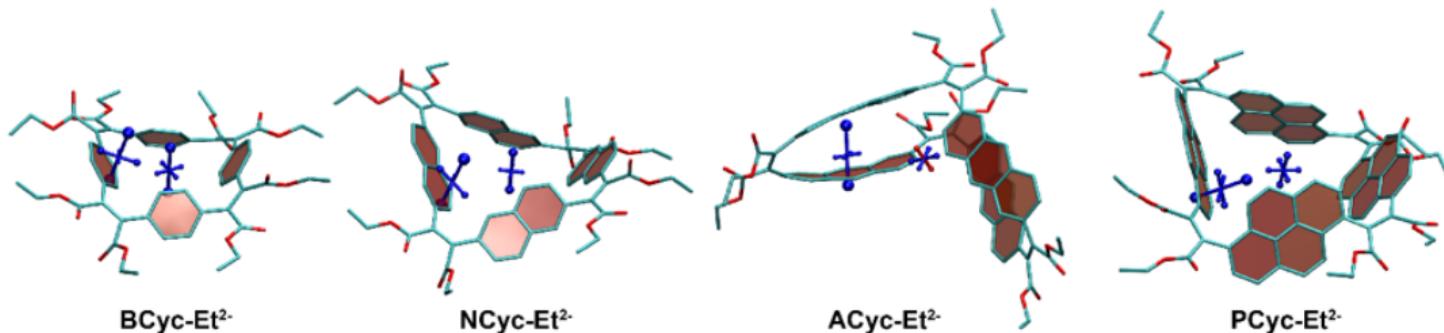


# Dianions

## ► Example: Dianions

- Local *vs* global aromaticity
- Balance changes with increasing system size → global aromaticity becomes “blurred”

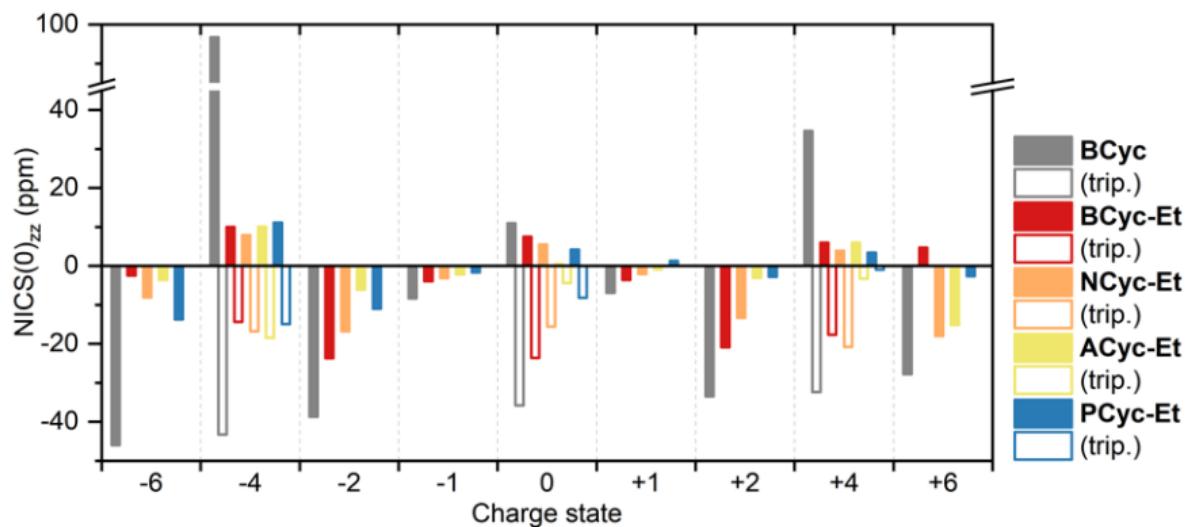
## Dianions



# NICS

- ▶ Compute **nucleus-independent chemical shift** for different states
  - NICS < 0 → **aromatic** / NICS > 0 → **antiaromatic**
  - Expected trends
  - Blurred for larger systems → strong **antiaromaticity** only for **BCyc +4/-4**

# NICS



# NICS vs ring currents

② How do the NICS values compare to **ring currents**

- Consider *conductor loop model*

## Conductor loop

$$B_{ind,z} = \frac{\mu_0}{2R} I$$

$$\text{NICS}(0)_{zz} = \frac{B_{ind,z}}{B_{ext,z}} = \frac{\mu_0}{2R} \frac{I}{B_{ext,z}}$$

