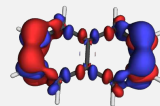
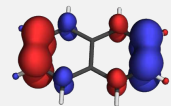


Tuning photophysical properties via excited-state aromaticity

Felix Plasser

Department of Chemistry, Loughborough University

Computational PhotoChemistry Online Meeting 2021
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Loughborough
University

Introduction

❓ Strategies for **tuning excitation energies**

▶ **Delocalisation**

- Larger molecule → Reduced confinement → Lower excitation energy

▶ **Electron donating/withdrawing substituents**

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

▶ **HOMO/LUMO overlap**

- Singlet-triplet splitting

☹ **Is that all there is?**

☹ **Not independent**

Aromaticity

(Excited-state) aromaticity¹

- ▶ New simple design rules
 - *Count electrons*
 - *Form disjoint Clar sextets*
- ▶ **Lowering of excitation energies**
 - Low excitation energies with large singlet-triplet gaps → **singlet fission**
 - **Biradicals**
 - Large **Stokes shifts** (*with structural flexibility*)
- ▶ Altered redox properties

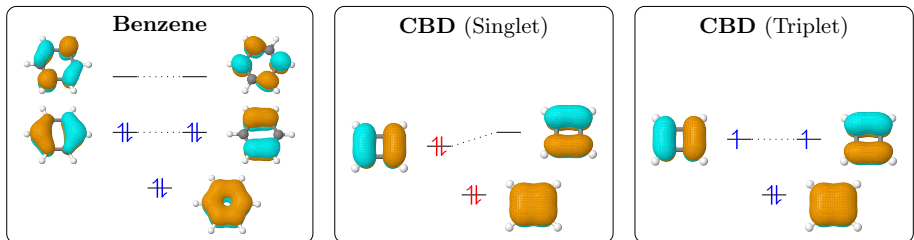
¹H. Ottosson, *Nat. Chem.* **2012**, 4, 969–971.

Outline

- 1 Biphenylene derivatives
→ **Tuning of excitation energies**
- 2 Polyaromatic hydrocarbons
→ **Biradical character**
- 3 Formally antiaromatic macrocycles
→ **Redox properties and Stokes shifts**
- 4 Conclusions

Molecular orbital picture

Cyclic π -systems



- ▶ Lowest π -orbital non-degenerate, higher π -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)
- ▶ Triplet: **Filled shells** with $4n$ electrons
- ▶ Singlet excited states: also stabilised due to low HOMO/LUMO gap
 - More complicated because of possible *double excitations*
 - Significant **exchange repulsion** → higher energy

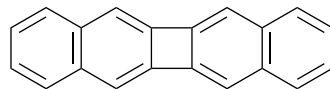
Triplet energies

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

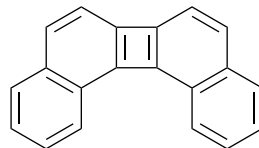
Vertical excitation energy (eV) – TDDFT/CAM-B3LYP

	1	2
T_1	2.74	1.56
S_1	3.71	2.63

❗ Energies shifted by **more than 1 eV**



Dibenzo[b,h]biphenylene (1)



Dibenzo[a,i]biphenylene (2)

¹FP, *Chemistry* **2021**, 3, 532.

Excited-state aromaticity

► Hückel's rule

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

► Baird aromaticity

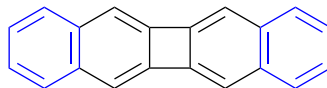
- Antiaromatic molecules become aromatic in their excited triplet state¹

► Resonance structures

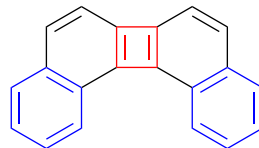
- **1** cannot have quartet and sextets at the same time
- **2** has quartet + two sextets

→ *Hypothesis*: **2** is more antiaromatic in its ground state and more aromatic in its excited states (see Ref. 2)

❓ How do we quantify/visualise aromaticity



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



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

¹N. C. Baird, *JACS* **1972**, 94, 4941–4948.

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

Nucleus independent chemical shift

- ▶ Perform **virtual NMR experiment**
 - Nucleus independent chemical shift¹
- **Shielding** for **aromatic** systems
- **Deshielding** for **antiaromatic** systems
- ⑦ How do we visualise a tensor
 - 3×3 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

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

Visualisation of chemical shielding tensors (VIST)

Eigenvalue decomposition

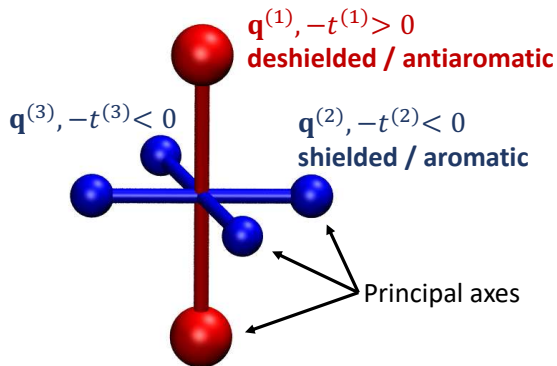
$$\underline{\sigma} \mathbf{q}^{(i)} = t^{(i)} \mathbf{q}^{(i)}$$

