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INTRODUCTION TO AROMATICITY & ANTIAROMATICITY

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AROMATICITY – AN IMPORTANT CONCEPT!

Balaban, Oniciu & Katritsky, *Chem. Rev.* 2004, *104*, 2777:

"Among approximately 20 million compounds identified by the end of the second millennium, more than two thirds are fully or partially aromatic, and approximately half are heteroaromatic"

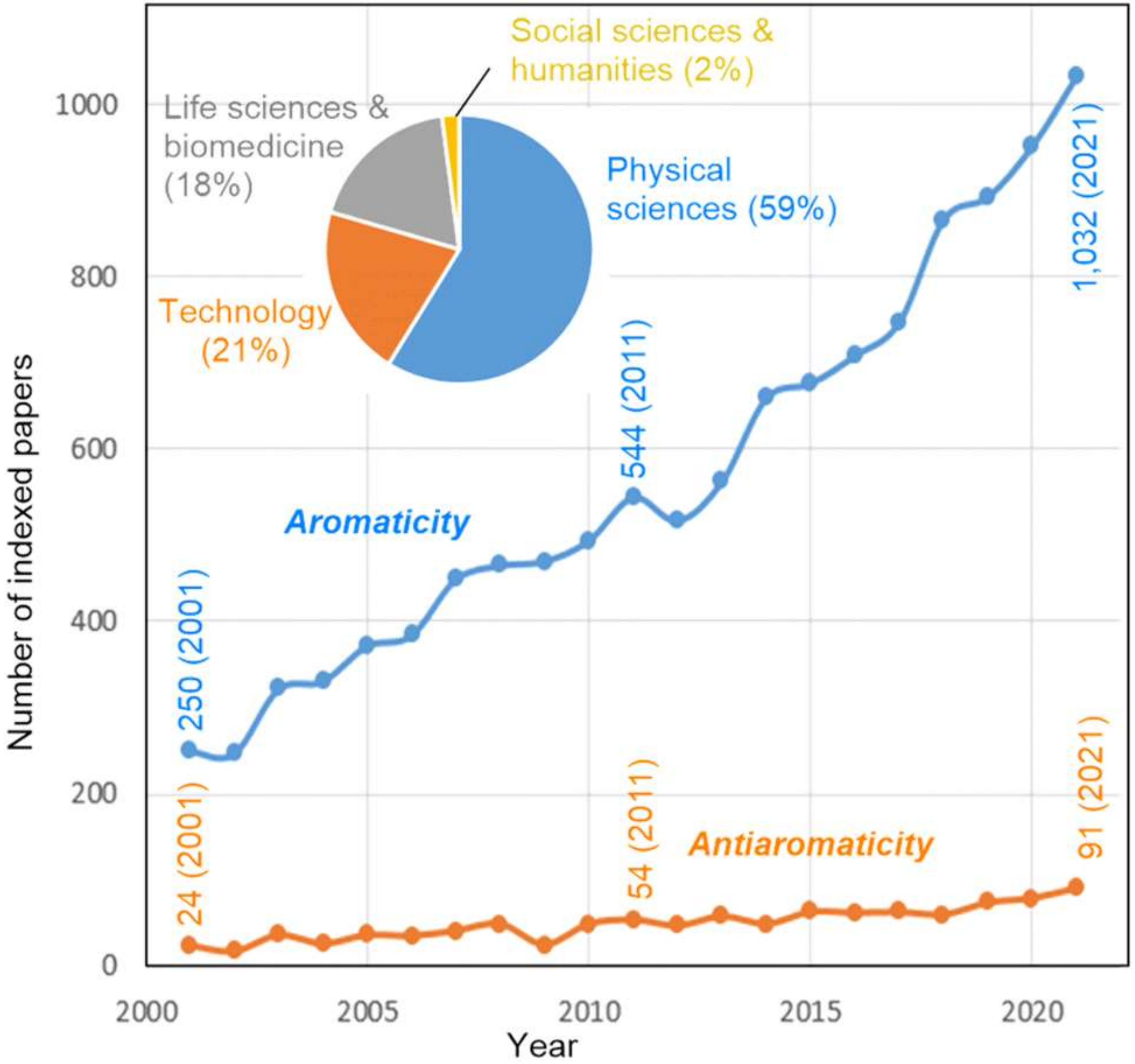
What molecules come to your mind if one says "aromatic",

and if one says "antiaromatic"?

AROMATICITY – AN IMPORTANT BUT VERY FUZZY CONCEPT!

Perspective by Merino *et al.*, ”Aromaticity: Quo Vadis”, *Chem. Sci.* **2023**, *14*, 5569

Commentary by Ottosson, ”A Focus on Aromaticity – Fuzzier than Ever Before?” *Chem. Sci.* **2023**, *14*, 5562.



AROMATICITY – AN IMPORTANT BUT VERY FUZZY CONCEPT!

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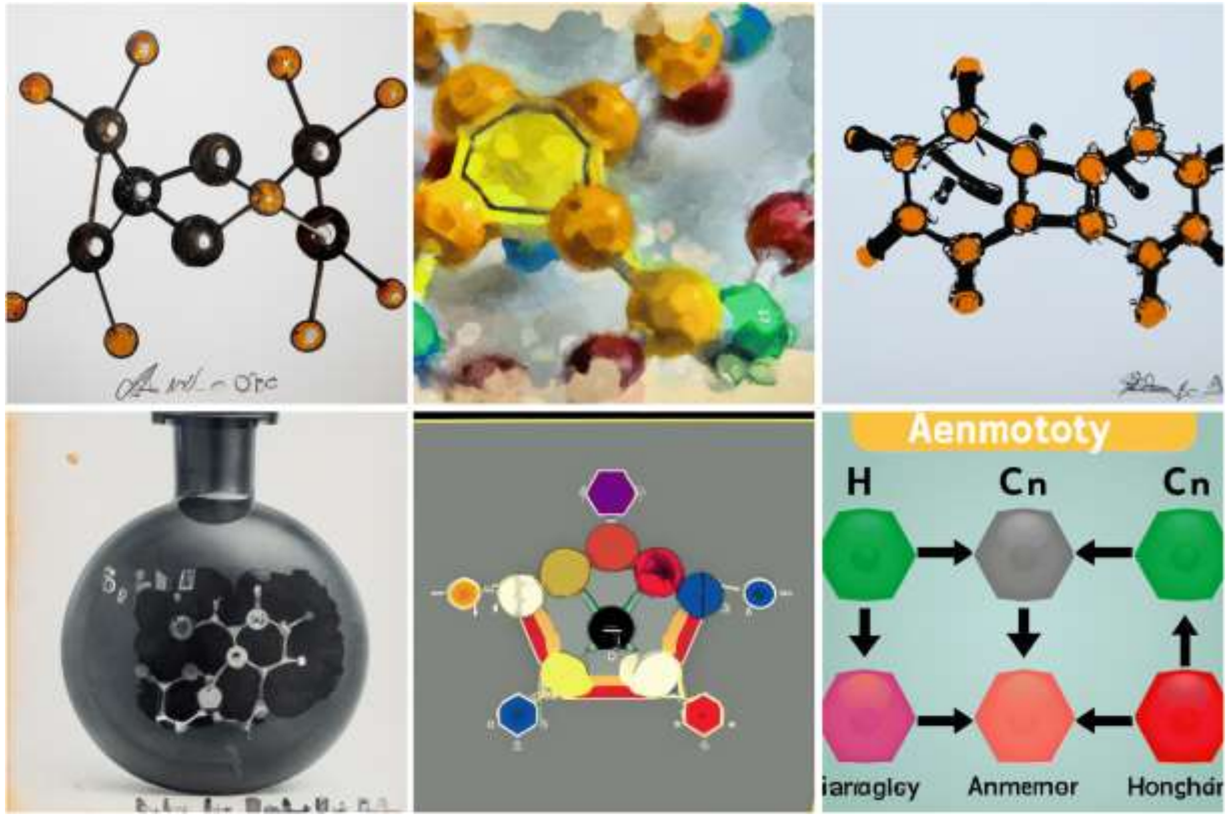
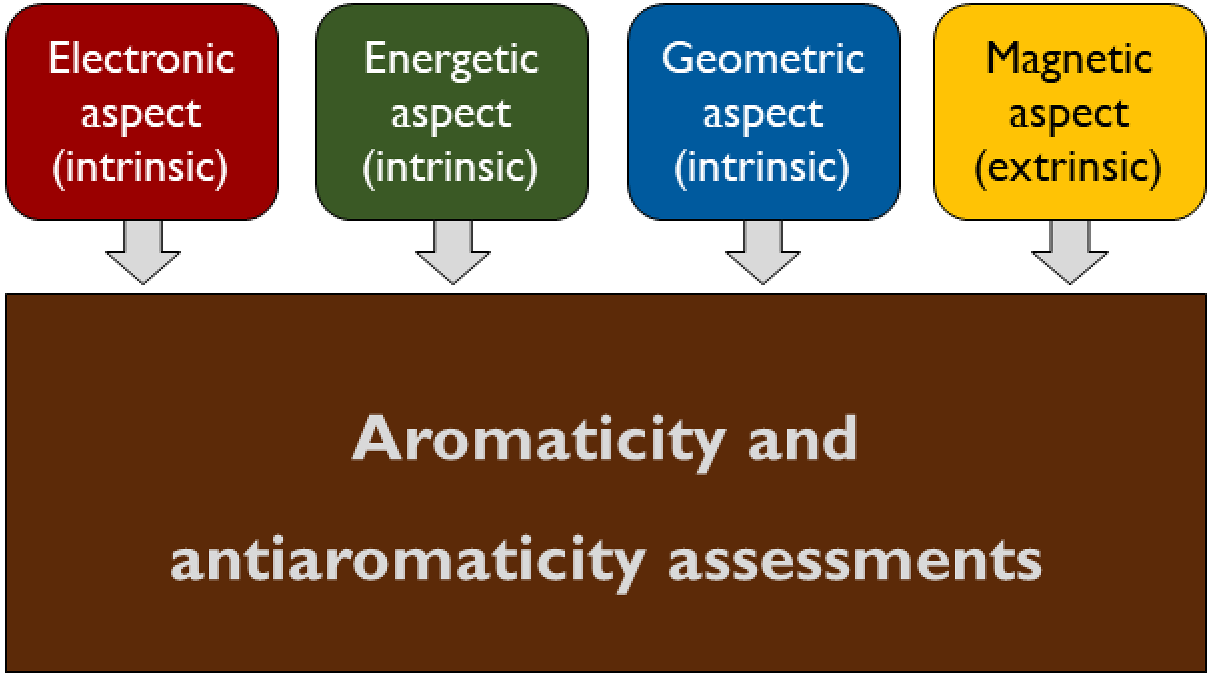


Why so fuzzy?

- **Aromaticity cannot be uniquely defined. No quantum mechanical operator corresponds to aromaticity.**
- **Four (five) aspects of aromaticity: Electronic, energetic (reactivity), geometric and magnetic aspects.**
- **Different aromaticity descriptors may give different answers for a molecule.**
- **A variety of forms: Hückel-, Möbius- (Heilbronner-type *vs.* Craig-type), Baird-, 3D-, σ-, spherical, … aromaticity.**

THE VARIOUS ASPECTS (CRITERIA) OF (ANTI)AROMATICITY

- **Energetic**; stabilization *vs.* destabilization relative a nonaromatic reference molecule.
- **Geometric**; bond length equalization *vs.* bond length alternation
- **Magnetic**; diamagnetic *vs.* paramagnetic ring currents when the molecule is placed in an applied magnetic field, e.g., in an NMR spectrometer.
- **Electronic**; electron delocalization *vs.* localization of π-electrons in cycle.
- There is also the reactivity aspect, but it is difficult to use for (anti)aromaticity assessments.


Electronic aspect (intrinsic)

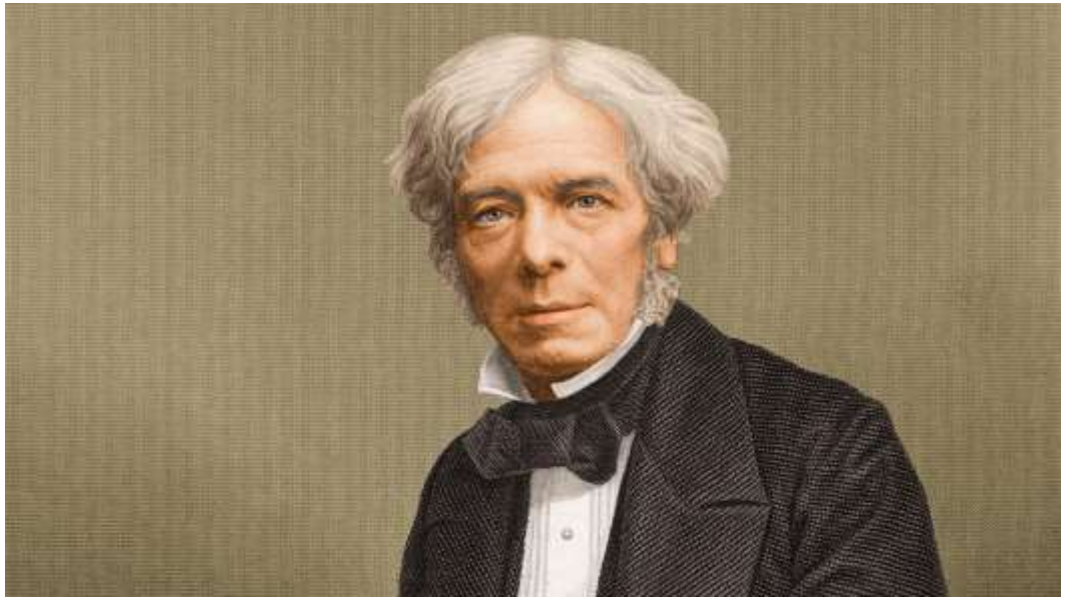
Energetic aspect (intrinsic)

Geometric aspect (intrinsic)

Magnetic aspect (extrinsic)

Aromaticity and antiaromaticity assessments

DISCOVERY OF BENZENE – THE AROMATIC PROTOTYPE MOLECULE

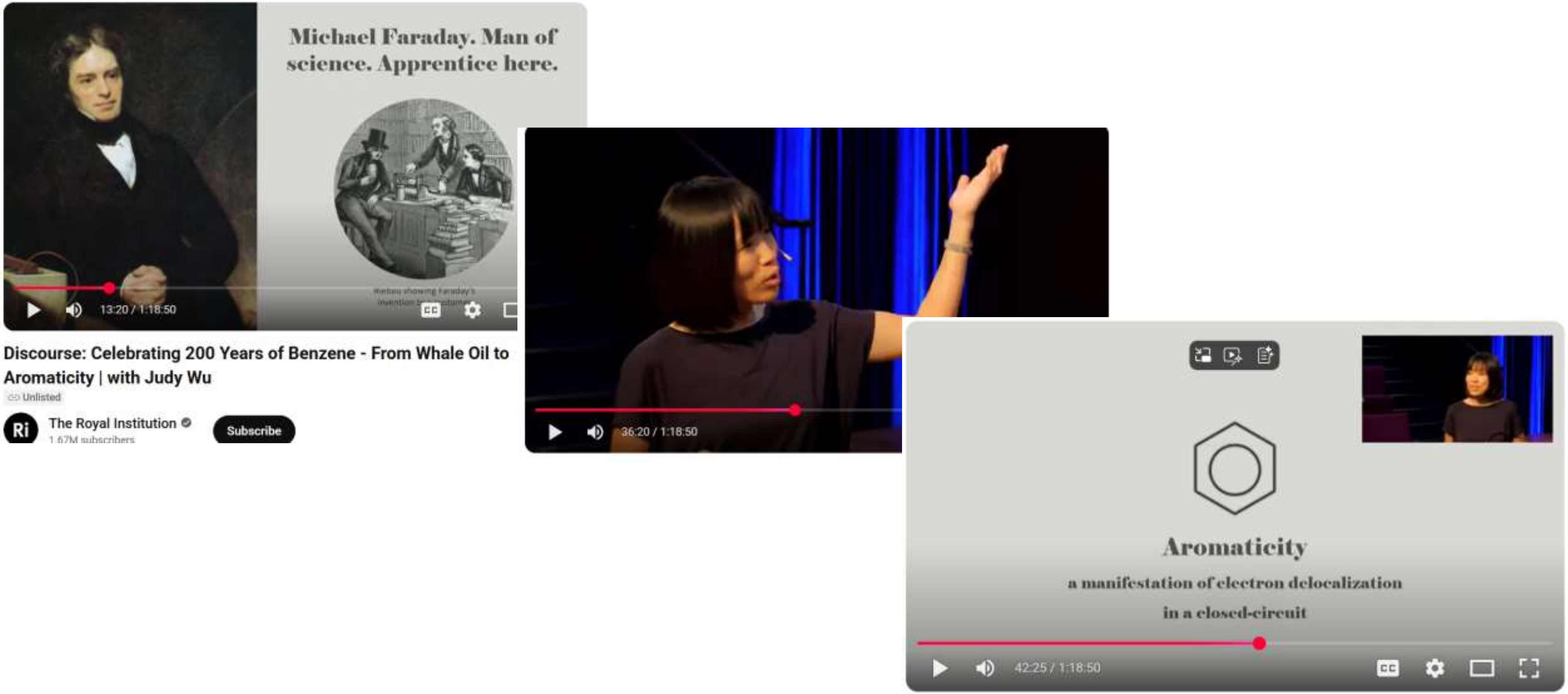


Michael Faraday 1791 – 1867

- **Benzene was discovered by Michael Faraday in 1825, as described here.**
- **He labelled it as *bicarburet of hydrogen* with a formula of C_6H_3, which was due to an incorrect mass of hydrogen at his time.**
- **Benzene was isolated from an oily by-product formed in the production of ”portable gas” from fish or whale oil.**

PROF. JUDY WU'S LECTURE AT THE ROYAL INSTITUTION, LONDON

Please view Prof. Judy Wu's lecture found on Youtube here



Michael Faraday. Man of science. Apprentice here.

Discourse: Celebrating 200 Years of Benzene - From Whale Oil to Aromaticity | with Judy Wu

Unlisted

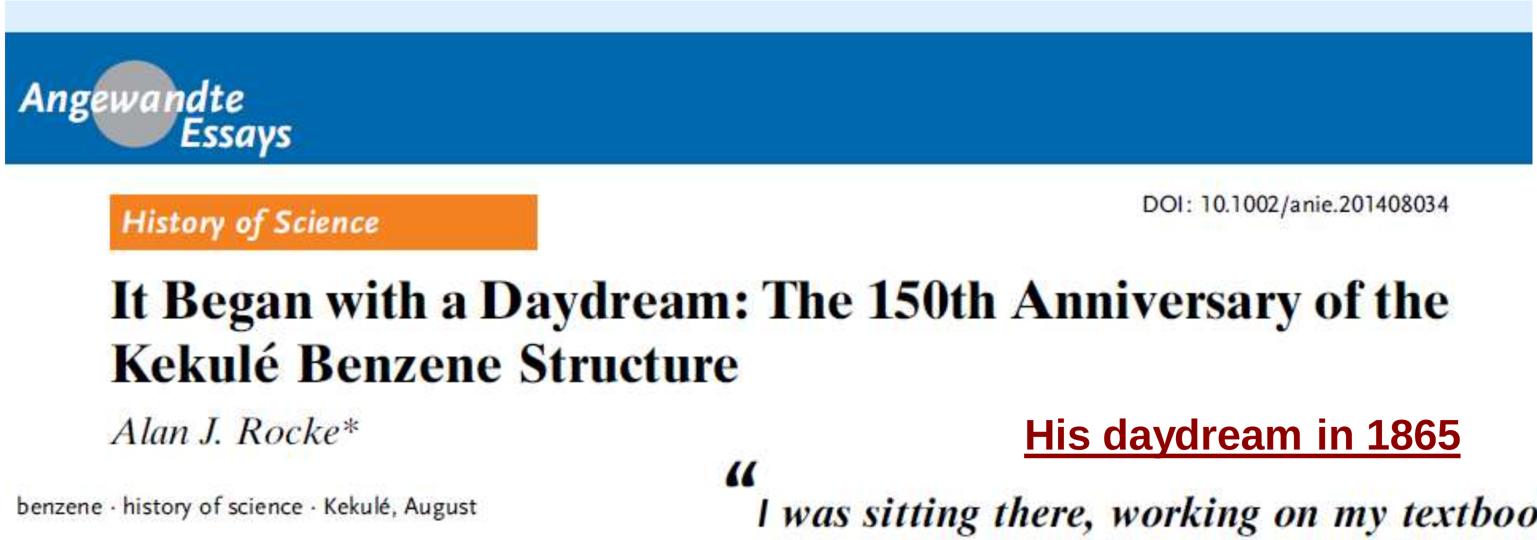
The Royal Institution

1.67M subscribers

Aromaticity

a manifestation of electron delocalization in a closed-circuit

AUGUST KEKULÉ'S DESCRIPTION OF BENZENE



Angewandte Essays

History of Science

DOI: 10.1002/anie.201408034

It Began with a Daydream: The 150th Anniversary of the Kekulé Benzene Structure

*Alan J. Rocke**

benzene · history of science · Kekulé, August

<u>**His daydream in 1865**</u>

> ***"I was sitting there, working on my textbook, but it was not going well; my mind was on other things. I turned my chair toward the fireplace and sank into half-sleep. Again the atoms fluttered before my eyes. This time smaller groups remained modestly in the background. My mind's eye, sharpened by repeated visions of a similar kind, now distinguished larger forms in a variety of shapes. Long lines, often combined more densely; everything in motion, twisting and turning like snakes. But look, what was that? One of the snakes had seized its own tail, and the figure whirled mockingly before my eyes. I awoke in a flash, and this time, too, I spent the rest of the night working out the consequences of the hypothesis.[1]"***

A. J. Rocke, *Angew. Chem. Int. Ed.* **2015**, *54*, 46.

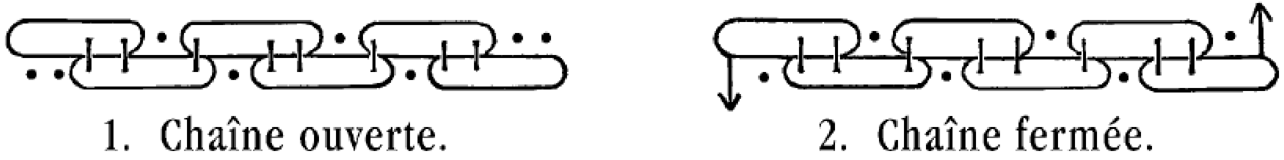
Figure 1. August Kekulé (1829–1896).