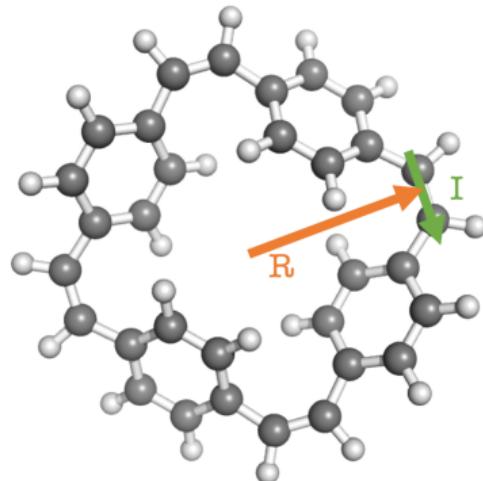
$B_{ind,z}$  Induced magn. field at center of loop

$\mu_0$  Bohr magneton

$R$  Radius

$I$  Current (from GIMIC)

## Conductor loop



<sup>1</sup>M. Rimmele, W. Nogala, et al., *Org. Chem. Front.* **2021**, 8, 4730.

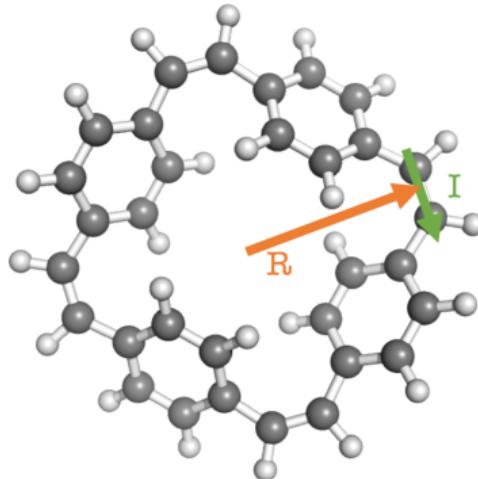
# NICS vs ring currents

## Conductor loop - BCyc

Charge	Current nA/T	NICS (model) ppm	NICS (DFT) ppm
-6	-36.2	-47.2	-46.0
-4	61.6	80.3	96.7
-2	-31.6	-41.2	-38.7
0	0.8	1.0	11.0
+2	-27.8	-36.2	-33.5
+4	18.5	24.1	34.6
+6	-24.1	-31.5	-27.7

- 😊 Good semi-quantitative agreement
- ▶ NICS (DFT) values generally higher than model
- More formal **antiaromaticity** from NICS (DFT)
  - Probably related to de-shielding from benzene rings

## Conductor loop

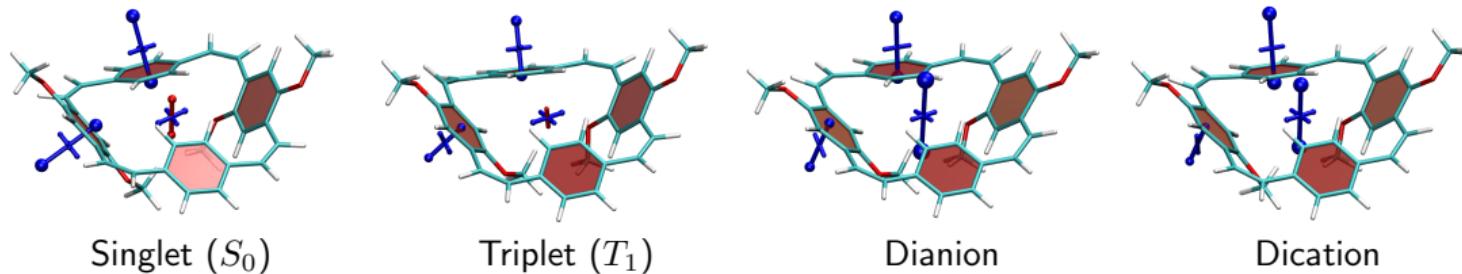


<sup>1</sup>M. Rimmele, W. Nogala, et al., *Org. Chem. Front.* **2021**, 8, 4730.