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

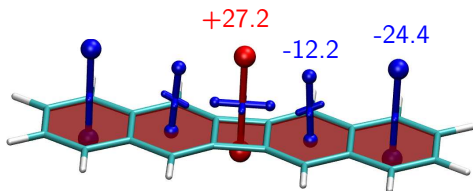
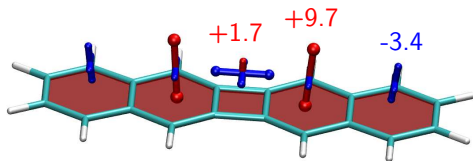
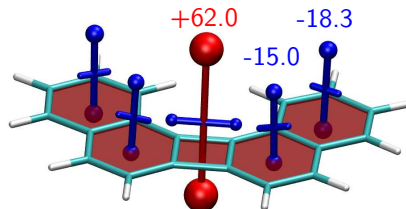
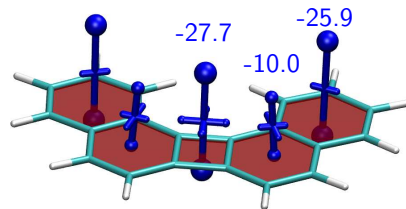
$t^{(i)}$ Eigenvalues

- ☺ **Full information** from local shielding tensor encoded graphically
- No a priori choice of a magnetisation axis
- Suitable even for **non-planar systems**¹

Visualisation of chemical shielding tensors (VIST)



¹FP, F. Glöcklhofer, *EJOC* **2021**, DOI: 10.1002/ejoc.202100352.

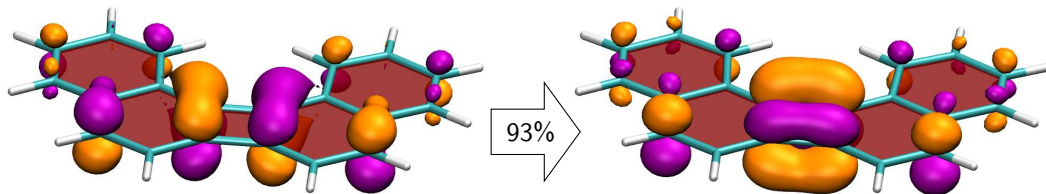
Molecule 1 – S_0 – RKS/TPSShMolecule 1 – T_1 – UKS/TPSShMolecule 2 – S_0 – RKS/TPSShMolecule 2 – T_1 – UKS/TPSSh

Excitation process

① Rigorous representation of the excitation process

- Natural transition orbitals¹
 - Singular value decomposition of the *transition density matrix*²

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



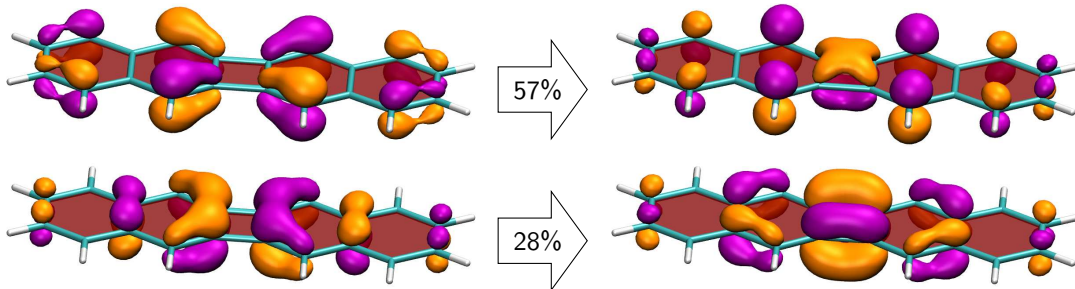
- Dominant transition around cyclobutadiene
- Fits with previous discussion on **Baird aromaticity**

¹R. L. Martin, *JCP* **2003**, 118, 4775–4777.

²FP, M. Wormit, A. Dreuw, *JCP* **2014**, 141, 024106.