<u>NOTE</u>: He was 36 years old when he had his daydream. He unlikely looked like this at that age.

AUGUST KEKULÉ'S DESCRIPTION OF BENZENE

His benzene descriptions evolved in the period 1865 – 1872.

In 1865:



1. Chaîne ouverte.

2. Chaîne fermée.

Figure 3. The 1865 "sausage" formulas showing open and closed chains in benzene (taken from reference [4]).

In 1866:

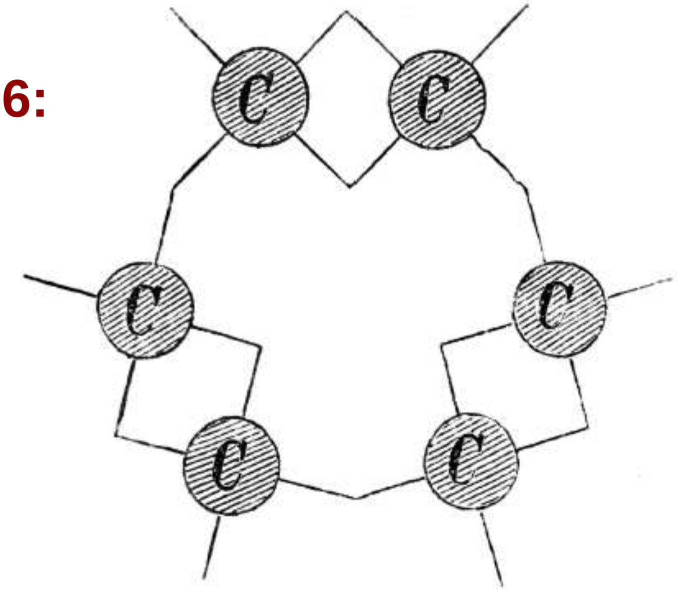


Figure 4. Kekulé's 1866 ball-and-stick benzene formula (taken from reference [26a].

And in 1872:

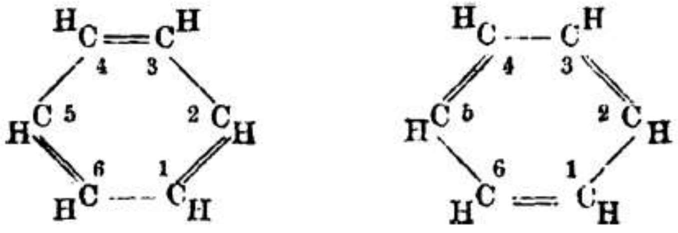


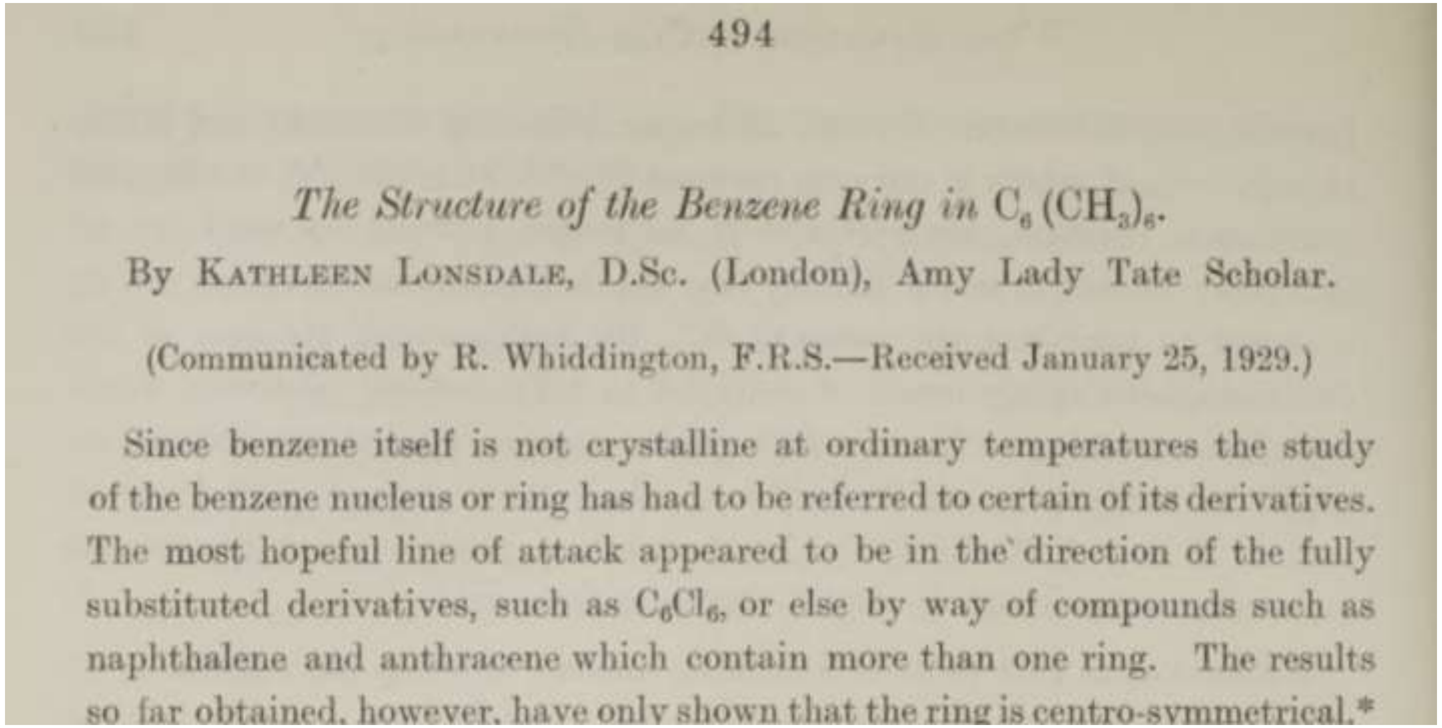
Figure 5. Kekule's 1872 oscillating single and double bonds in benzene (taken from reference [27]).

A. J. Rocke, *Angew. Chem. Int. Ed.*
2015, *54*, 46.

FIRST OBSERVATION THAT THE BENZENE RING IS A HEXAGON

K. Lonsdale, *Proc. R. Soc. A* **1929**, *123*, 494.

Dame Kathleen Lonsdale



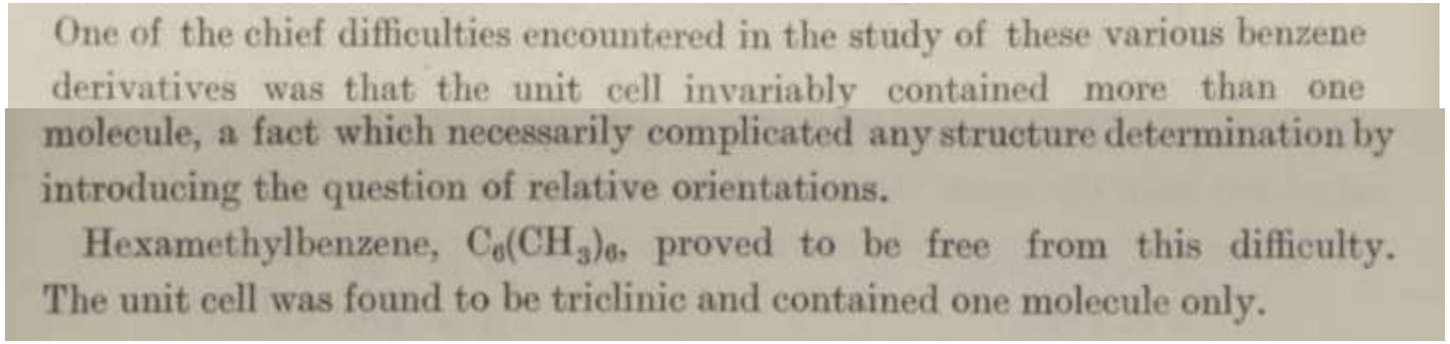
494

The Structure of the Benzene Ring in $C_6(CH_3)_6$.

By Kathleen Lonsdale, D.Sc. (London), Amy Lady Tate Scholar.

(Communicated by R. Whiddington, F.R.S.—Received January 25, 1929.)

Since benzene itself is not crystalline at ordinary temperatures the study of the benzene nucleus or ring has had to be referred to certain of its derivatives. The most hopeful line of attack appeared to be in the direction of the fully substituted derivatives, such as C_6Cl_6, or else by way of compounds such as naphthalene and anthracene which contain more than one ring. The results so far obtained, however, have only shown that the ring is centro-symmetrical.*



One of the chief difficulties encountered in the study of these various benzene derivatives was that the unit cell invariably contained more than one molecule, a fact which necessarily complicated any structure determination by introducing the question of relative orientations.

Hexamethylbenzene, $C_6(CH_3)_6$, proved to be free from this difficulty. The unit cell was found to be triclinic and contained one molecule only.

- **In 1929, Kathleen Lonsdale verified that the benzene ring is a planar hexagon.**
- **She carefully selected hexamethylbenzene as the compound to target.**

FIRST OBSERVATION THAT THE BENZENE RING IS A HEXAGON

K. Lonsdale, *Proc. R. Soc. A* **1929**, *123*, 494.

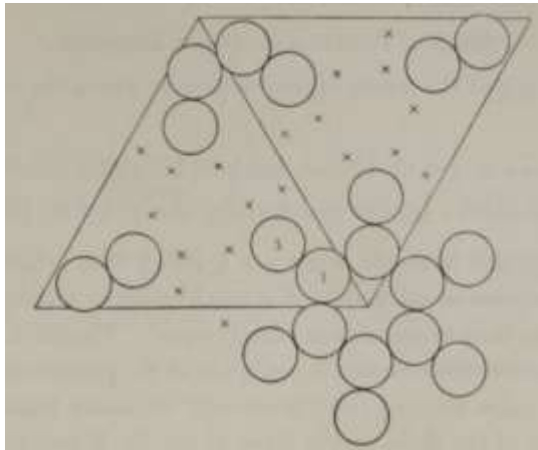
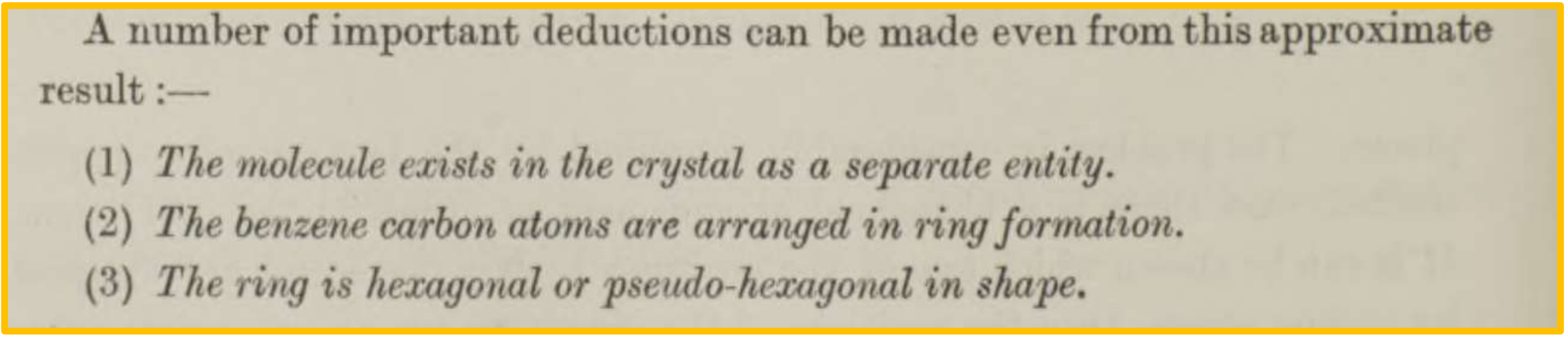


Fig. 7.



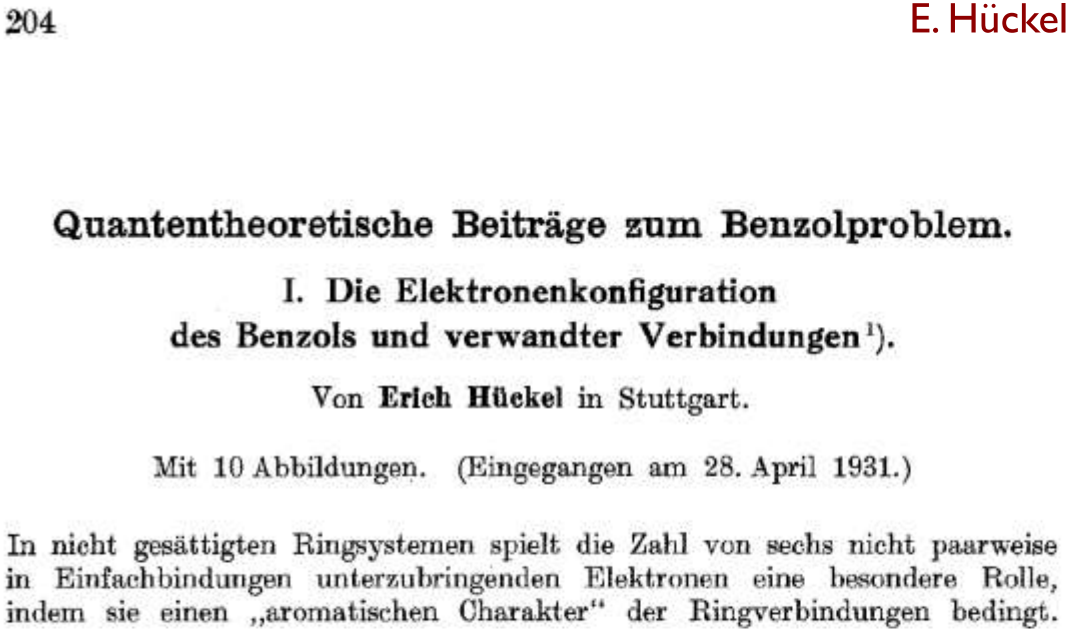
A number of important deductions can be made even from this approximate result :—

(1) *The molecule exists in the crystal as a separate entity.*
(2) *The benzene carbon atoms are arranged in ring formation.*
(3) *The ring is hexagonal or pseudo-hexagonal in shape.*

- **The structural determination settled the controversy on a potential oscillation between two benzene structures.**
- **It lay the foundation of the latter theories by Erich Hückel, and also by Linus Pauling.**

HÜCKEL’S THEORY FOR π-CONJUGATED HYDROCARBONS

E. Hückel, *Z. Physik* **1931**, *70*, 204.



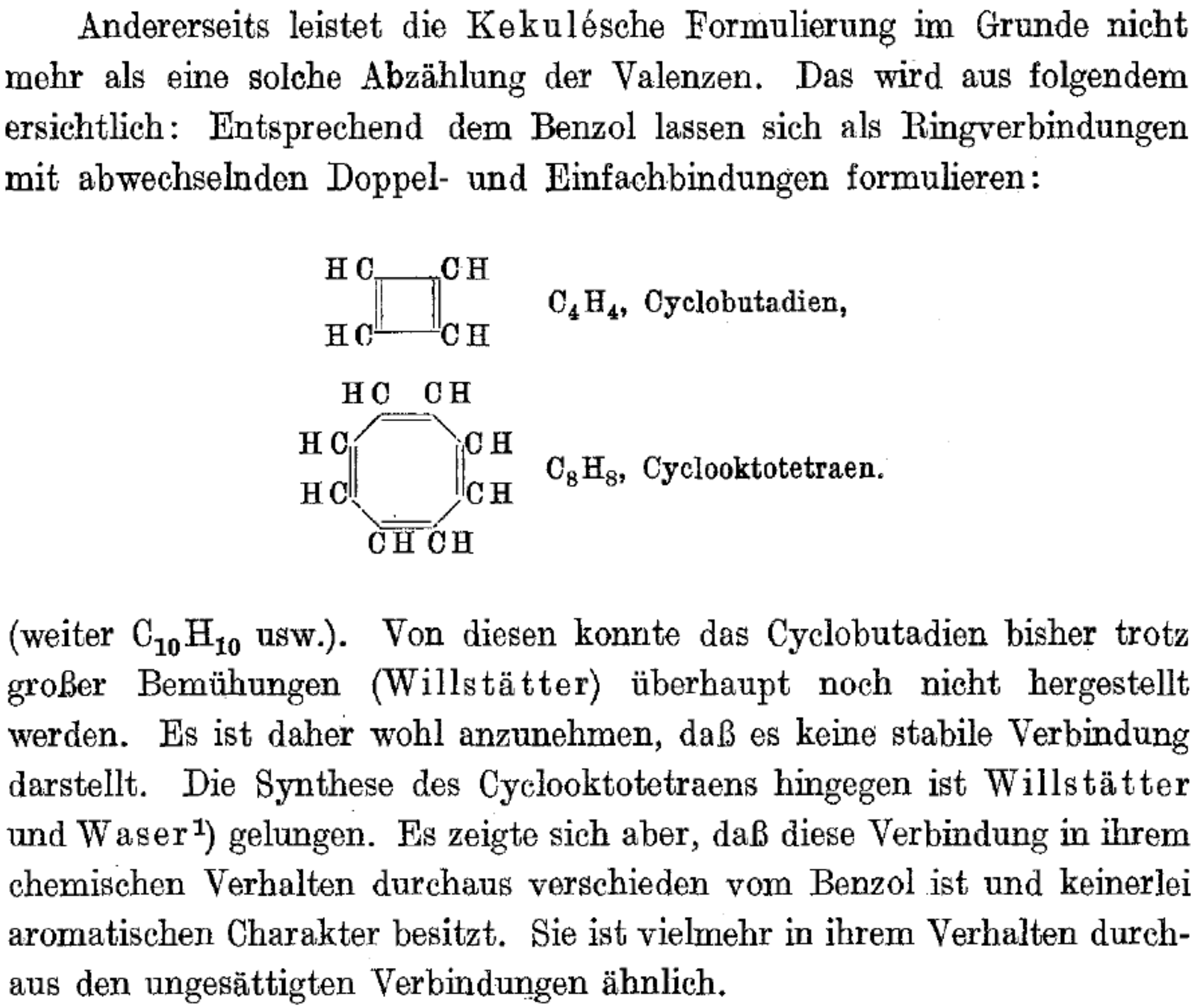
Quantentheoretische Beiträge zum Benzolproblem.

I. Die Elektronenkonfiguration des Benzols und verwandter Verbindungen[1]).

Von **Erich Hückel** in Stuttgart.

Mit 10 Abbildungen. (Eingegangen am 28. April 1931.)

In nicht gesättigten Ringsystemen spielt die Zahl von sechs nicht paarweise in Einfachbindungen unterzubringenden Elektronen eine besondere Rolle, indem sie einen „aromatischen Charakter“ der Ringverbindungen bedingt.



Andererseits leistet die Kekulésche Formulierung im Grunde nicht mehr als eine solche Abzählung der Valenzen. Das wird aus folgendem ersichtlich: Entsprechend dem Benzol lassen sich als Ringverbindungen mit abwechselnden Doppel- und Einfachbindungen formulieren:

C_4H_4, Cyclobutadien,

C_8H_8, Cyclooktotetraen.

(weiter $C_{10}H_{10}$ usw.). Von diesen konnte das Cyclobutadien bisher trotz großer Bemühungen (Willstätter) überhaupt noch nicht hergestellt werden. Es ist daher wohl anzunehmen, daß es keine stabile Verbindung darstellt. Die Synthese des Cyclooktotetraens hingegen ist Willstätter und Waser[1]) gelungen. Es zeigte sich aber, daß diese Verbindung in ihrem chemischen Verhalten durchaus verschieden vom Benzol ist und keinerlei aromatischen Charakter besitzt. Sie ist vielmehr in ihrem Verhalten durchaus den ungesättigten Verbindungen ähnlich.

HÜCKEL'S MO THEORY FOR π-CONJUGATED HYDROCARBONS

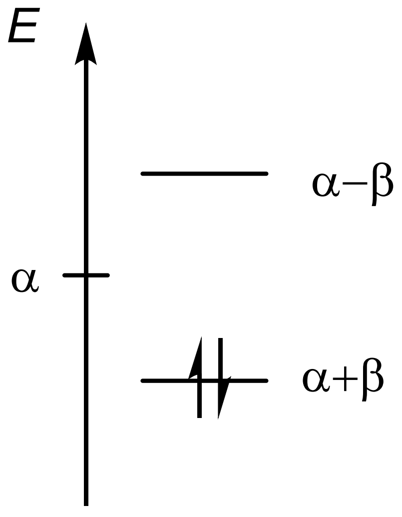
What are the basic assumptions of Hückel MO theory?

- There is an energy separation between σ- and π-MOs, whereby they can be treated separately.
- All sp^2 C atoms involved in the π-conjugation of a particular molecule are considered to be equivalent, whereby their atomic orbital energies for their p_z AOs are all equal to α.
- There are only interactions between a C atoms and its nearest neighboring C atoms, and this interaction is the same between each pair of neigboring C atoms. The interaction is labelled β.
- There is no orbital overlap between the p_z AOs of C atoms which are neighbors.
- This simplifies the matrix equation so substantially that it can be solved analytically.

BENZENE HAS A RESONANCE STABILIZATION OF 2β WITH HMO-THEORY

The orbital energies are given in terms of α, called Coulomb integral, and β, called resonance integral.