# Methoxy derivatives

- ▶ Methoxy substituted derivatives
    - Singlet – local **aromaticity** / weak global **antiaromaticity**
    - Dianion, dication – global **aromaticity**
- ② Why is the triplet not Baird aromatic

## VIST plots

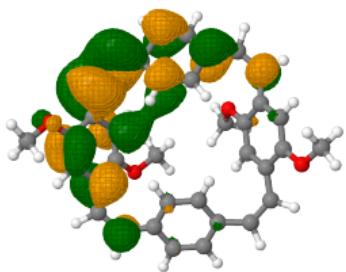


<sup>1</sup>M. Pletzer, FP, et al., *Open Res. Eur.* **2021**, 1, 111.

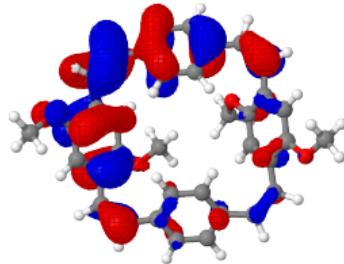
# Methoxy derivatives

- ▶ Look at electronic structure through **natural difference orbitals**
  - Obtained as eigenvectors of difference density matrix
- Available for **non-orthogonal orbitals** and between states with **different electron number**
- ▶ **Symmetric structure** for dianion and dication → 12 nodal planes each
- ▶ **Symmetry broken** for triplet

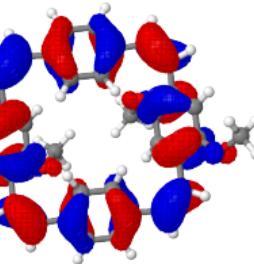
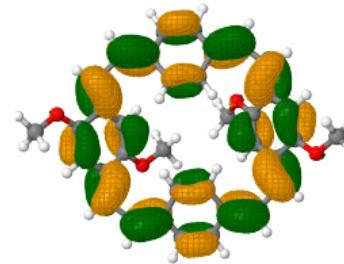
## Natural difference orbitals



Triplet ( $T_1$ )



Dianion

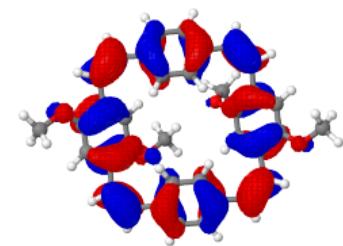
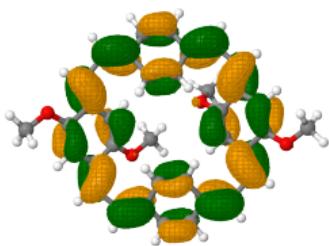


Dication

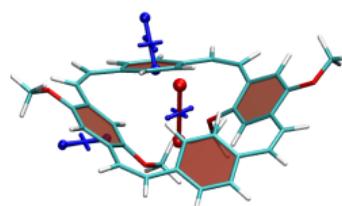
# Methoxy derivatives

- (?) What about the  $S_1$  state
- (:( Cannot compute shielding tensors for  $S_1$
- (: Can compute natural difference orbitals and shielding tensors in  $S_0$  and  $T_1$ 
  - Both support excited-state aromaticity

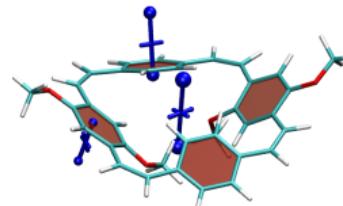
## $S_1$ state



Natural difference orbitals



$S_0 @ S_1$



$T_1 @ S_1$

# Summary

## ► Aromaticity

- Design strategy for tuning photophysical and electrochemical properties
- Clear structure/property relationships
  - Biphenylene derivatives
  - Formally antiaromatic macrocycles

## ► Tools

- Visualization of **chemical shielding tensors**
- Natural transition/difference **orbitals**
- Implemented in the open-source **TheoDORE** package<sup>1</sup>

<sup>1</sup><https://theodore-qc.sourceforge.io/>

## Acknowledgements

# Loughborough

P. Kimber



Loughborough  
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A. Dreuw

Vienna

M. Menger

L. González

## Vienna/Lubbock/Tianjin

H. Lischka



FWF

Slides available at: <https://fplasser.sci-public.lboro.ac.uk>