Natural transition orbitals

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



- Two interacting configurations
 - Only second one around cyclobutadiene
- **Reduced Baird aromaticity**

Summary

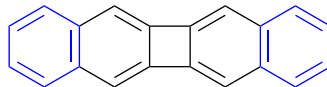
► Consistent picture

→ **Baird aromaticity** enhanced for **2**

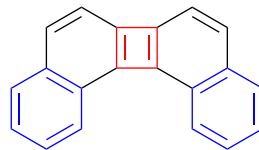
- Quartets/sextets
- Excitation energies
- Chemical shielding tensors
- Natural transition orbitals

► Interpretation in MO picture

- **Low** HOMO/LUMO gap with **large** spatial overlap



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



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

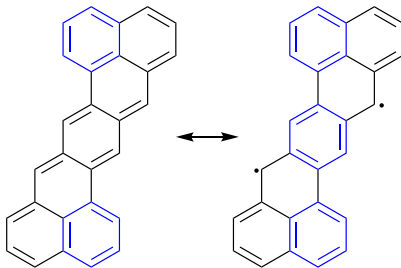
¹FP, F. Glöcklhofer, *EJOC* **2021**, DOI: 10.1002/ejoc.202100352.

²FP, *Chemistry* **2021**, 3, 532.

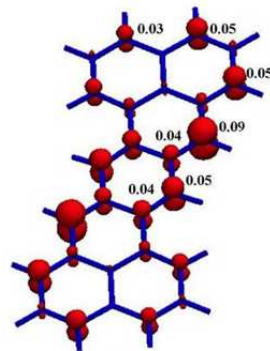
Related chemistry

- Fused benzene rings
 - Maximal number of sextets only with **biradical formation**

Zethrenes¹



Unpaired electrons

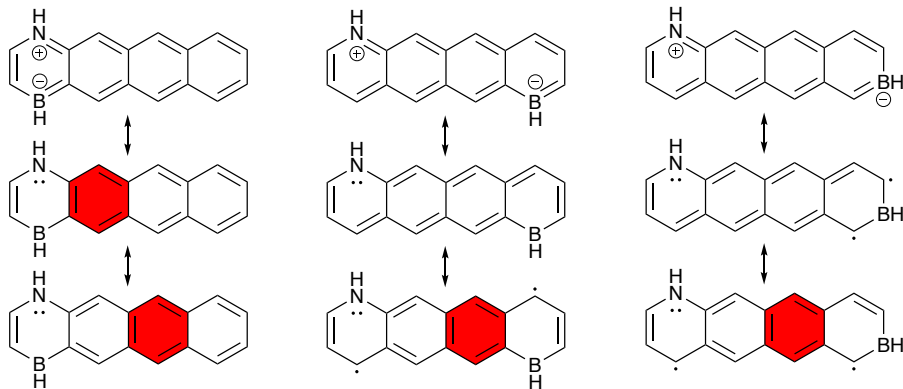


¹A. Das, T. Müller, FP, H. Lischka, *JPCA* **2016**, 120, 1625–1636.

Related chemistry

- Doping with heteroatoms
 - *Ionic* / *biradical* resonance structures vs sextets

Heteroatoms – BN-doped tetracenes

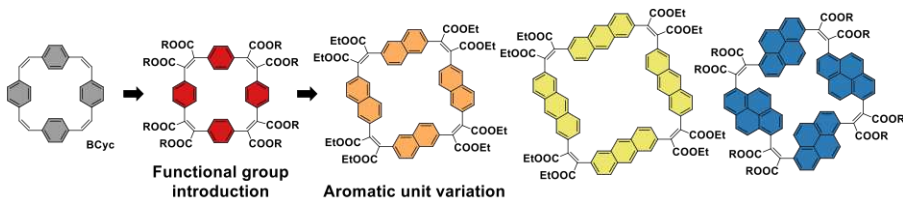


¹M. Pinheiro, F. B. C. Machado, FP, A. J. A. Aquino, H. Lischka, *JMCC* **2020**, 8, 7793–7804.

Macrocycles

- ▶ Synthesis of different macrocycles
 - All with a **formally antiaromatic** $4n$ π -electron perimeter
- ▶ Consequences
 - Doubly charged states become **aromatic** → Multielectron reduction → Batteries
 - Excited states become **aromatic** → Stokes shifts

Macrocycles



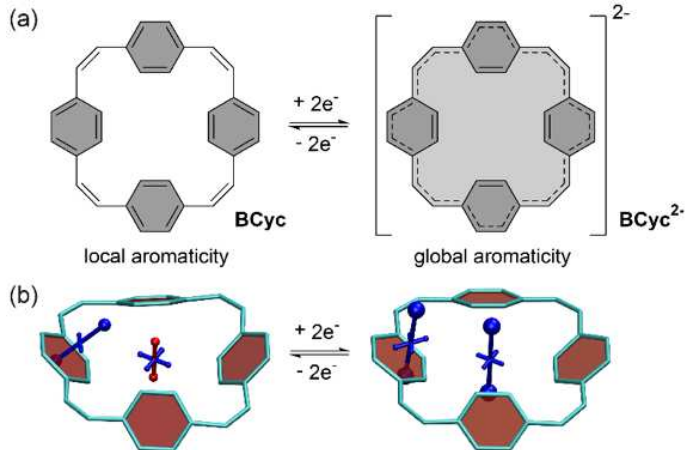
¹M. Rimmele, W. Nogala, et al., *Org. Chem. Front.* **2021**, DOI: 10.1039/D1QO00901J.