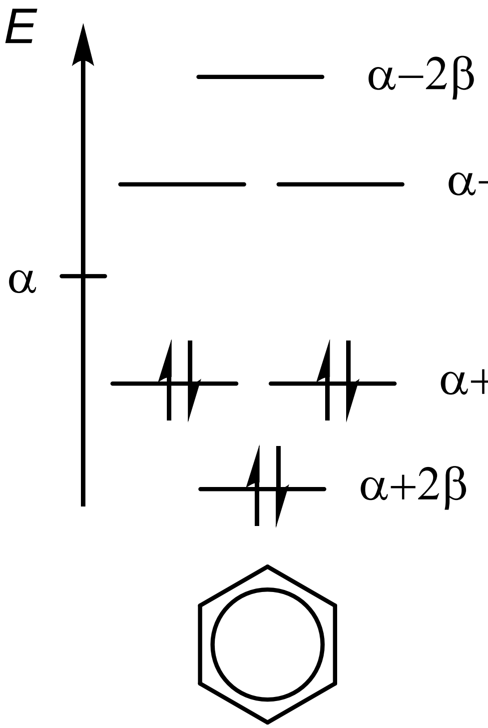
Ethylene: Two π-electrons in a localized π-bond



$H_2C{=}CH_2$

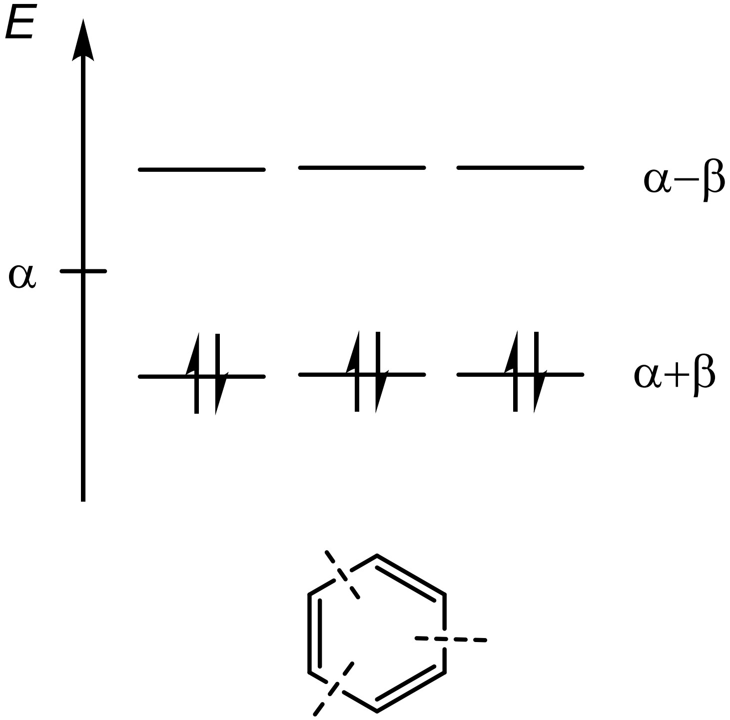
Hückel energy (HE): 2α+2β

Benzene: Six π-electrons delocalized in hexagon



6α+8β

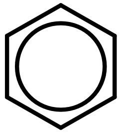
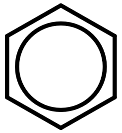
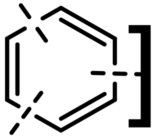
Hypothetical "1,3,5-cyclohexatriene": Six π-electrons in localized π-bonds



6α+6β

BENZENE HAS A RESONANCE STABILIZATION OF 2β WITH HMO-THEORY

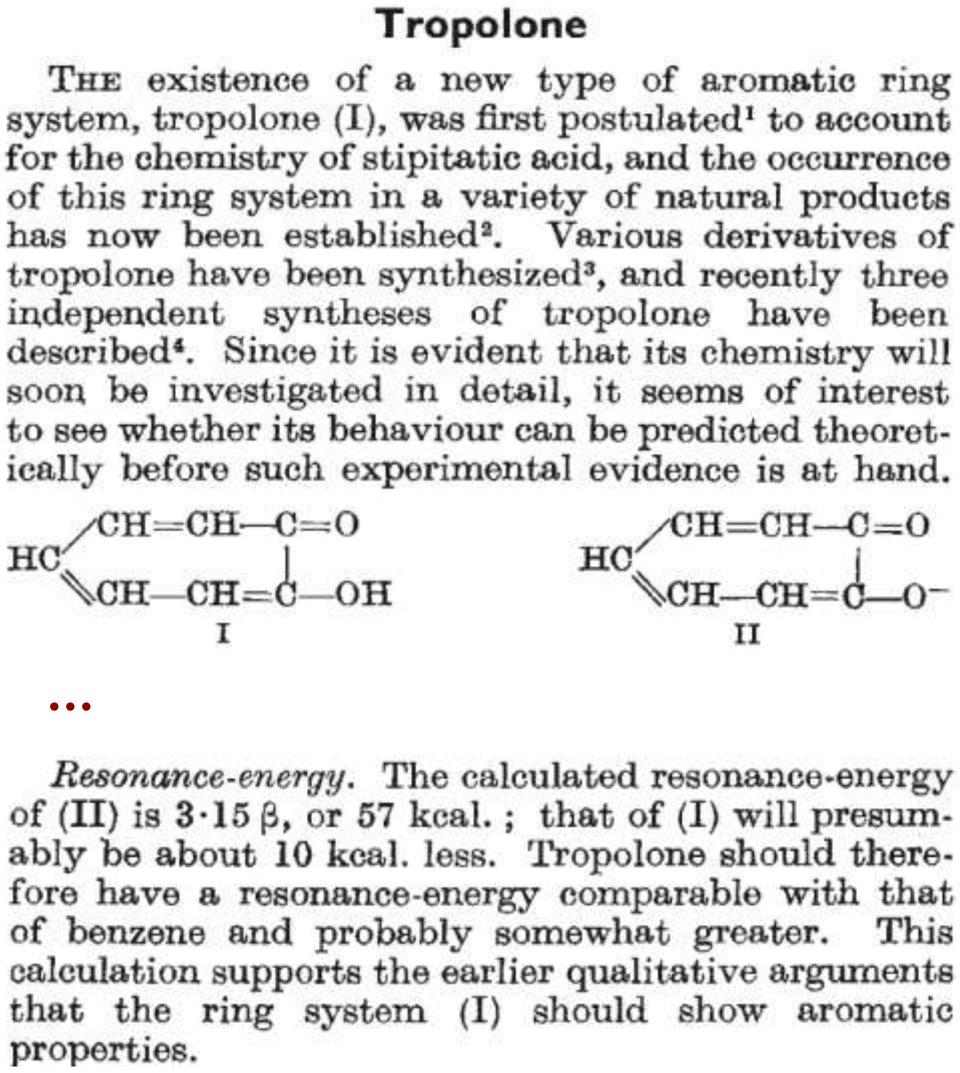
The Hückel resonance energy (HRE) of benzene is given as the difference in Hückel energies between benzene with six delocalized π-electrons and the one with six localized π-electrons, *i.e.*, "1,3,5-cyclohexatriene" (see previous page).

HRE[**] = HE[****] - HE[****] = 2β**

HÜCKEL’S MO THEORY DID NOT GET IMMEDIATE ATTENTION

- **Erich Hückel was educated as a theoretical physicist, however, worked on description of organic molecules. Neither his theoretical physicist colleagues nor organic chemists at that time appreciated the theory he deduced.**
- **It took two decades, until the early 1950s, before the HMO theory started to be used. Yet, then it eventually got its well-deserved recognition.**
- **But he was also a socially difficult person who could be arrogant.**
- **He recieved the Otto Hahn Prize in 1966, and he received an Honorary Doctorate at Uppsala University in 1973.**
- **He passed away in 1980.**

THE “2 + 4*n*” RULE WAS USED FIRST IN 1951, WITH REFERENCE TO DEWAR



Tropolone

THE existence of a new type of aromatic ring system, tropolone (I), was first postulated[1] to account for the chemistry of stipitatic acid, and the occurrence of this ring system in a variety of natural products has now been established[2]. Various derivatives of tropolone have been synthesized[3], and recently three independent syntheses of tropolone have been described[4]. Since it is evident that its chemistry will soon be investigated in detail, it seems of interest to see whether its behaviour can be predicted theoretically before such experimental evidence is at hand.

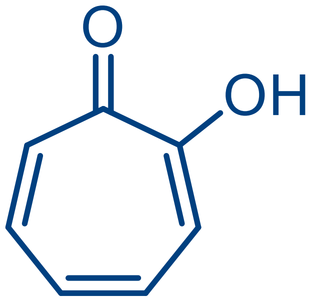
$$\mathrm{HC}\begin{array}{l}\diagup\mathrm{CH{=}CH{-}C{=}O}\\ \diagdown\mathrm{CH{-}CH{=}C{-}OH}\end{array}\qquad \mathrm{HC}\begin{array}{l}\diagup\mathrm{CH{=}CH{-}C{=}O}\\ \diagdown\mathrm{CH{-}CH{=}C{-}O^-}\end{array}$$

I II

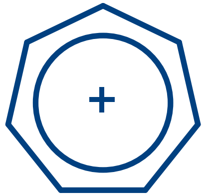
…

Resonance-energy. The calculated resonance-energy of (II) is 3·15 β, or 57 kcal.; that of (I) will presumably be about 10 kcal. less. Tropolone should therefore have a resonance-energy comparable with that of benzene and probably somewhat greater. This calculation supports the earlier qualitative arguments that the ring system (I) should show aromatic properties.

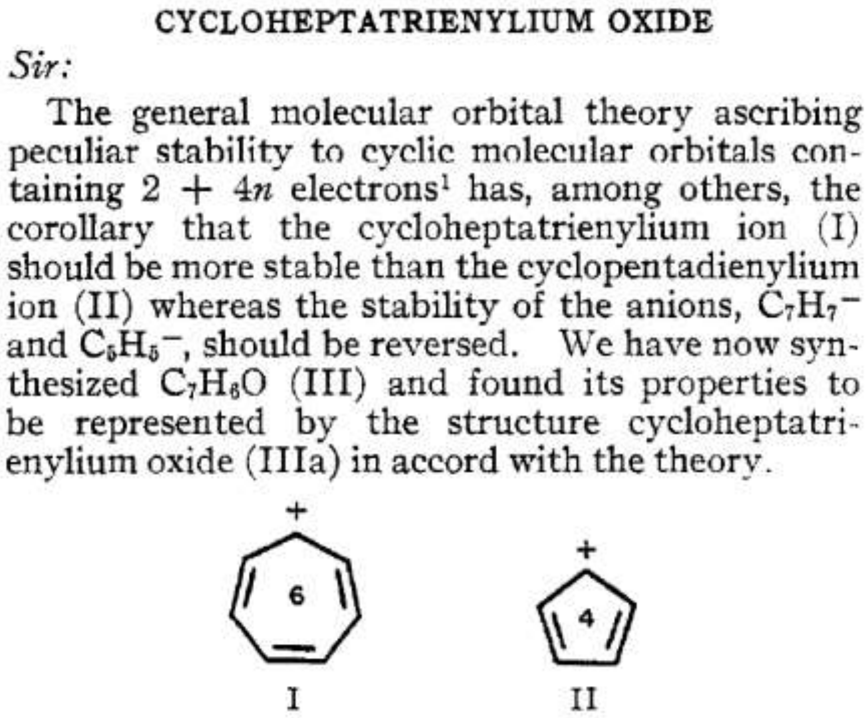
M. J. S. Dewar, *Nature* **1950**, *166*, 790



Tropolone



Tropylium cation



CYCLOHEPTATRIENYLIUM OXIDE

Sir:

The general molecular orbital theory ascribing peculiar stability to cyclic molecular orbitals containing 2 + 4*n* electrons[1] has, among others, the corollary that the cycloheptatrienylium ion (I) should be more stable than the cyclopentadienylium ion (II) whereas the stability of the anions, $C_7H_7^-$ and $C_5H_5^-$, should be reversed. We have now synthesized C_7H_6O (III) and found its properties to be represented by the structure cycloheptatrienylium oxide (IIIa) in accord with the theory.

I II

W. von E. Doering, F. L. Detert,
J. Am. Chem. Soc **1951**, *73*, 876

MAGNETIC FIELDS, AROMATICITY, AND NMR SPECTROSCOPY

In 2001, P. v. R. Schleyer writes in the Editorial for his Special Issue on Aromaticity in *Chemical Reviews*:

Chem. Rev. **2001**, *101*, 1115–1118.

*”**In 1910**, Pascal devised the first increment system for relating the magnitude of diamagnetic repulsion the magnetic susceptibility to molecular structures. The repulsions of benzene compounds by the magnetic field were “exalted”, i.e., unusually large based on the increment-sum expectations.*

….

*In **1936**, Linus Pauling (and, independently, Dame Kathleen Lonsdale) suggested that induced “ring currents” of the six benzene π electrons were responsible for this exaltation.*

…

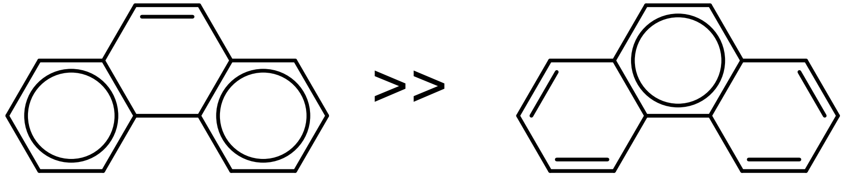
*In **1956**, Pople applied ring current theory to explain the downfield chemical shift of benzene protons (relative to those of vinyl H’s).”*

In 1946, NMR was discovered independently by Edward Purcell and Felix Bloch. *They received the Nobel price in Physics in 1952.*

CLAR'S RULE FOR POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

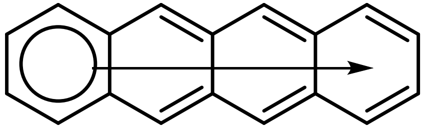
Clar's rule is first described in the book "*The Aromatic Sextet*" by Erich Clar, 1972.

- **The resonance structure with the most number of isolated benzene sextets (Clar sextets) is the most important one.**
- **This explains why the two terminal hexagons of phenanthrene are less reactive than the middle one.**

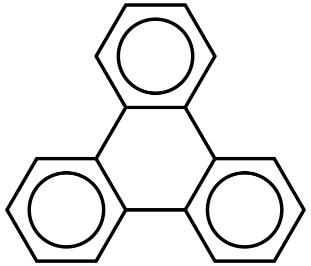


Two Clar sextets **One Clar sextet**

- **Among isomeric PAHs, the isomer for which most Clar sextets can be drawn is the most stable isomer.**
- **This explains why tetracene is easily oxidized while triphenylene has a very low reactivity.**



Tetracene has one (migrating) Clar sextet



Triphenylene has three Clar sextets

MÖBIUS AROMATICITY – HEILBRONNER 1964

Tetrahedron Letters No.29, pp. 1923-1928, 1964. Pergamon Press Ltd.
Printed in Great Britain.

HÜCKEL MOLECULAR ORBITALS OF MÖBIUS-TYPE CONFORMATIONS OF ANNULENES

E.Heilbronner
Laboratorium für organische Chemie der Eidg. Technischen Hochschule, Zürich

(Received 1 June 1964)

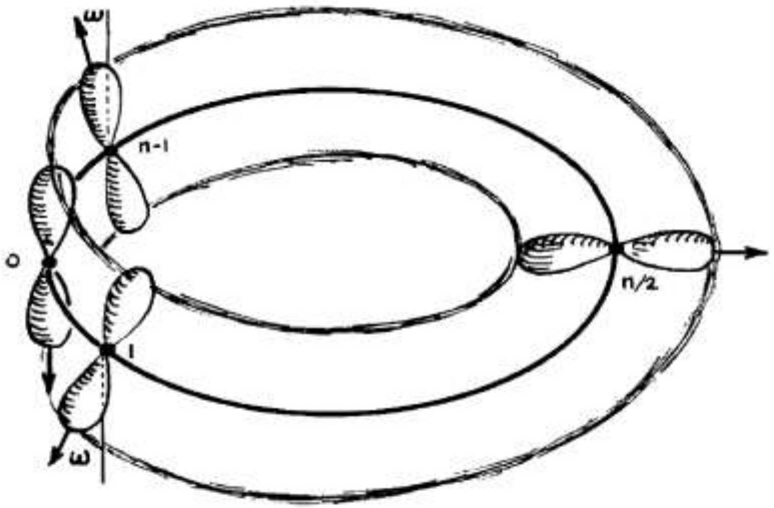


Figure 1

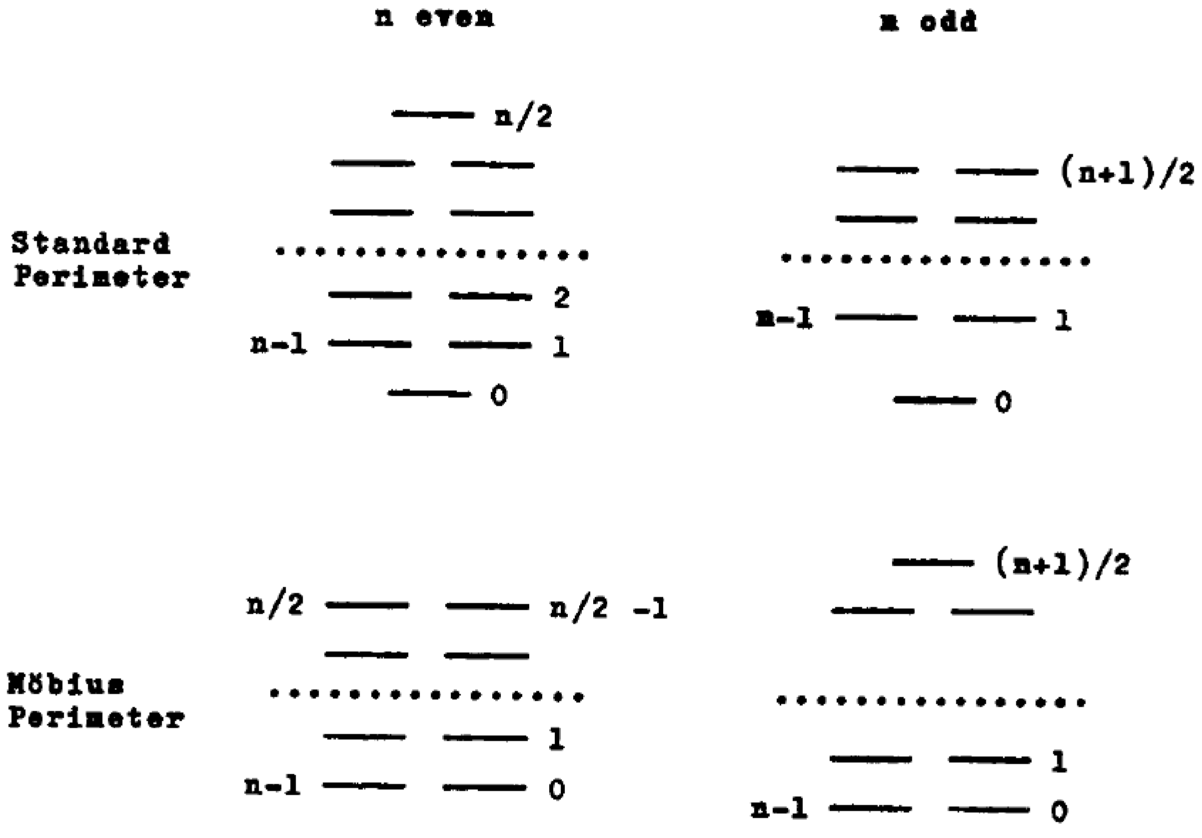


Figure 2

MÖBIUS AROMATICITY – HEILBRONNER 1964

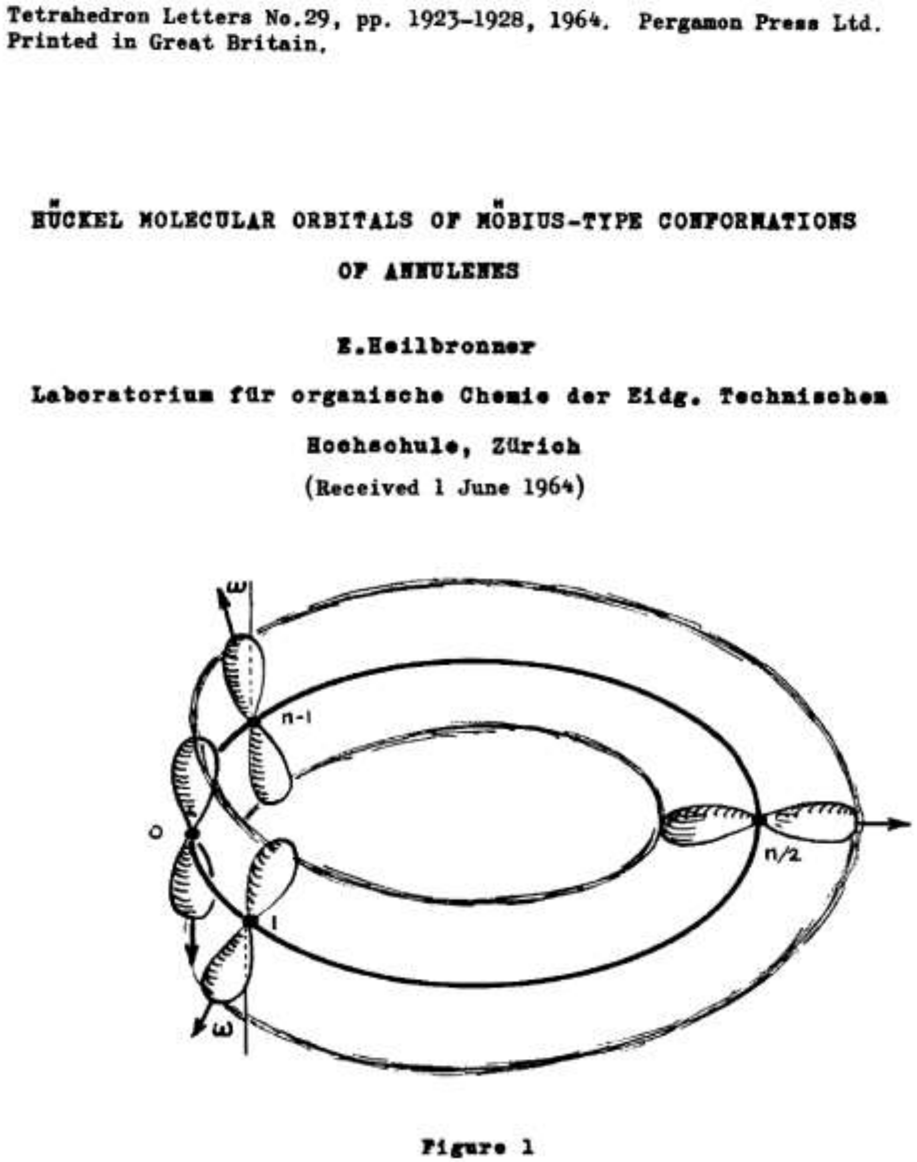


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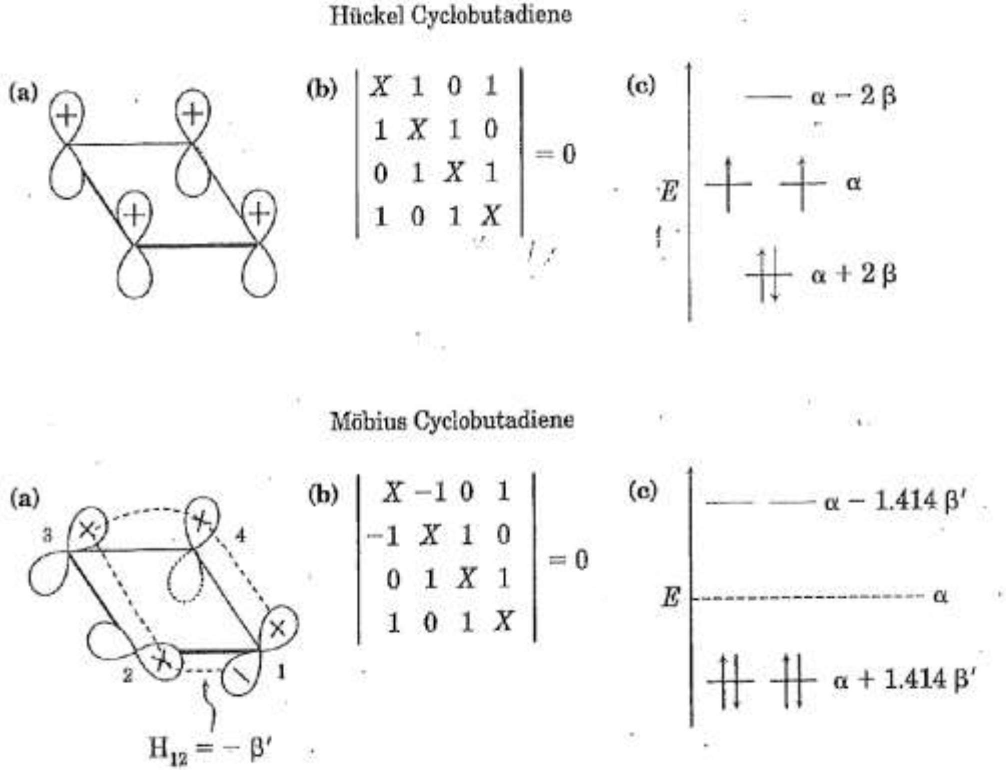
Figure 1

Figure 11.97
(a) Basis set orbitals, (b) secular determinant, and (c) energy levels for Hückel cyclobutadiene (top) and Möbius cyclobutadiene (bottom).



Hückel (b):

$$\begin{vmatrix} X & 1 & 0 & 1 \\ 1 & X & 1 & 0 \\ 0 & 1 & X & 1 \\ 1 & 0 & 1 & X \end{vmatrix} = 0$$

Möbius (b):

$$\begin{vmatrix} X & -1 & 0 & 1 \\ -1 & X & 1 & 0 \\ 0 & 1 & X & 1 \\ 1 & 0 & 1 & X \end{vmatrix} = 0$$

Because of the phase-shift between C1 and C2 in the Möbius cyclobutadiene, there will be a negative interaction (negative β) between these two C atoms, reflected in the secular determinant.

HÜCKEL *vs.* MÖBIUS AROMATICITY WITH FROST'S CIRCLE MNEMONIC

The π-orbital energies can be derived by a mnemonic by Frost and Musulin from 1953.

- **Inscribe a polygon corresponding to the annulene into a circle with radius 2β.**
- **For an annulene with Hückel-topology, place one vertex at 6:00 pm (18:00)**
- **For an annulene with Möbius-topology place instead one side downwards.**
- **To get the π-MO energies, project the vertices onto a vertical energy scale that ranges from α+2β to α-2β, then compute the energies through regular trigonometrics.**

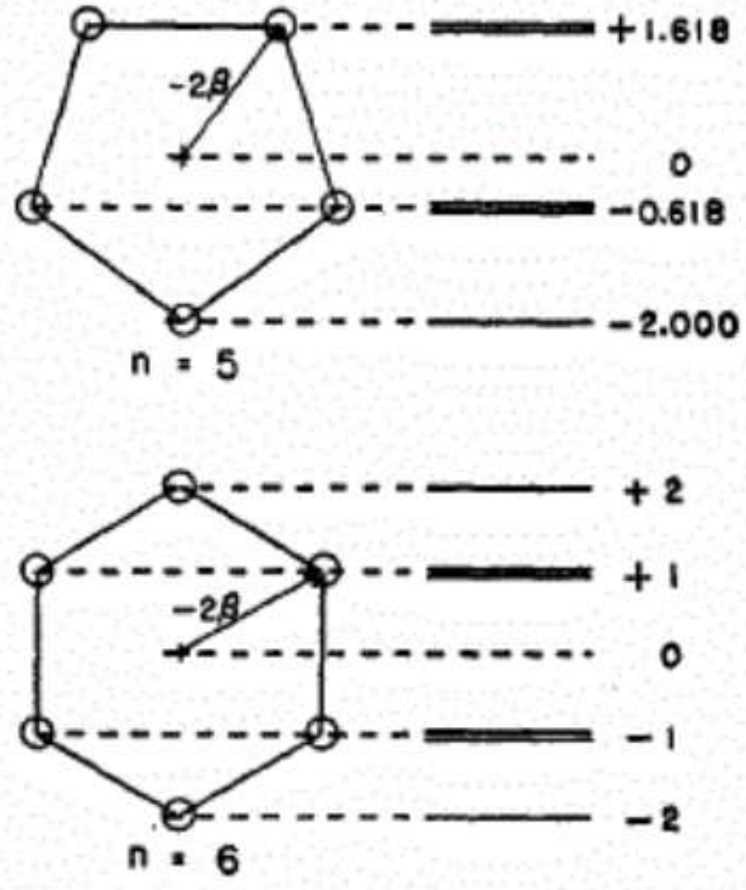
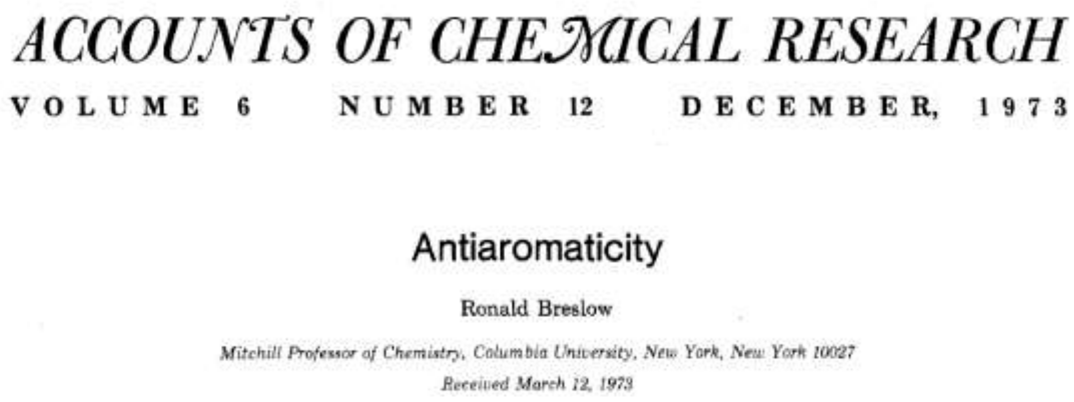


Fig. 1. Projection scheme for construction of energy level diagram of ring compounds. Resonance energies, unit: −β.

Frost & Musulin, *J. Chem. Phys.* **1953**, *21*, 572.

BRESLOW INTRODUCES THE *ANTIAROMATICITY* CONCEPT IN 1965



ACCOUNTS OF CHEMICAL RESEARCH
VOLUME 6 NUMBER 12 DECEMBER, 1973

Antiaromaticity

Ronald Breslow
Mitchill Professor of Chemistry, Columbia University, New York, New York 10027

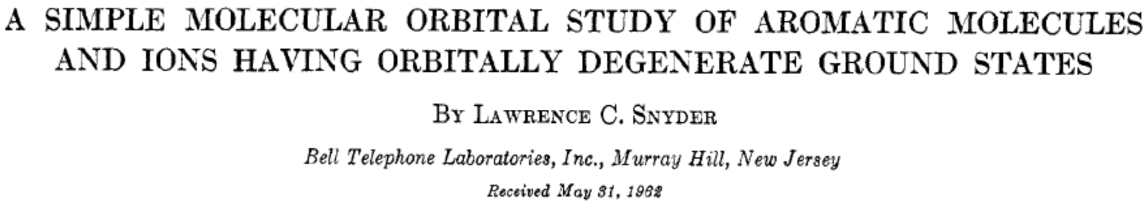
Received March 12, 1973

”… However, both theory and experiment suggest that for at least some members of the 4n series cyclic delocalization of π electrons leads to strong destabilization of the compound, in contrast to the stabilization characteristic of aromaticity. ***For this reason, we proposed[4] the term “antiaromatic” to describe such systems.***

A cyclic conjugated system is considered to be antiaromatic if its π electron energy is higher than that of a suitable reference compound which is not cyclically delocalized. Thus antiaromaticity is a particular aspect of antibonding, just as aromaticity is a particular aspect of bonding. In both cases, the definition assumes that there are ways of assigning the total energy of a given molecule to various compartments, one of which reflects the result of cyclic delocalization of its π electrons. …”

FIRST DESCRIPTION OF THE EXCITED STATES OF [4*n*]ANNULENES

L. C. Snyder, *J. Phys. Chem.* **1962**, *66*, 2299



A SIMPLE MOLECULAR ORBITAL STUDY OF AROMATIC MOLECULES AND IONS HAVING ORBITALLY DEGENERATE GROUND STATES

By Lawrence C. Snyder

Bell Telephone Laboratories, Inc., Murray Hill, New Jersey

Received May 31, 1962

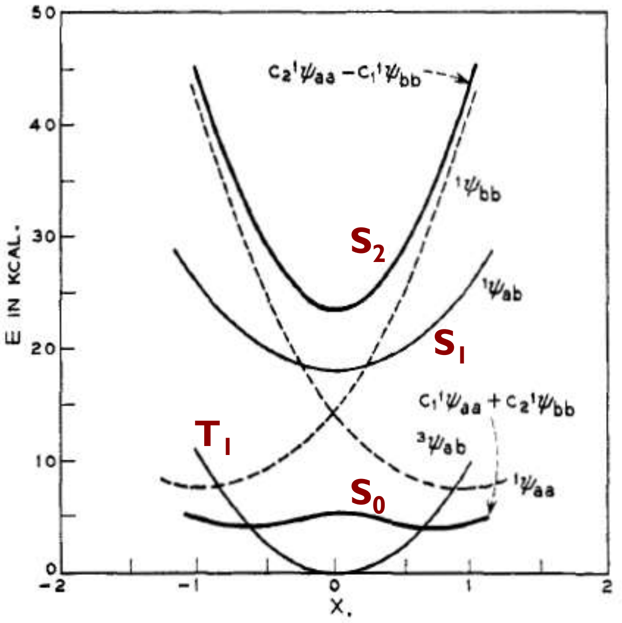
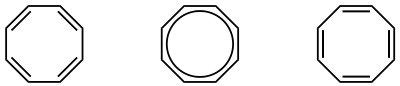
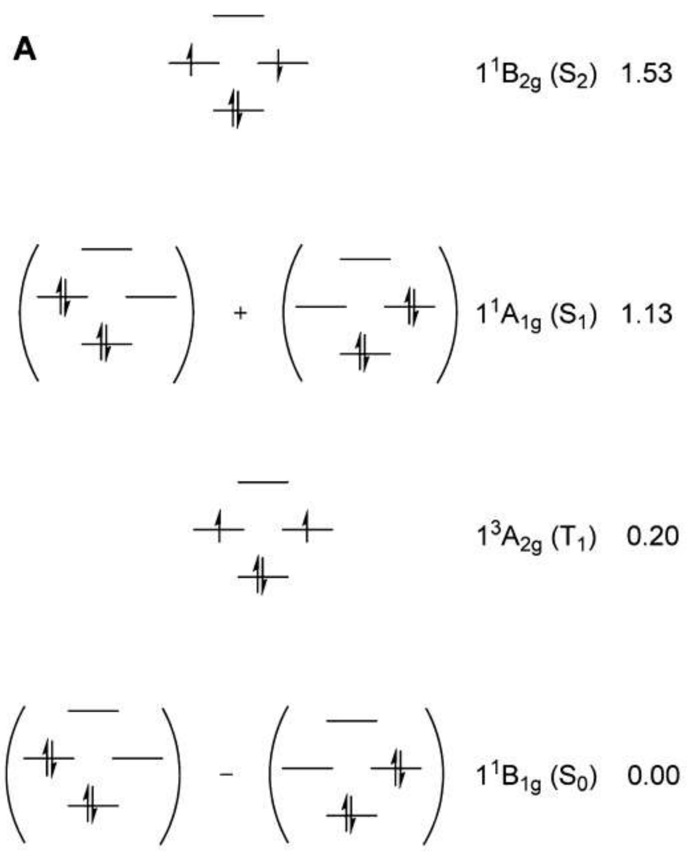


Fig. 6.—Geometrical stability of C_8H_8 states after configuration interaction.

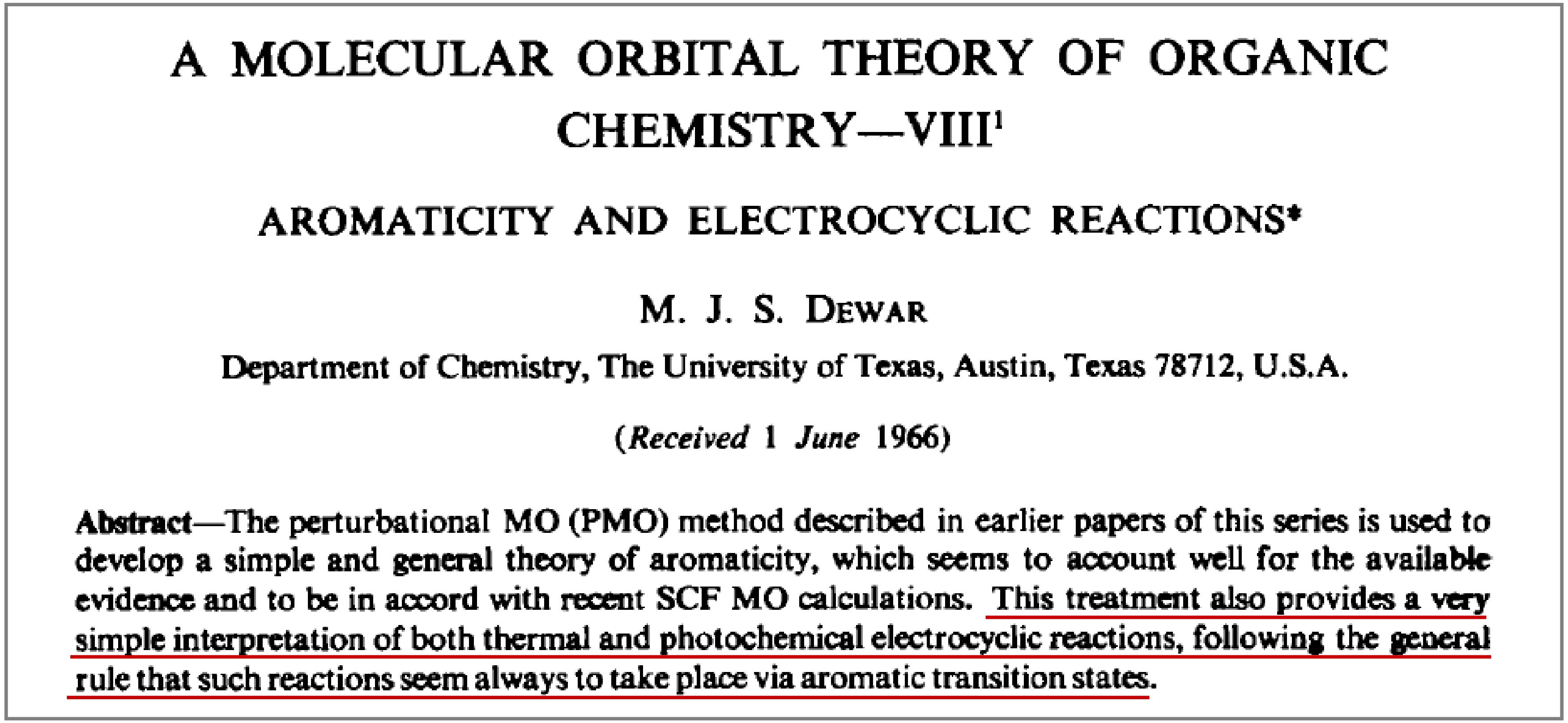


- **Cyclobutadiene in the T_1, S_1 and S_2 states is D_{4h} symmetric, and**
- **Cyclooctatetraene in the T_1, S_1 and S_2 states is D_{8h} symmetric**



DEWAR & ZIMMERMAN: ALLOWED PERICYCLIC REACTIONS PROCEED OVER AROMATIC TRANSITION STATES, BOTH IN GROUND & EXCITED STATES

M. J. S. Dewar, *Tetrahedron Suppl.* **1966**, *8*, 75; H. E. Zimmermann, *J. Am. Chem. Soc.* **1966**, *88*, 1564, *ibid.* **1966**, *88*, 1566.



A MOLECULAR ORBITAL THEORY OF ORGANIC CHEMISTRY—VIII[1]

AROMATICITY AND ELECTROCYCLIC REACTIONS*

M. J. S. Dewar

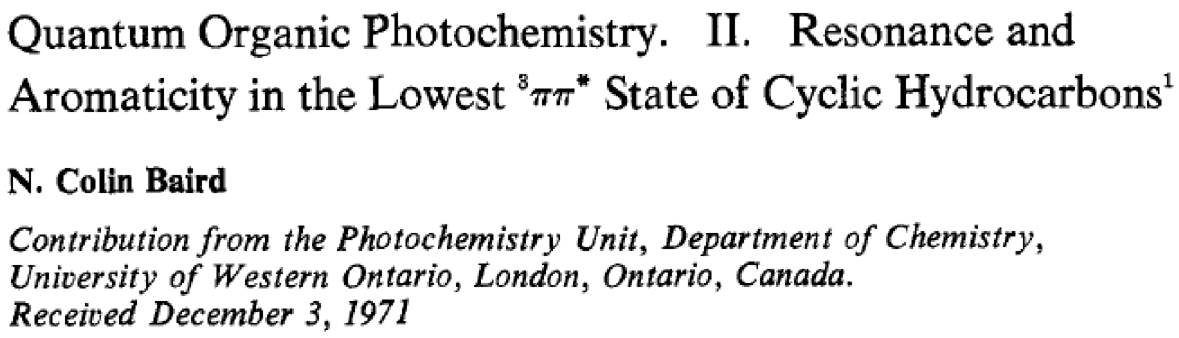
Department of Chemistry, The University of Texas, Austin, Texas 78712, U.S.A.

(*Received* 1 *June* 1966)

Abstract—The perturbational MO (PMO) method described in earlier papers of this series is used to develop a simple and general theory of aromaticity, which seems to account well for the available evidence and to be in accord with recent SCF MO calculations. This treatment also provides a very simple interpretation of both thermal and photochemical electrocyclic reactions, following the general rule that such reactions seem always to take place via aromatic transition states.

THEORY ON T_1 STATE AROMATICITY & ANTIAROMATICITY (1972)

N. C. Baird *J. Am. Chem. Soc.* **1972**, *94*, 4941.



Quantum Organic Photochemistry. II. Resonance and Aromaticity in the Lowest $^3\pi\pi^*$ State of Cyclic Hydrocarbons[1]

N. Colin Baird

Contribution from the Photochemistry Unit, Department of Chemistry,
University of Western Ontario, London, Ontario, Canada.
Received December 3, 1971

"Arguments based on simple perturbation theory indicate that the rules for ground state aromaticity are reversed in the $^3\pi\pi^*$ state, *i.e.*, 4*n* rings display "aromatic" character whereas 4*n*+2 rings display "antiaromatic""

ORGANIC PHOTOCHEMISTRY

Exciting excited-state aromaticity

In 1972, Baird published rules describing aromaticity and antiaromaticity in the lowest triplet excited states of annulenes. The fortieth anniversary of Baird's rules — which are the reverse of Hückel's rules for aromaticity and antiaromaticity in the ground state — ought to be celebrated before 2012 comes to an end.