Macrocycles

- ▶ Neutral state
 - Local **aromaticity** / weak global **antiaromaticity**
- ▶ Dianion
 - Global **aromaticity**

⑦ How about the other cycles

Two-electron reduction

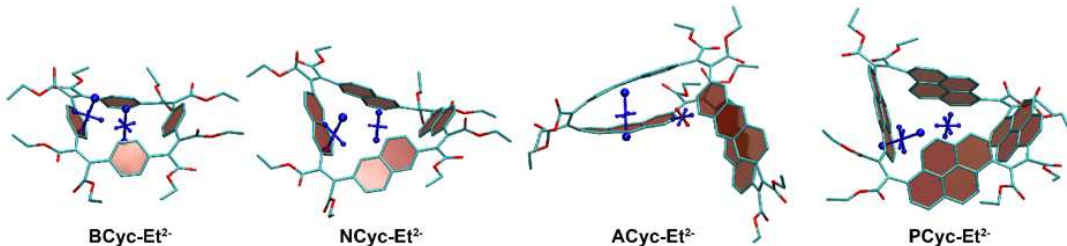


Dianions

► Example: **Dianions**

- Local **vs** global aromaticity
- Balance changes with increasing system size

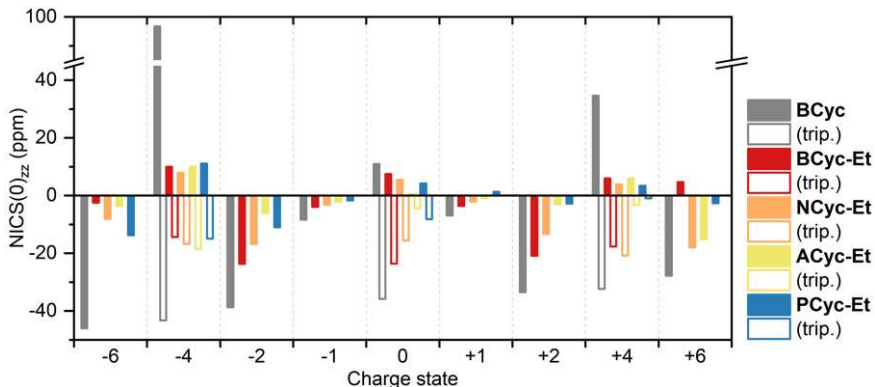
Dianions



NICS

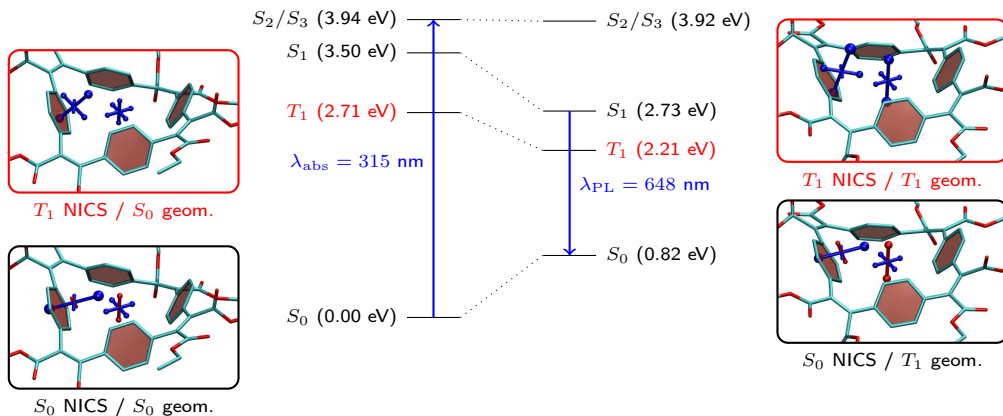
- Compute **nucleus-independent chemical shift** for different states
 - $\text{NICS} < 0 \rightarrow$ **aromatic** / $\text{NICS} > 0 \rightarrow$ **antiaromatic**
 - Expected trends but blurred for larger systems

NICS



Stokes Shifts

- ⑦ Why are the **Stokes shifts** so large
- Global (anti-)aromaticity only after geometry relaxation
 - *also*: Relaxation to dark S_1 state



Summary

► Aromaticity

- Structure/property relationships

► Chemical shielding tensors

- Good compromise: intuitive *vs* rigorous

► Visualisation of chemical shielding tensors

- Compact representation identifying **aromatic** and **antiaromatic** regions
- Info about **local variation** and **anisotropy**

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