Henrik Ottosson

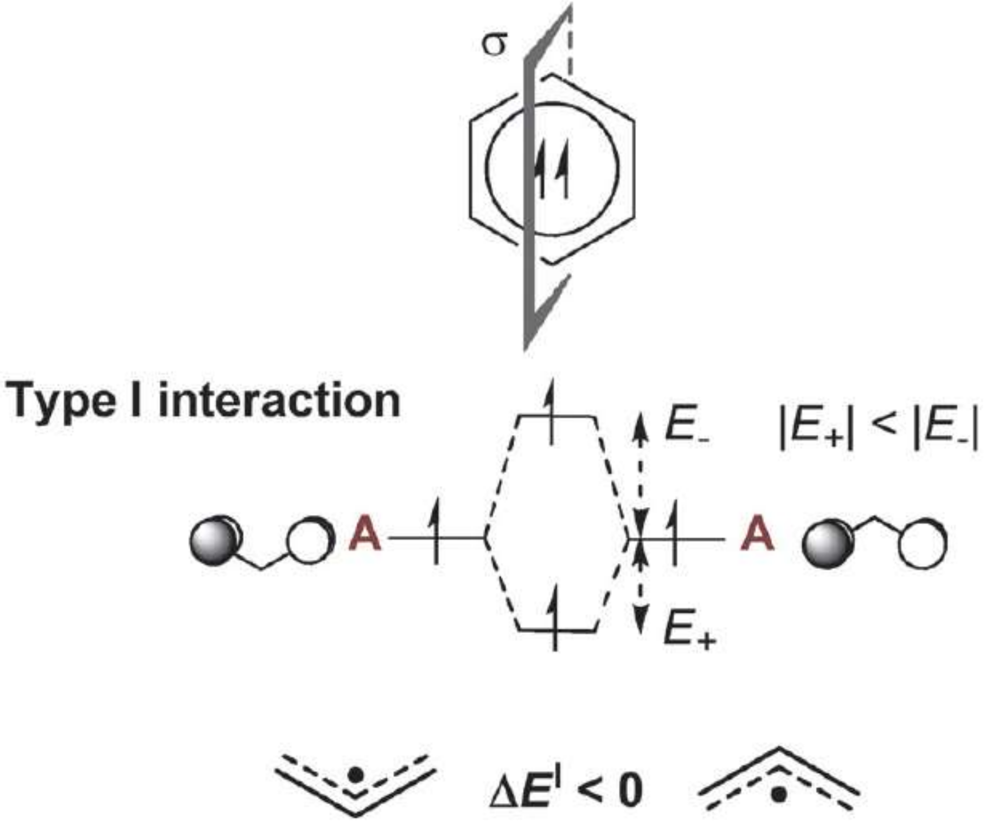
H. Ottosson *Nat. Chem.* **2012**, *4*, 969 (News & Views article)

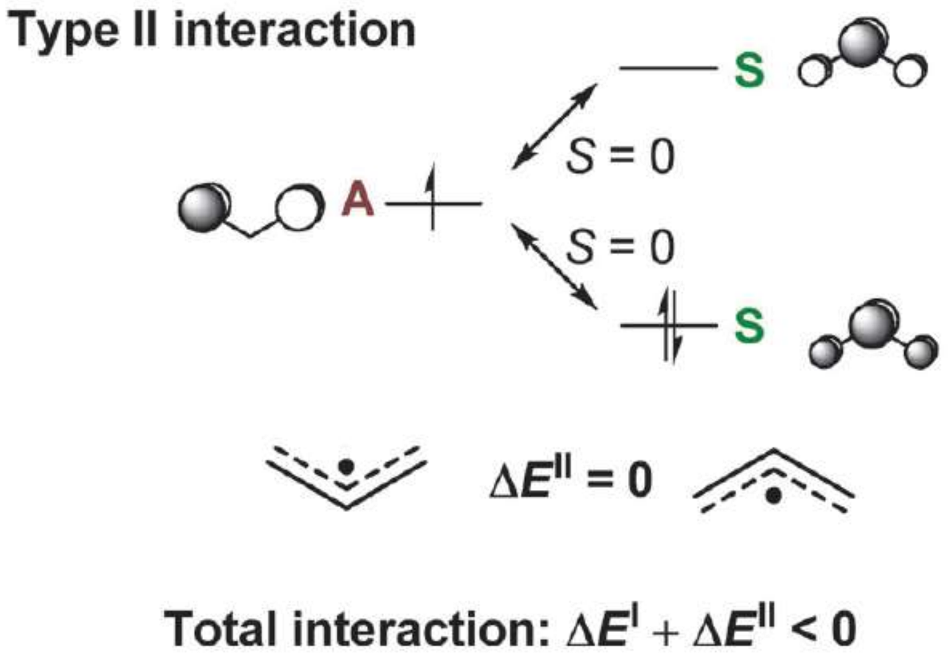
QUALITATIVE MO THEORETICAL RATIONALIZATION

N. C. Baird *J. Am. Chem. Soc.* **1972**, *94*, 4941.

Construct annulene triplet states from two linear polyenyl monoradicals. We first consider triplet state benzene, and construct this from two allyl radicals.

Question: Is there a stabilization or destabilization upon this process?





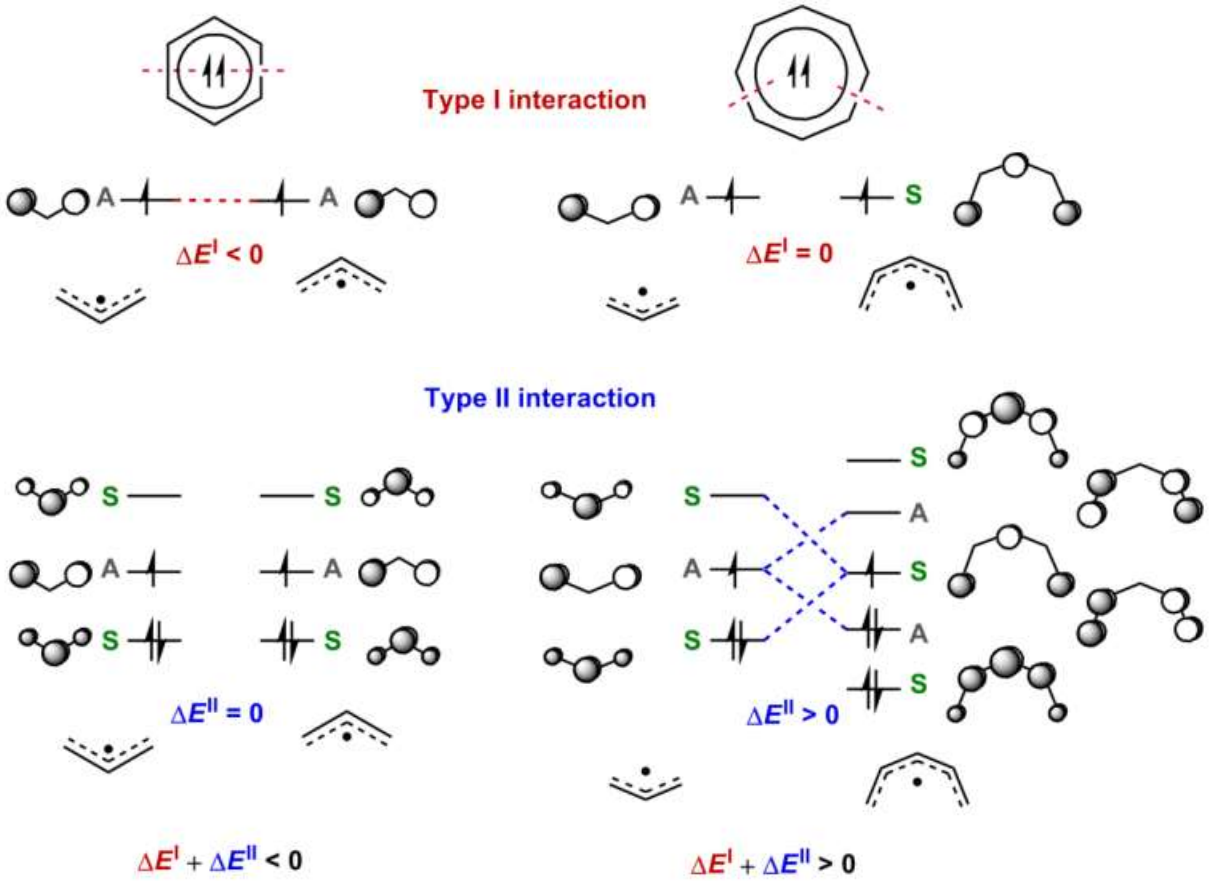
QUALITATIVE MO THEORETICAL RATIONALIZATION

N. C. Baird *J. Am. Chem. Soc.* **1972**, *94*, 4941.

Construct annulene triplet states from two linear polyenyl monoradicals

Type I interaction:
Interaction between the two SOMOs.

Type II interaction:
Interaction of the SOMO of one fragment with the vacant and doubly occupied π-MOs of other fragment

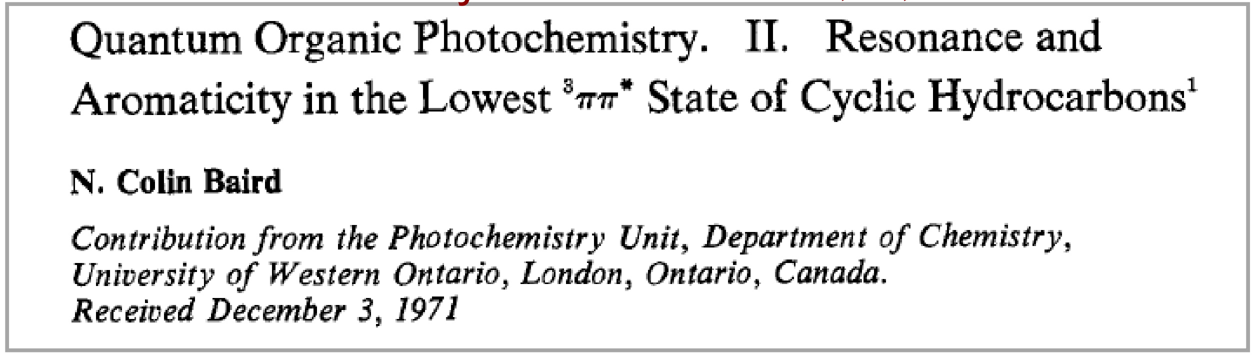


Energy loss upon cyclization
Antiaromatic

Energy gain upon cyclization
Aromatic

PROF. N. COLIN BAIRD -
FROM PHOTOCHEMISTRY TO ENVIRONMENTAL CHEMISTRY, AND BACK

N. C. Baird *J. Am. Chem. Soc.* **1972**, *94*, 4941.



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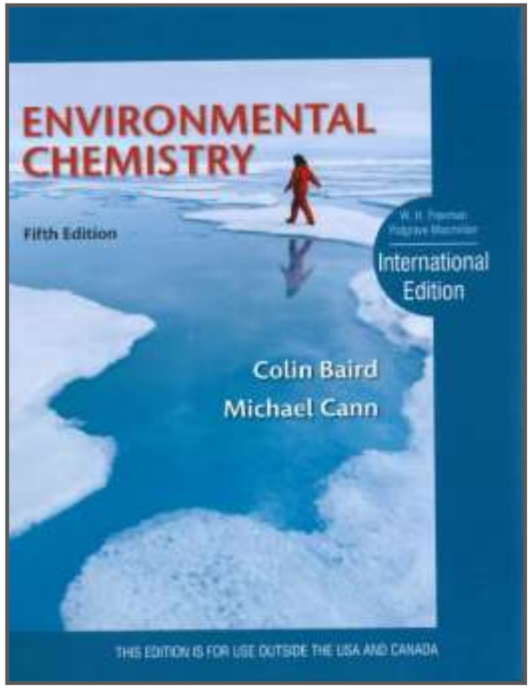


London (ON), March 2013.

Baird, *J. Phys. Org. Chem.*, **2023**, *36*, e4459

Received: 29 July 2022 | Revised: 9 October 2022 | Accepted: 17 October 2022

DOI: 10.1002/poc.4459

Journal of Physical Organic Chemistry WILEY

PERSPECTIVE

Organic triplets as free radical pairs: Everything old is new again

N. Colin Baird

Department of Chemistry, University of Western Ontario, London, Ontario, Canada

Correspondence
Norman Colin Baird, Department of Chemistry, University of Western Ontario, London, Ontario N6A 5B7, Canada.
Email: ncolinbaird@gmail.com

Abstract

More than a half-century ago, Michael Dewar devised a theoretical construct whereby the aromatic stabilization of conjugated hydrocarbon rings could be analyzed by imagining them to be formed by combining free radical chains. From the analysis, he also predicted that the rings would reverse their aromaticity in their first excited states. By taking the construct more literally, we were able to calculate the ground state-to-triplet energies of twisted conjugated

AROMATICITY & ANTIAROMATICITY AS FUNCTION OF ORBITAL TOPOLOGY, ELECTRONIC STATE, AND NUMBER OF π-ELECTRONS

J.-i. Aihara, *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1788:

"… either conformation of any annulene in the excited state can be predicted to have an aromatic character opposite to that in the ground state".

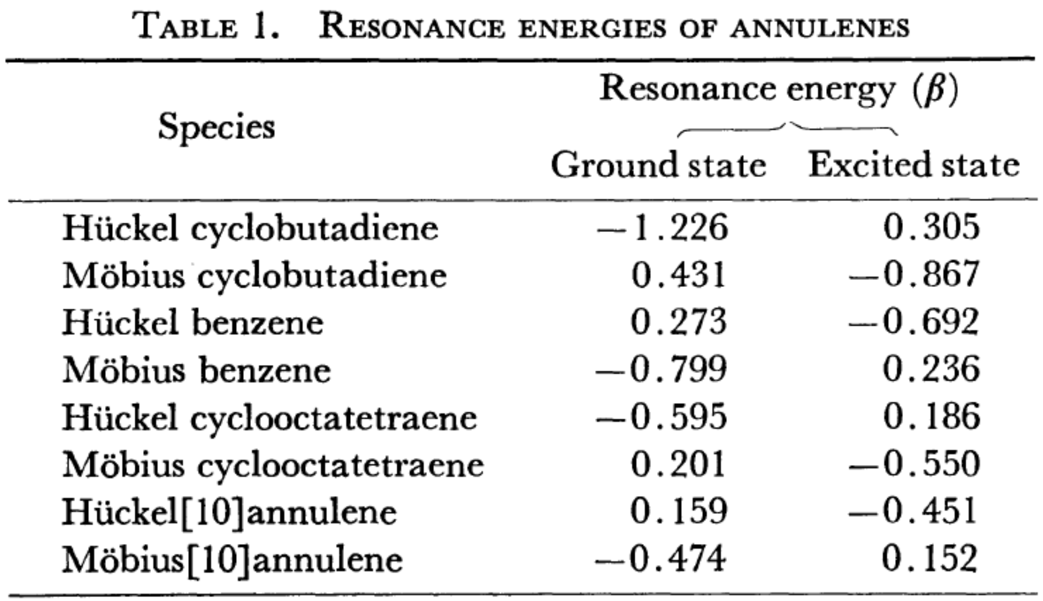
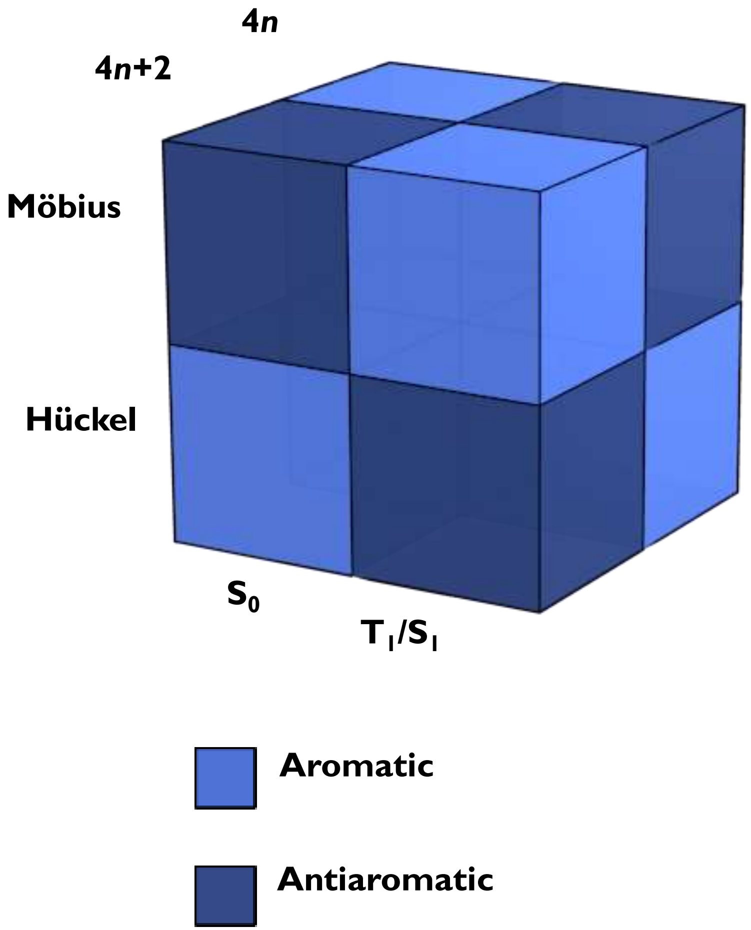


TABLE 1. RESONANCE ENERGIES OF ANNULENES

Species	Resonance energy (β) Ground state	Resonance energy (β) Excited state
Hückel cyclobutadiene	−1.226	0.305
Möbius cyclobutadiene	0.431	−0.867
Hückel benzene	0.273	−0.692
Möbius benzene	−0.799	0.236
Hückel cyclooctatetraene	−0.595	0.186
Möbius cyclooctatetraene	0.201	−0.550
Hückel[10]annulene	0.159	−0.451
Möbius[10]annulene	−0.474	0.152



QUALITATIVE VALENCE BOND THEORY OF [4*n*]ANNULENES

Zilberg & Haas, *J. Phys. Chem. A* **1998**, *102*, 10851.

A [4*n*]annulene in its closed-shell singlet state has

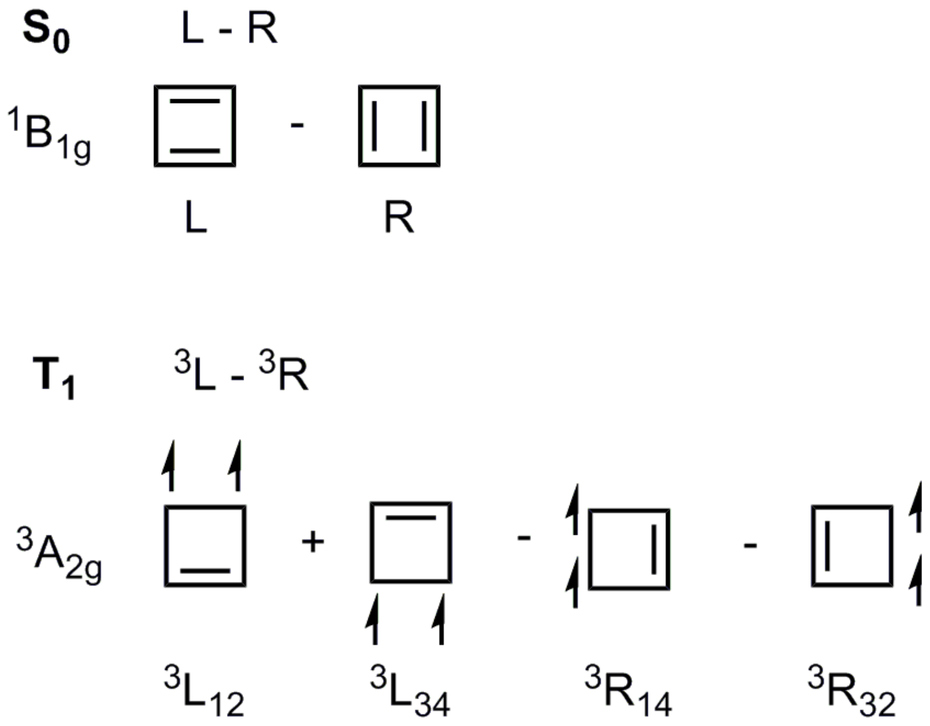
- **2*n* π_α electrons and**
- **2*n* π_β electrons**

leading to 2*n* π-bonds …

… while in its triplet state it has

- **2*n* + 1 π_α electrons and**
- **2*n* - 1 π_β electrons**

which gives only 2*n* - 1 π-bonds.

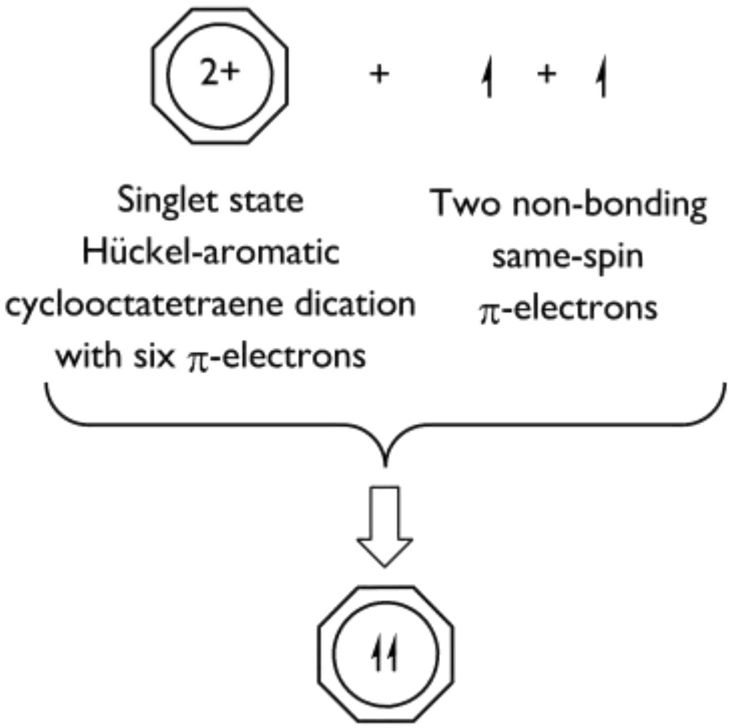


Thus, the triplet state [4*n*]annulene can be viewed a Hückel aromatic (4*n* - 2)π-electron cycle plus two nonbonding same-spin π-electrons

INTERPRETATION OF BAIRD’S RULE IN TERMS OF HÜCKEL’S RULE

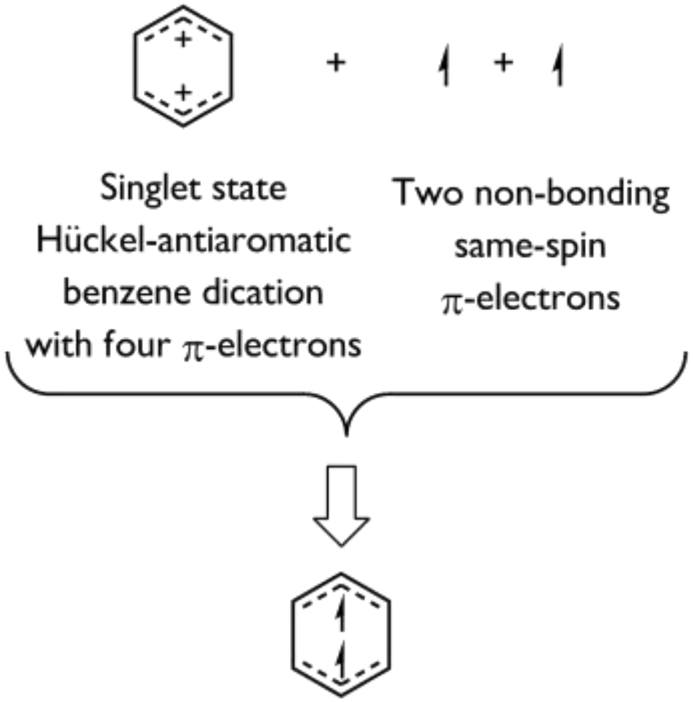
Triplet state cyclooctatetraene:

Five π_α-electrons and three π_β-electrons give three π-bonds.



Triplet state benzene:

Four π_α-electrons and two π_β-electrons give two π-bonds.



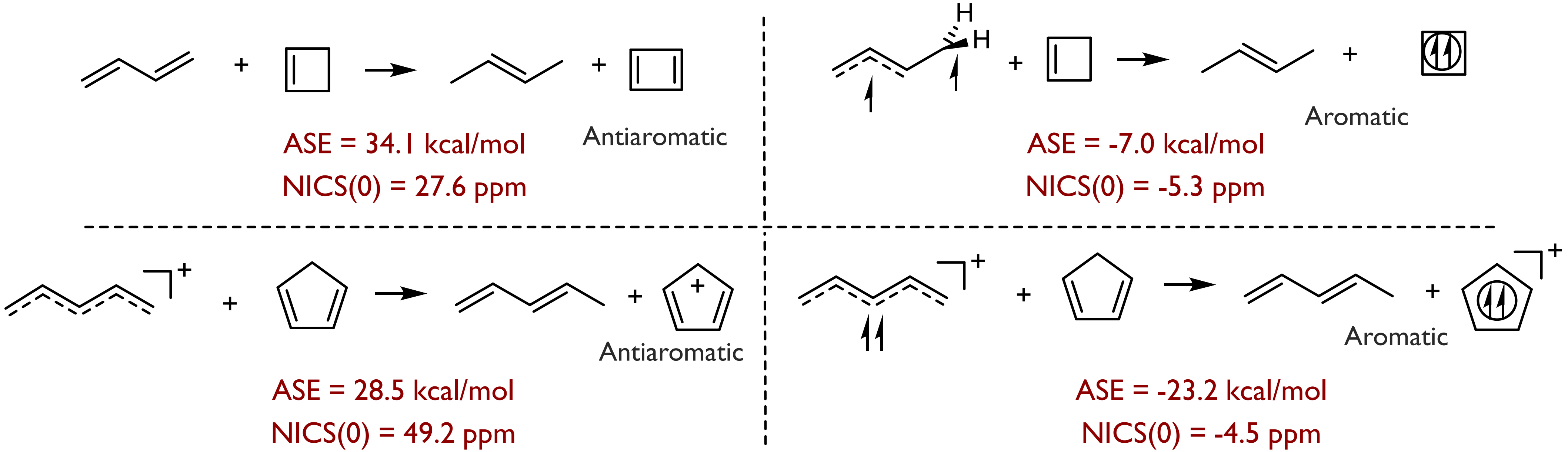
AROMATIC STABILIZATION ENERGIES OF 4*n*π-ELECTRON CYCLES

Aromatic: Negative aromatic stabilization energies (ASEs) and negative nucleus independent chemical shifts (NICSs).

Antiaromatic: Positive ASE and positive NICS values.

Lowest singlet state

Lowest triplet state



ASE = 34.1 kcal/mol
NICS(0) = 27.6 ppm

Antiaromatic

Aromatic

ASE = -7.0 kcal/mol
NICS(0) = -5.3 ppm

Antiaromatic

ASE = 28.5 kcal/mol
NICS(0) = 49.2 ppm

Aromatic

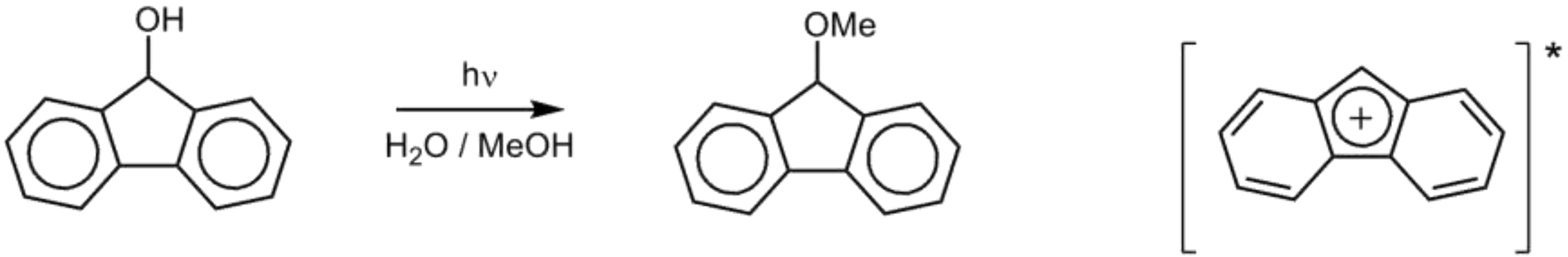
ASE = -23.2 kcal/mol
NICS(0) = -4.5 ppm

ASE at CCSD(T)/cc-pVDZ level and NICS at GIAO-HF/6-31G(d) level.

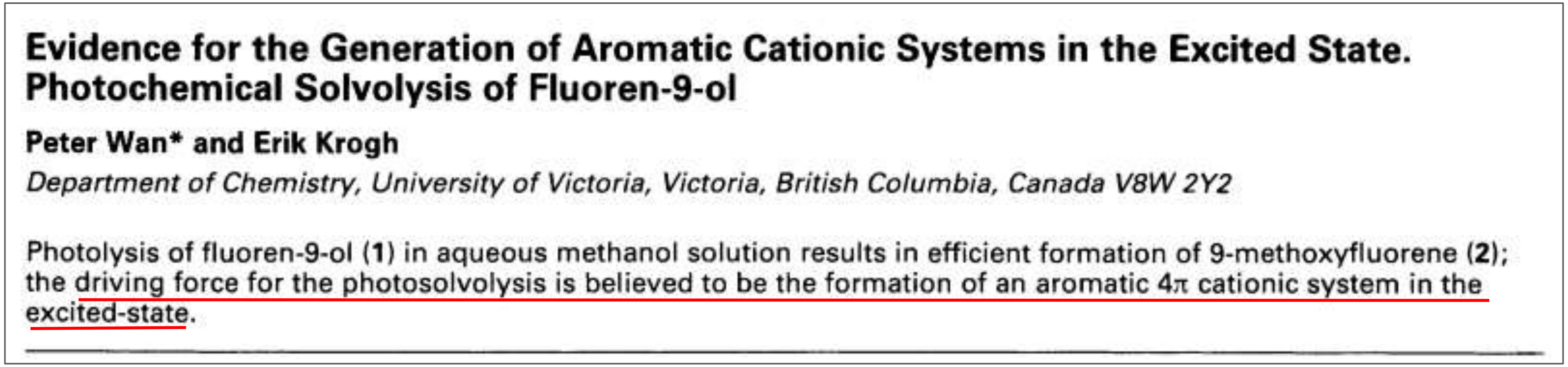
Gogonea, Schleyer & Schreiner, *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1945.

FIRST EXPERIMENT ON EXCITED STATE AROMATICITY (1985)

Wan & Krogh, *J. Chem. Soc., Chem. Commun.* **1985**, 1207.



Prof. Peter Wan



Evidence for the Generation of Aromatic Cationic Systems in the Excited State. Photochemical Solvolysis of Fluoren-9-ol

Peter Wan* and Erik Krogh

Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada V8W 2Y2

Photolysis of fluoren-9-ol (**1**) in aqueous methanol solution results in efficient formation of 9-methoxyfluorene (**2**); the driving force for the photosolvolysis is believed to be the formation of an aromatic 4π cationic system in the excited-state.

SCOPE OF EXCITED STATE AROMATICITY & ANTIAROMATICITY EXPANDS

N. C. Baird *J. Am. Chem. Soc.* **1972**, *94*, 4941

Quantum Organic Photochemistry. II. Resonance and Aromaticity in the Lowest $^3\pi\pi^*$ State of Cyclic Hydrocarbons[1]

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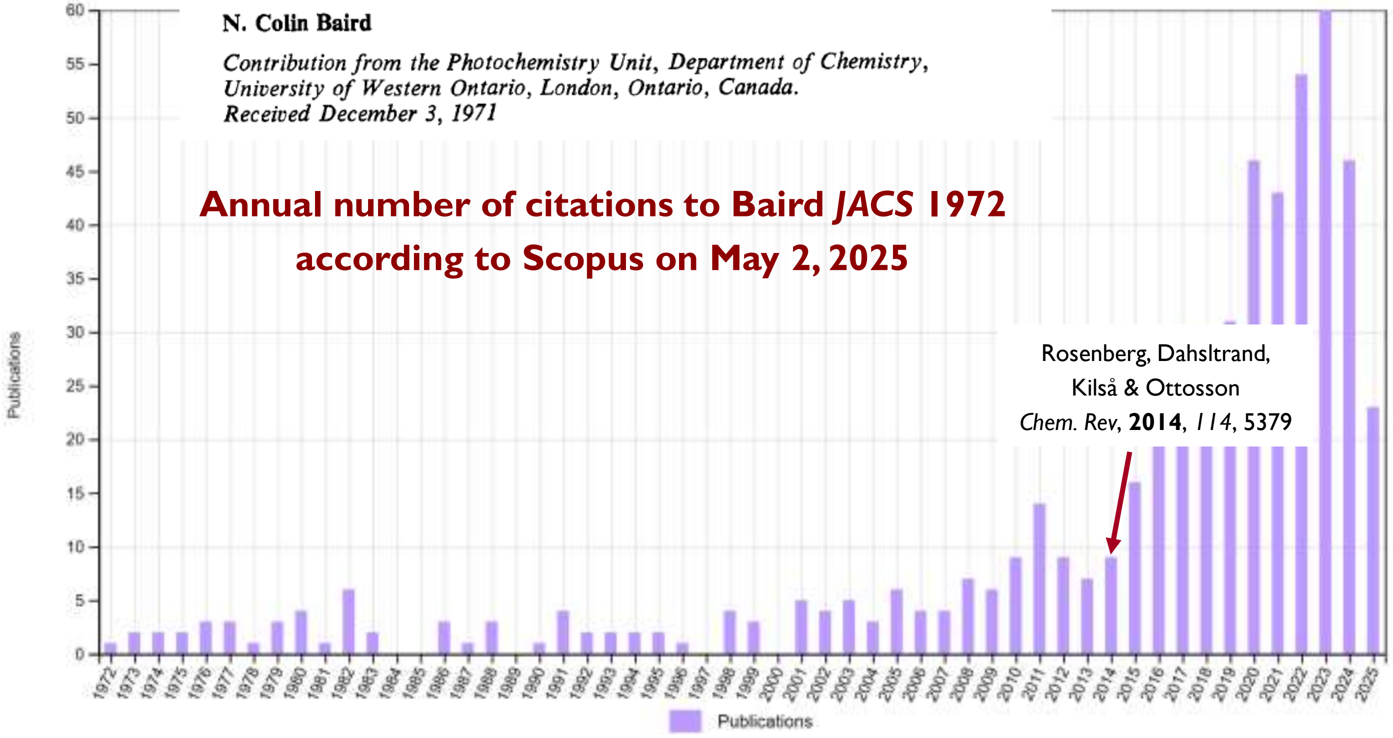
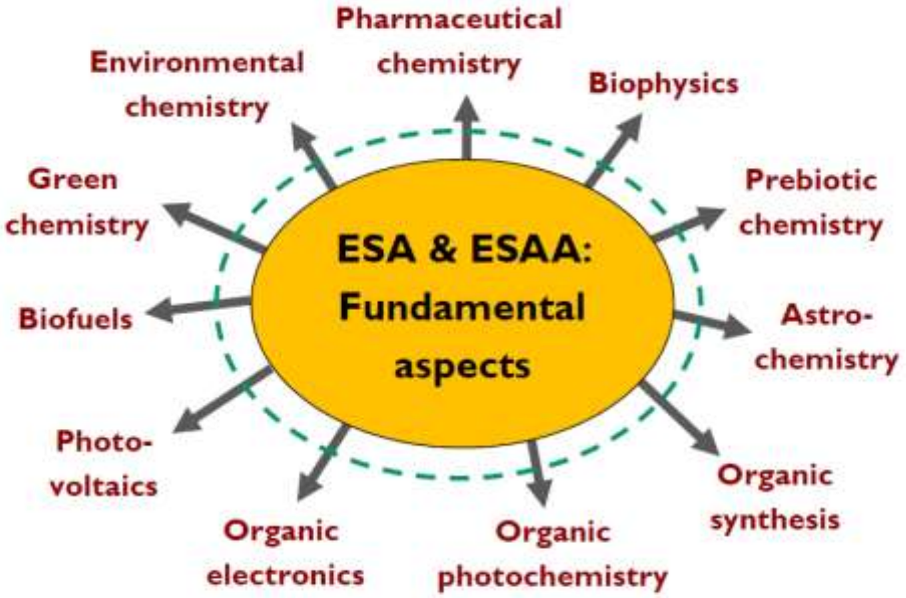


Annual number of citations to Baird *JACS* 1972 according to Scopus on May 2, 2025

Rosenberg, Dahsltrand,
Kilså & Ottosson
Chem. Rev, **2014**, *114*, 5379



ESA & ESAA: Fundamental aspects

Pharmaceutical chemistry

Environmental chemistry

Biophysics

Green chemistry

Prebiotic chemistry

Biofuels

Astro-chemistry

Photo-voltaics

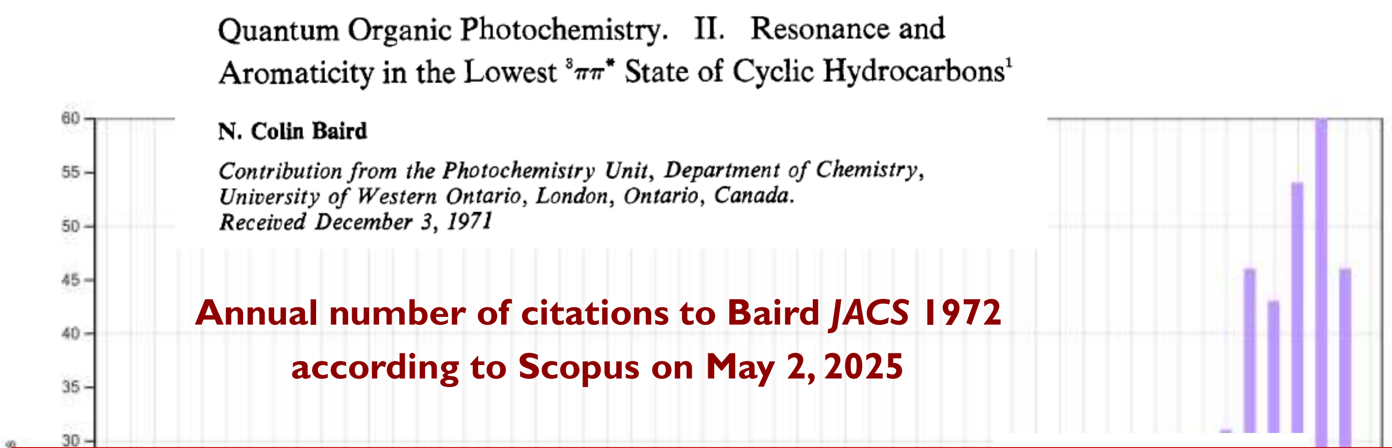
Organic synthesis

Organic electronics

Organic photochemistry

SCOPE OF EXCITED STATE AROMATICITY & ANTIAROMATICITY EXPANDS

N. C. Baird *J. Am. Chem. Soc.* **1972**, *94*, 4941



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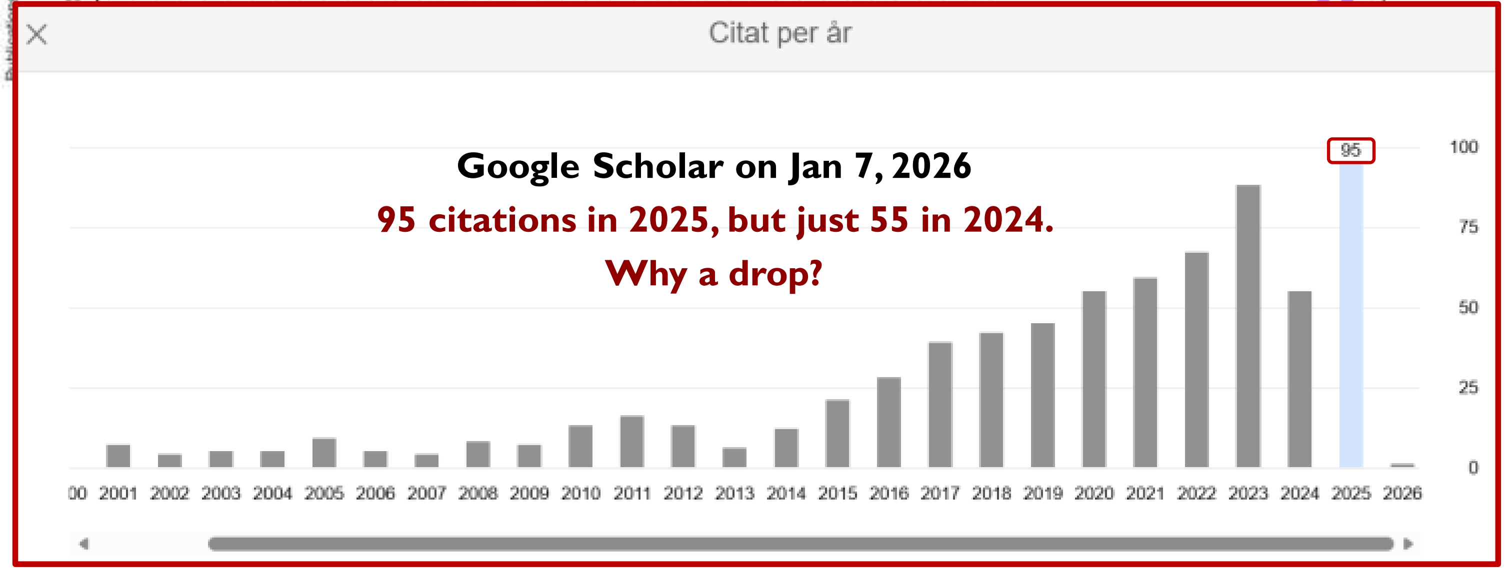
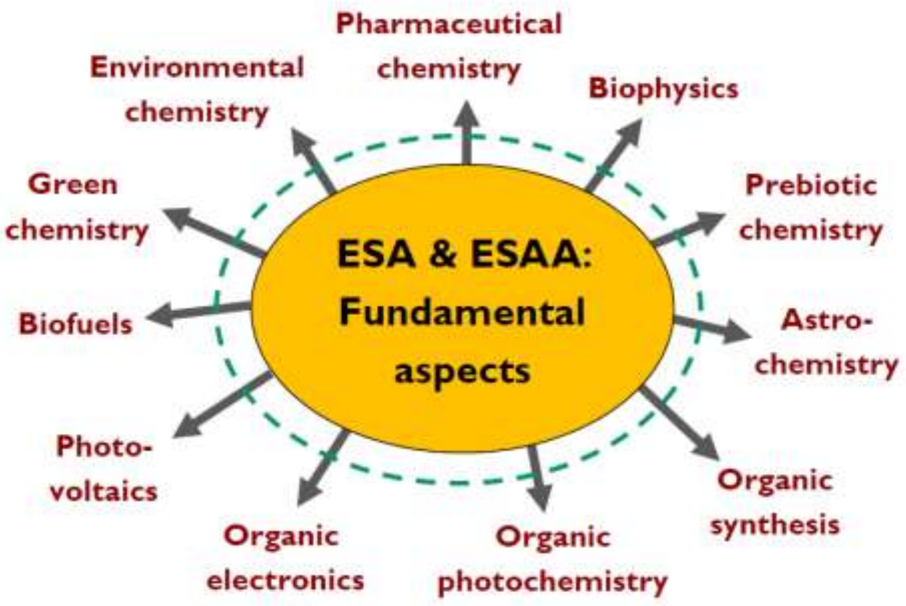


Citat per år

Google Scholar on Jan 7, 2026

95 citations in 2025, but just 55 in 2024.

Why a drop?



ESA & ESAA: Fundamental aspects

Environmental chemistry

Pharmaceutical chemistry

Biophysics

Green chemistry

Prebiotic chemistry

Biofuels

Astro-chemistry

Photo-voltaics

Organic electronics

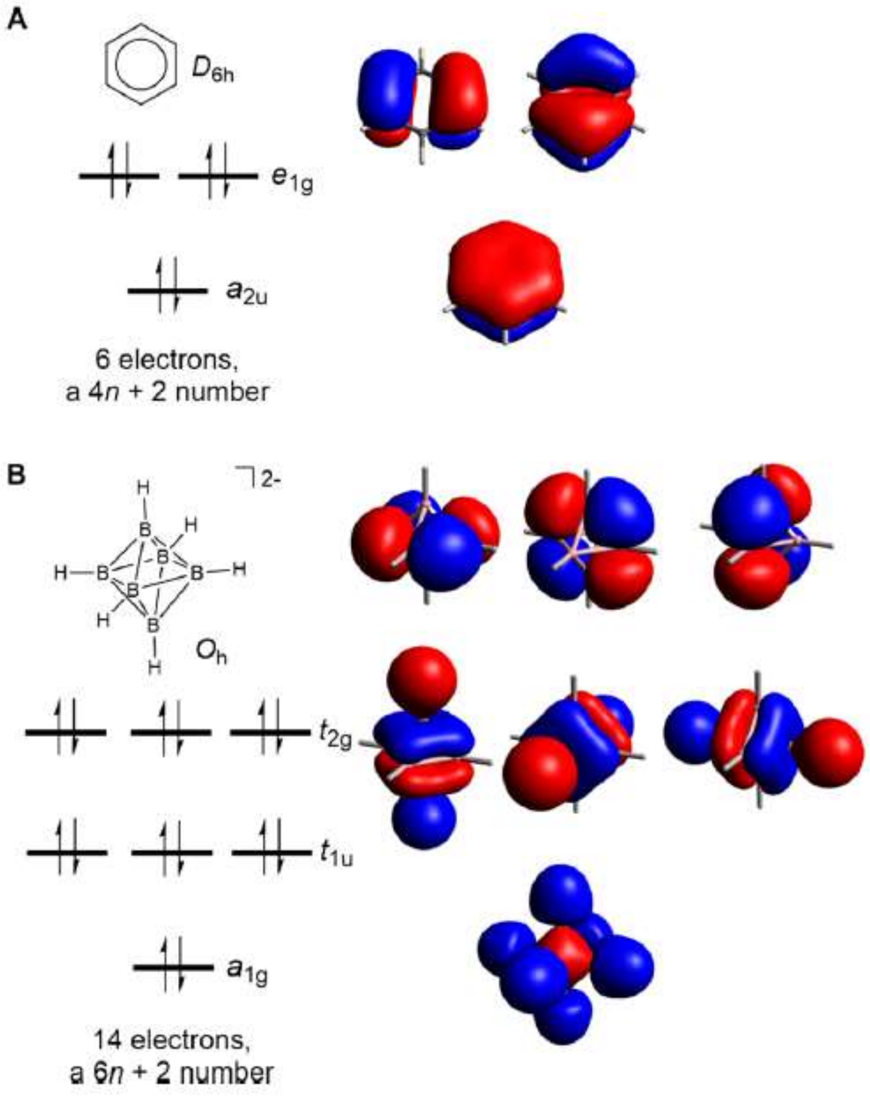
Organic photochemistry

Organic synthesis

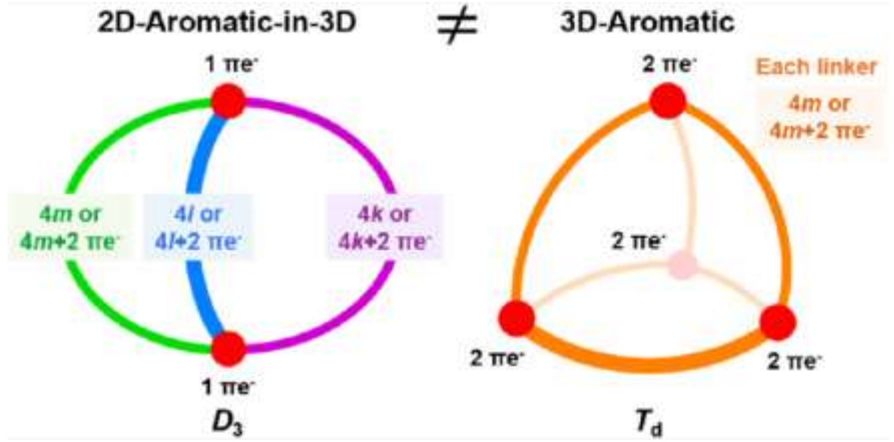
THREE-DIMENSIONAL AROMATICITY (3D-AROMATICITY)

2D-aromaticity of benzene

3D-aromaticity of the *closo*-borane B_6H_6



NOTE 1: Aromaticity in three dimensions is not necessarily 3D-aromaticity.



NOTE 2: A molecule can exhibit several locally aromatic circuits which when added together are perceived as one globally aromatic system.

El Bakouri, Szczepanik, Jorner, Ayub, Bultinck, Solà & Ottosson

J. Am. Chem. Soc. **2023**, *144*, 8560.

σ-AROMATICITY

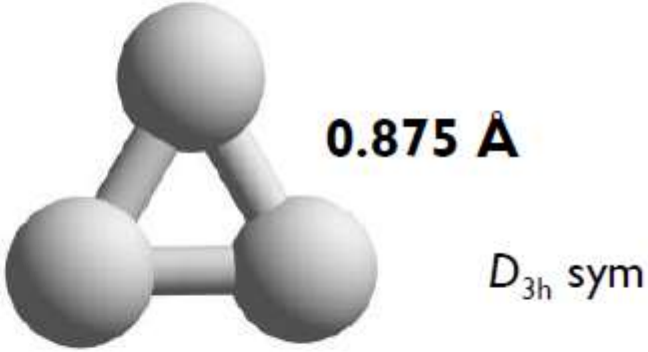
False conclusion on σ-aromaticity

- **Cyclopropane has 6 σ-electrons in the C-C bonded triangular framework.**
- **In 1979, Dewar postulated that cyclopropane is σ-aromatic in order to explain some NMR spectral observation, however, this was later disproven by Schleyer and co-workers.**

Correct conclusion on σ-aromaticity

- **Two electrons in σ-orbital**
- **Equilateral triangle**
- **Diatropic ring current in an applied magnetic field**

➡ Hückel σ-aromatic



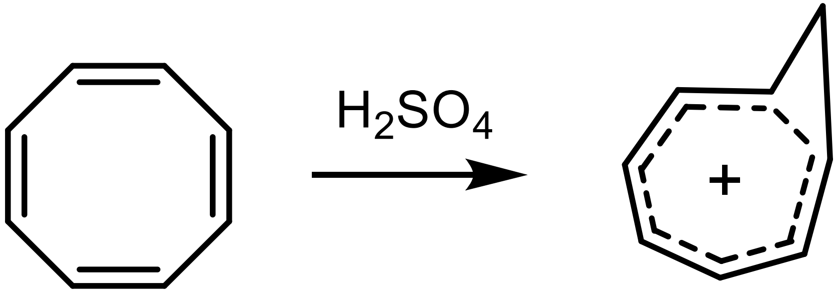
The most abundant aromatic molecule in the Universe.

HOMOAROMATICITY (AROMATICITY PARTIALLY THROUGH-SPACE)

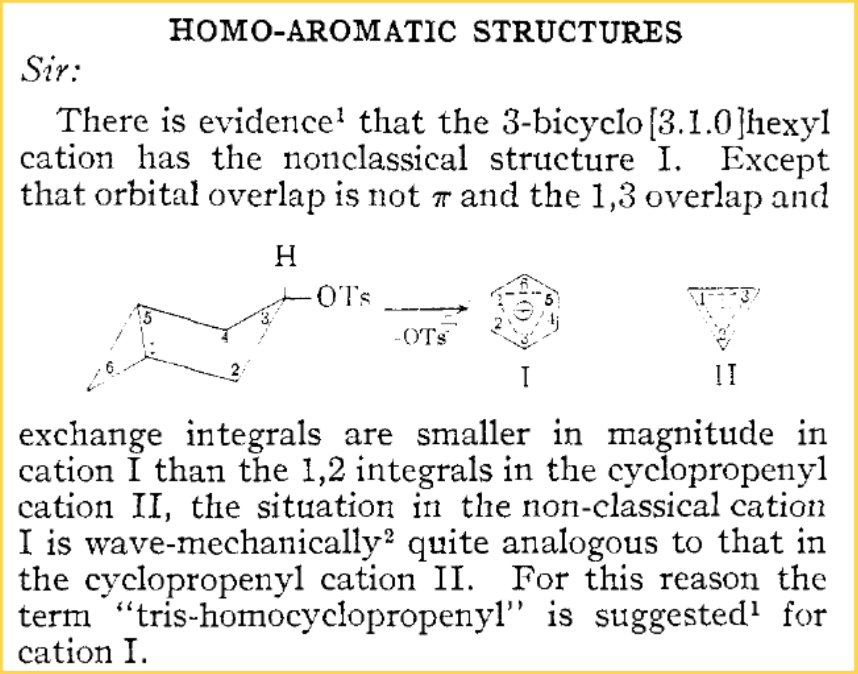
Homotropylium cation in S_0 state:

A 6π-electron cycle with one through-space

π---π interaction.



Childs *Acc. Chem. Res.* **1984**, *17*, 347.



HOMO-AROMATIC STRUCTURES

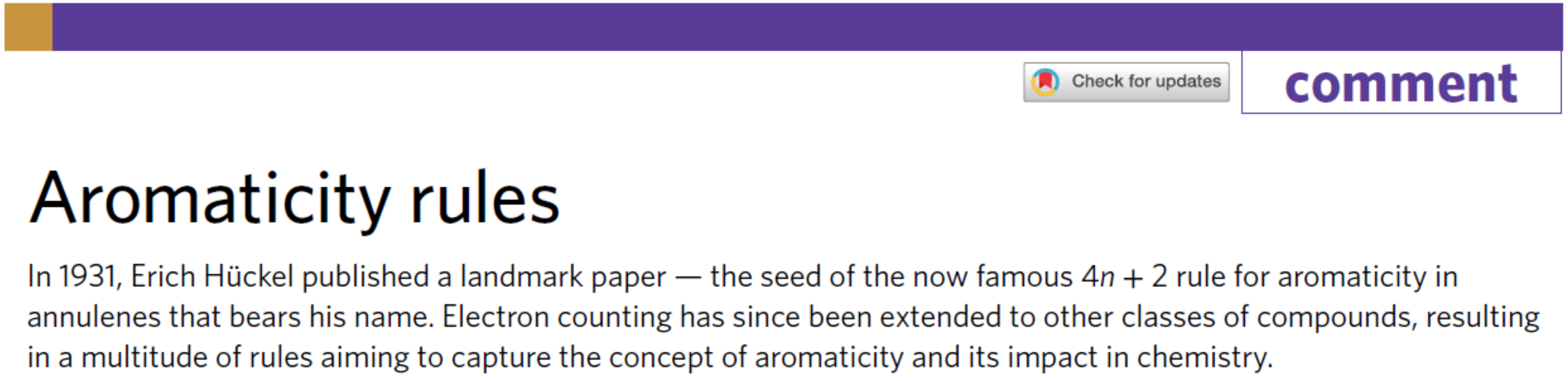
Sir:

There is evidence[1] that the 3-bicyclo[3.1.0]hexyl cation has the nonclassical structure I. Except that orbital overlap is not π and the 1,3 overlap and exchange integrals are smaller in magnitude in cation I than the 1,2 integrals in the cyclopropenyl cation II, the situation in the non-classical cation I is wave-mechanically[2] quite analogous to that in the cyclopropenyl cation II. For this reason the term "tris-homocyclopropenyl" is suggested[1] for cation I.

Winstein *J. Am. Chem. Soc.* **1959**, *81*, 6524.

- **Homoaromaticity first proposed by Saul Winstein in 1959 to explain observations made in some solvolysis experiments.**
- **Yet, the existence of homoaromaticity was long disputed. Resolved first in the 1990s through combined experimental NMR and quantum chemical studies.**

ON THE RULES OF AROMATICITY, OR BETTER, *AROMATICITY RULES!*



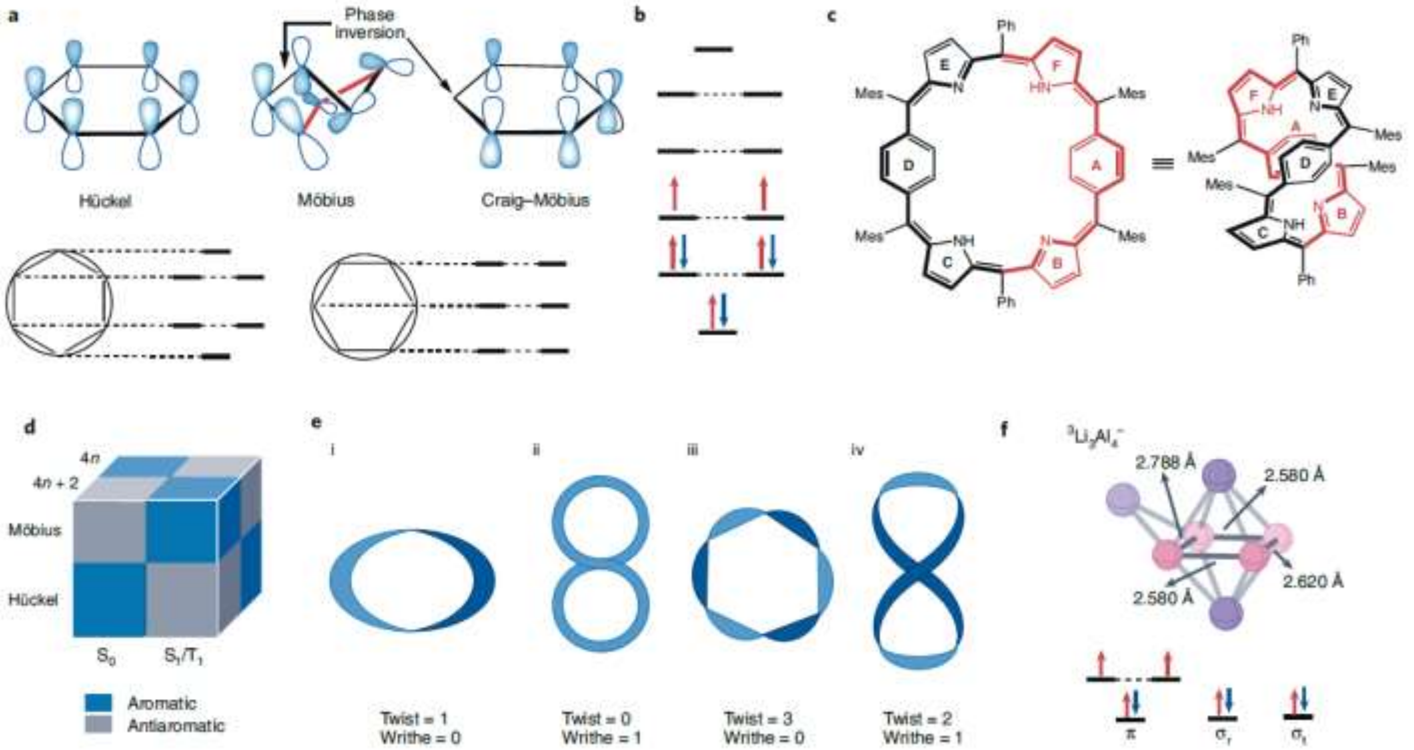
Aromaticity rules

In 1931, Erich Hückel published a landmark paper — the seed of the now famous 4*n* + 2 rule for aromaticity in annulenes that bears his name. Electron counting has since been extended to other classes of compounds, resulting in a multitude of rules aiming to capture the concept of aromaticity and its impact in chemistry.

Miquel Solà

M. Solà, *Nat. Chem.* **2022**, *14*, 585-590.

Please read for a further introduction to the various forms of aromaticity that exist.



THE IUPAC DEFINITION OF AROMATICITY (GOLD BOOK)

The concept of spatial and electronic structure of cyclic molecular systems displaying the effects of cyclic electron delocalization which provide for their enhanced thermodynamic stability (relative to acyclic structural analogues) and tendency to retain the structural type in the course of chemical transformations. A quantitative assessment of the degree of aromaticity is given by the value of the resonance energy. It may also be evaluated by the energies of relevant isodesmic and homodesmotic reactions. Along with energetic criteria of aromaticity, important and complementary are also a structural criterion (the lesser the alternation of bond lengths in the rings, the greater is the aromaticity of the molecule) and a magnetic criterion (existence of the diamagnetic ring current induced in a conjugated cyclic molecule by an external magnetic field and manifested by an exaltation and anisotropy of magnetic susceptibility). Although originally introduced for characterization of peculiar properties of cyclic conjugated hydrocarbons and their ions, the concept of aromaticity has been extended to their homoderivatives (see homoaromaticity), conjugated heterocyclic compounds (heteroaromaticity), saturated cyclic compounds (σ-aromaticity) as well as to three-dimensional organic and organometallic compounds (three-dimensional aromaticity). A common feature of the electronic structure inherent in all aromatic molecules is the close nature of their valence electron shells, *i.e.*, double electron occupation of all bonding MOs with all antibonding and delocalized nonbonding MOs unfilled. The notion of aromaticity is applied also to transition states.

THE IUPAC DEFINITION OF ANTIAROMATICITY (GOLD BOOK)

Those cyclic molecules for which cyclic electron delocalization provides for the reduction (in some cases, loss) of thermodynamic stability compared to acyclic structural analogues are classified as antiaromatic species. In contrast to aromatic compounds, antiaromatic ones are prone to reactions causing changes in their structural type, and display tendency to alternation of bond lengths and fluxional behavior (see fluxional molecules) both in solution and in the solid. Antiaromatic molecules possess negative (or very low positive) values of resonance energy and a small energy gap between their highest occupied and lowest unoccupied molecular orbitals. In antiaromatic molecules, an external magnetic field induces a paramagnetic electron current. Whereas benzene represents the prototypical aromatic compound, cyclobuta-1,3-diene exemplifies the compound with most clearly defined antiaromatic properties.

Electronic Aromaticity Descriptors

Irene Casademont Reig

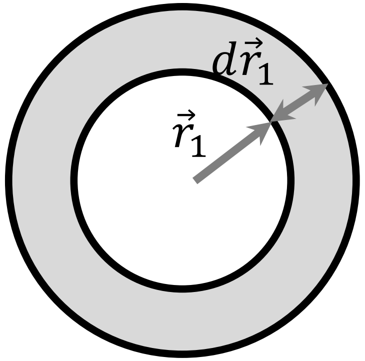
08 – 01 – 2026

Born Interpretation

Born: the probability of finding one electron at d$_1$ (d$\mathbf{r}_1$ with σ_1) is

$$P(\mathbf{1})d_1 = \int d_{\mathbf{2}} \int d_{\mathbf{3}} \ldots \int \boldsymbol{d_N} |\psi(\mathbf{1}, \mathbf{2}, \ldots, \boldsymbol{N})|^2 d_{\mathbf{1}}$$

regardless the position of the other N-1 electrons.



From the latter we define the electron density,

$$\rho(\mathbf{1}) = N \cdot P(\mathbf{1})$$

That integrated over Ω it gives the average number of electrons in Ω.

$$N_\Omega \equiv \langle\psi|\widehat{N}|\psi\rangle_\Omega = \langle\psi| \textstyle\sum_i a_i^\dagger a_i |\psi\rangle_\Omega = N \cdot (\Omega) = \int_\Omega \rho(\mathbf{1}) d_{\mathbf{1}}$$

This is the basis of electron population analysis.

The Electron Density

- The electron density is the central quantity in DFT and QTAIM.
- It is an observable obtained from X-ray spectroscopy analysis.
- It depends on three coordinates (vs. wfn that depends on 3N)
- It can be constructed from the molecular orbitals:

$$\rho(\mathbf{1}) = \sum_{i}^{N} \phi_i^*(\mathbf{1})\phi_i(\mathbf{1}) = \sum_{i}^{N} |\phi_i(\mathbf{1})|^2$$

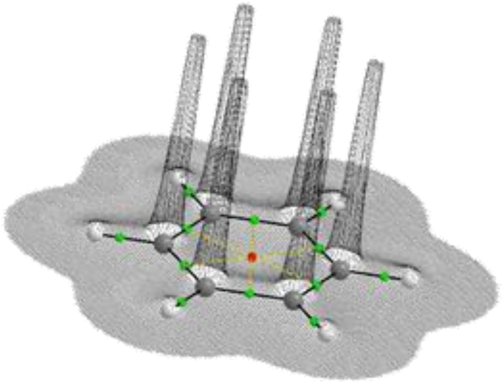
- Extention of Born interpretation: Pair density $[\rho_2(\mathbf{1},\mathbf{2})]$

$$P(1,2)d_1 d_2 = \int d_3 \ldots \int d_n |\psi(\mathbf{1},\mathbf{2},\ldots \boldsymbol{N})|^2 d_1 d_2$$

$$\rho_2(\mathbf{1},\mathbf{2}) = N(N-1)P(\mathbf{1},\mathbf{2})$$

An Atom in a Molecule

- Need to characterize an atom inside a molecule → atomic partition
- From an atomic partition we can define atomic properties
- There is not a unique atomic partition, there have been many suggestions
- Two main groups:
  - Hilbert-space based
  - Real space partitioning



→ Quantum Theory of Atoms in Molecules (**QTAIM**)

- Another useful tool to study electron distribution within a molecule:

Population Analysis (for AIMs)

$$N_A = \int_A \rho(\mathbf{1}) d_1 = \sum_i n_i \int_A |\phi_i(\mathbf{1})|^2 d_1 = \sum_i n_i S_{ii}(A)$$

$$S_{ij}(A) = \int_A \phi_i^*(\mathbf{1}) \phi_j(\mathbf{1}) d_1$$

Bader, R.F.W., Atoms in Molecules: A Quantum Theory, Oxford University Press, Oxford, **1990**

Gatti, C. *Zeit. Kristallogr.* **2005**, *220*, 399

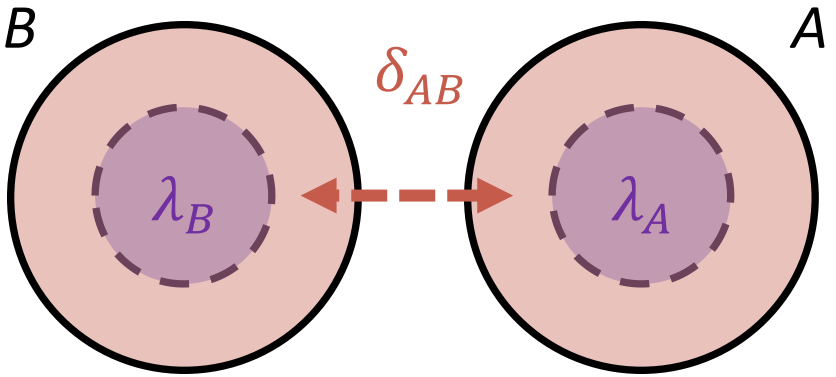
The Electron Sharing Indices (ESI)

- All the electrons in a molecule are either localized in an atom or delocalized with other atoms.

- The **delocalization index** (DI):

$$\boldsymbol{\delta_{AB}} = -cov(N_A, N_B) = 2\int_A \int_B d_1 d_2 \rho_{XC}(1,2)$$

$$\rho_{XC}(1,2) = \rho(1)\rho(2) - \rho_2(1,2)$$



- The **localization index** (LI):

$$\boldsymbol{\lambda_A} = N_A - \sigma^2[N_A] = \frac{\delta(A,A)}{2} = \int_A \int_A d_1 d_2 \rho_{XC}(1,2)$$

Aromaticity

- It refers to **several properties** not necessarily mutually related.

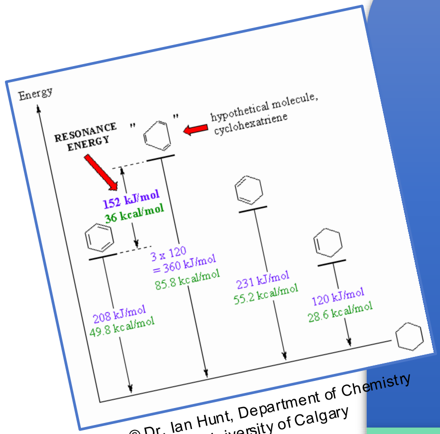
> A compound is considered to be aromatic if there is a measurable degree of delocalization of a π-electron system in the ground state of the molecule.
>
> F. Sondheimer (1964)

- Organic chemists use **aromaticity to elucidate phenomena** such as chemical stability/reactivity, bond length equalization/alternation, etc.

Katritzky A.R., *et al., J. Am. Chem Soc.* **1989**, *111*, 7

Feixas, F., *et al.*, *Chem. Soc. Rev.* **2015**, *44*, 6434

Aromaticity



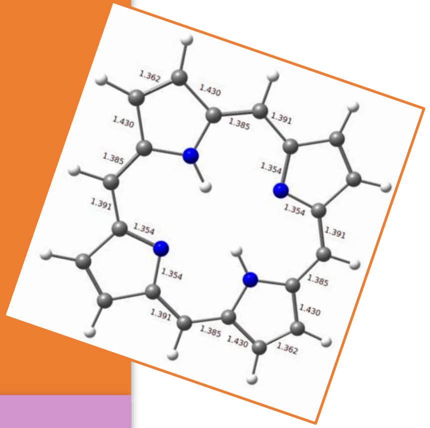
© Dr. Ian Hunt, Department of Chemistry
University of Calgary

Energetic:

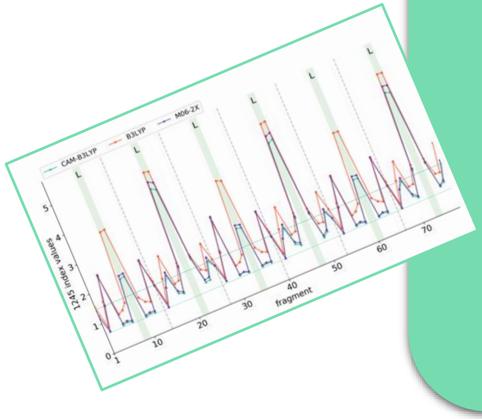
ASE

Geometric:

HOMA, BLA



INDICES

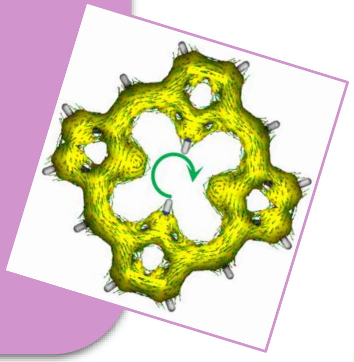


Electronic:

FLU, BOA, I_{ring}, MCI, AV1245 & AV_{min}

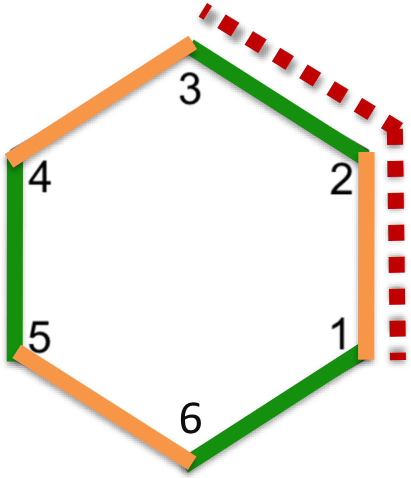
Magnetic:

ACID & NICS



Electronic Aromaticity Measures

Ring structure of *n* atoms, represented by the following string $\mathcal{A}=\{A_1, A_2, \ldots, A_n\}$:



Based on bond-orders:

$$BOA(\mathcal{A}) = \frac{1}{n_1}\sum_{i=1}^{n_1}\boxed{\delta(A_{2i-1}, A_{2i})} - \frac{1}{n_2}\sum_{i=1}^{n_2}\boxed{\delta(A_{2i}, A_{2i+1})}$$

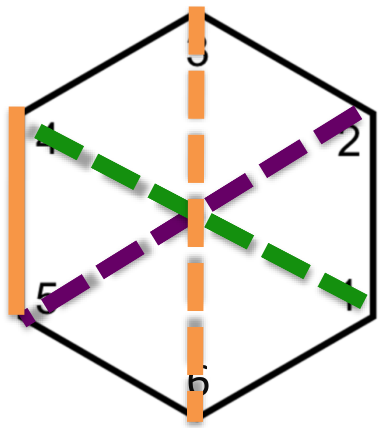
Problems with odd nº atoms

BOA(1)

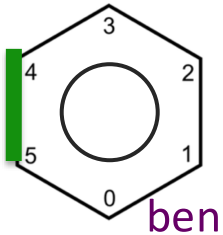
$$BOA(\mathcal{A}) = \frac{1}{2n}\sum_{i=1}^{n}\underline{\boxed{\delta(A_i, A_{i+1})} - \boxed{\delta(A_{i+1}, A_{i+2})}}$$

Electronic Aromaticity Measures

Ring structure of *n* atoms, represented by the following string $\mathcal{A}=\{A_1, A_2, \ldots, A_n\}$:



Based on bond-orders:



benzene

$$BOA(\mathcal{A}) = \frac{1}{2n}\sum_{i=1}^{n}|\delta(A_i, A_{i+1}) - \delta(A_{i+1}, A_{i+2})|$$

$$FLU(\mathcal{A}) = \frac{1}{n}\sum_{i=1}^{n}\left[\left(\frac{\delta(A_i)}{\delta(A_{i-1})}\right)^{\alpha}\left(\frac{\boxed{\delta(A_i, A_{i-1})} - \boxed{\delta_{ref}(A_i, A_{i-1})}}{\delta_{ref}(A_i, A_{i-1})}\right)\right]^2$$

$$PDI(\mathcal{A}) = \frac{\boxed{\delta(A_1, A_4)} + \boxed{\delta(A_2, A_5)} + \boxed{\delta(A_3, A_6)}}{3}$$

Electronic Aromaticity Measures

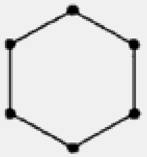
$\mathcal{A}=\{A_1, A_2, \ldots, A_n\}$:

Based on multicenter quantities:

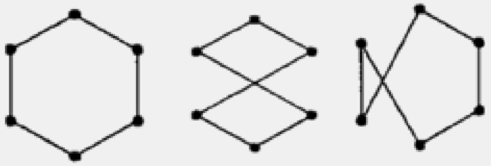
I_{ring}

$$I_{\text{ring}}(\mathscr{A}) = 2^{n-1} \sum_{i_1 i_2 \ldots i_n} S_{i_1 i_2}(A_1) \cdots S_{i_n i_1}(A_n)$$

Only the Kekulé structure considered



MCI



etc.

$$\text{MCI}(\mathscr{A}) = \frac{1}{2n} \sum_{\mathscr{P}(\mathscr{A})} I_{\text{ring}}(\mathscr{A})$$

$$S_{ij}(A_1) = \int_{A_1} d\mathbf{1}\,\phi_i^*(\mathbf{1})\phi_j(\mathbf{1})$$

MCI is related to the *n*-central moment of the n-variate probability distribution $\rho_n(\mathbf{1},\ldots,\mathbf{n})$ integrated into $A_1,\ldots,A_n$

Original definition I_{ring}: Giambiagi, M., *et al. Phys. Chem. Chem. Phys.* **2000**, *2*, 3381

Original definition MCI: Bultinck, P., *et al. J. Phys. Org. Chem.* **2005**, *111*, 7

Ring-size consistent: Cioslowski, J., Matito, E., Solà, M. *J. Phys. Chem. A* **2007**, *111*, 6521

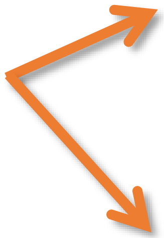
Text book examples

Molecule	DI (C_1-C_2)	DI (C_2-C_3)	FLU	BOA	Iring	Iring$^{1/n}$	MCI	MCI$^{1/n}$	AV1245	AV$_{min}$
Benzene	1.39	1.39	0.000	0.000	0.048	0.603	0.072	0.646	10.71	10.71
Cyclohexane	0.98	0.98	0.090	0.000	0.000	0.256	0.000	0.260	-0.01	0.01
Cyclohexatriene a/b=0.9	1.11	1.62	0.034	0.511	0.032	0.564	0.044	0.594	7.43	7.43
Cyclohexatriene a/b=0.7	0.86	1.90	0.138	1.038	0.007	0.436	0.007	0.438	1.76	1.76

Computational level: CAM-B3LYP/6-311G(d,p)

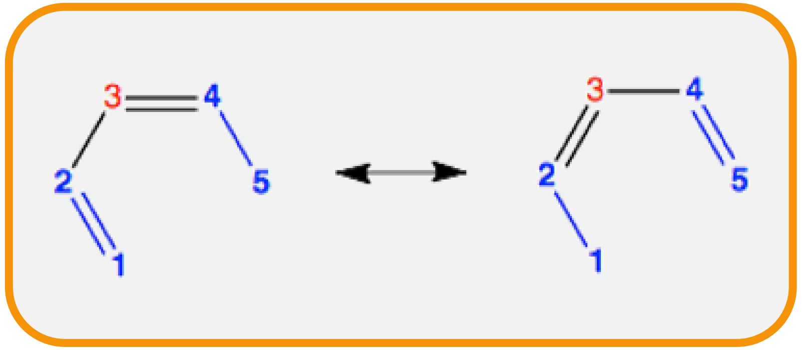
AV1245

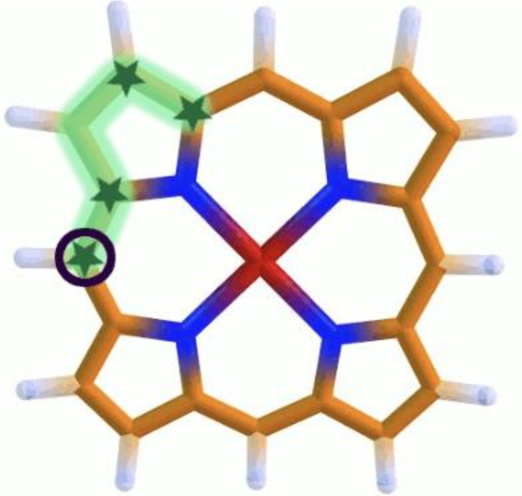
- Electronic aromaticity index for **large systems**
- I_{ring} and **MCI** cannot be used in large circuits



I_{ring}: measures the delocalization along the ring

MCI: also accounts for the delocalization across the ring

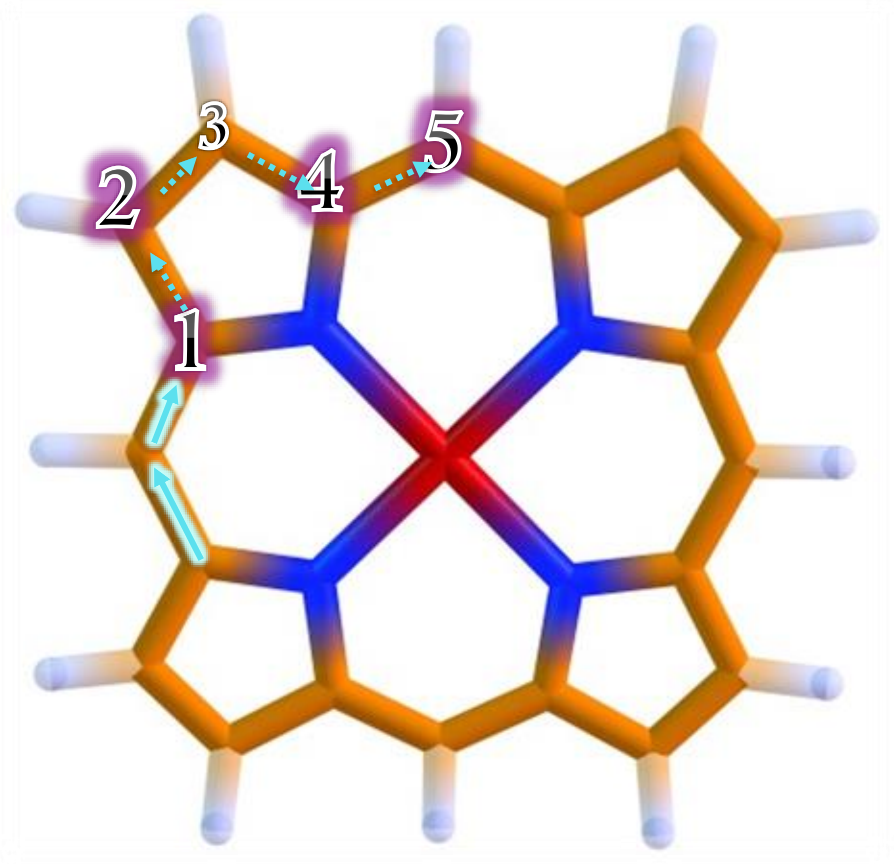




Matito E., *Phys. Chem. Chem. Phys.*, **2016**, *18*, 11839
Feixas, F., *et al.*, *Chem. Soc. Rev.*, **2015**, *44*, 6434
García-Fernández, C., *et al.*, *J. Phys. Chem. C*, **2017**, *121*, 27118

AV1245 & AV_{min}

- Electronic aromaticity index for **large systems**
- I_{ring} and **MCI** cannot be used in large circuits
- **Average** of 4-center **MCI**
- Large values will identify **aromatic** species
- **AV_{min}**: minimal (multicenter) delocalization
  - BOA
  - 1245-index distribution profile



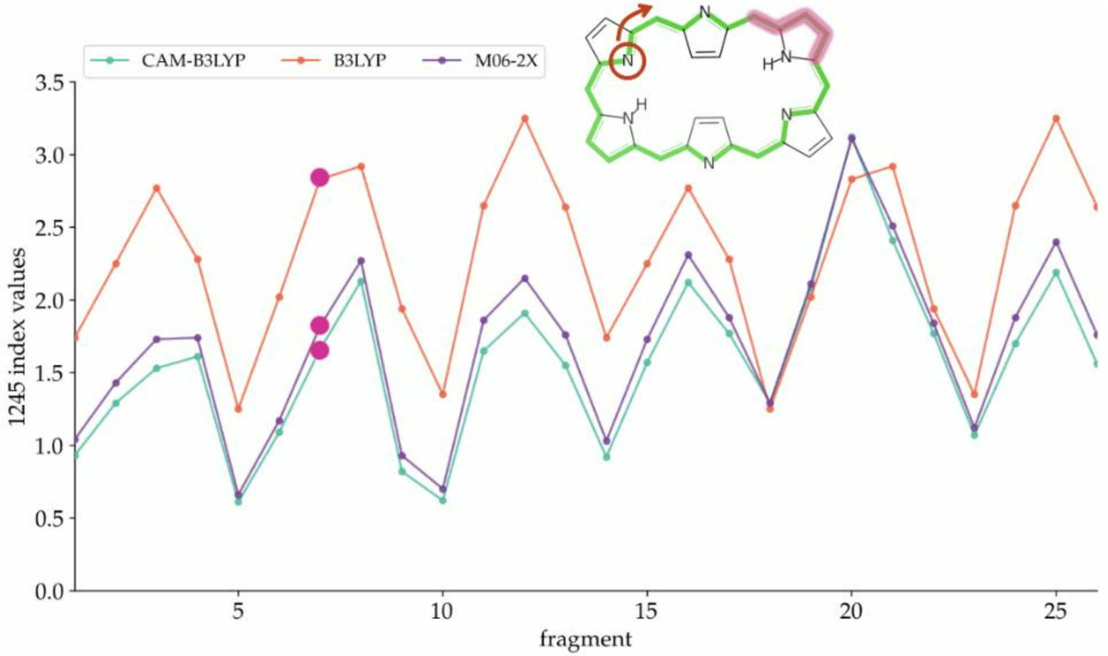
Matito E., *Phys. Chem. Chem. Phys.*, **2016**, *18*, 11839

Feixas, F., *et al.*, *Chem. Soc. Rev.*, **2015**, *44*, 6434

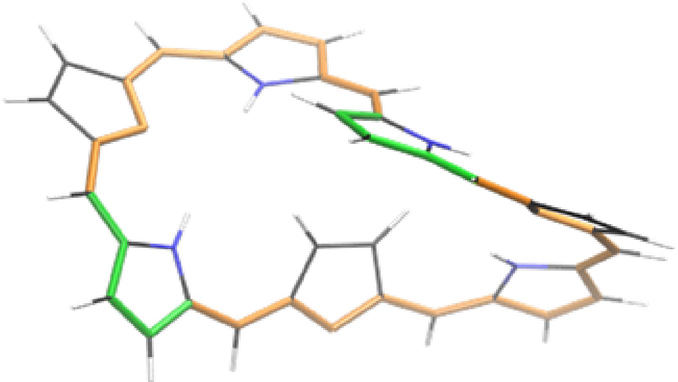
García-Fernández, C., *et al.*, *J. Phys. Chem. C*, **2017**, *121*, 27118

AV1245 & AV$_{min}$

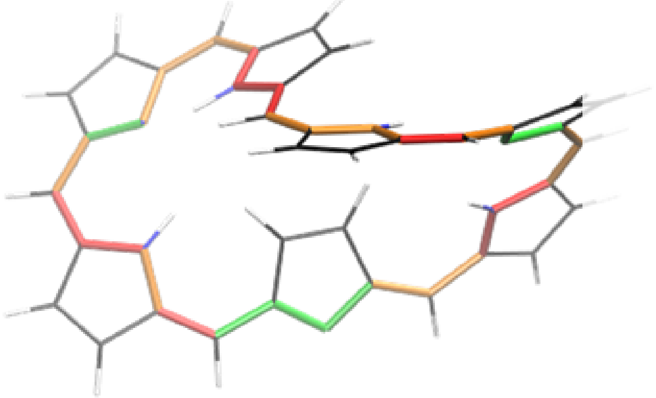
1245-index distribution profile of 26H



AV1245 Colored representation of 32M



annulene path

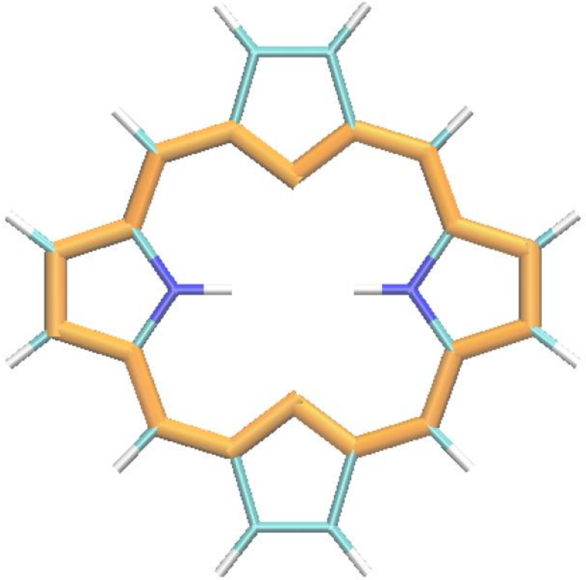


inner path

Casademont-Reig, I., *et al.*, in Aromaticity. Modern computational methods and applications, *Elsevier*, **2021**, pp. 235

Level of theory: CAM-B3LYP/6-311G(d,p)

Annulene Model

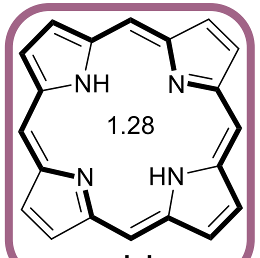


“The most aromatic circuit follows the **annulene-like conjugation pathway** and determines the macrocyclic aromaticity of the porphyrin.”

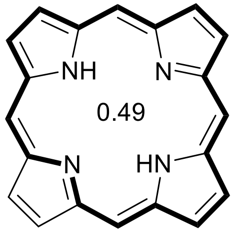
The annulene-like pathway **follows the internal circuit except** when it passes through a **pyrrole ring**

Aihara, J., *et al. J. Phys. Chem. A*, **2012**, *116*, 11718

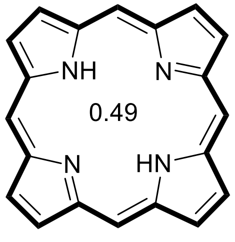
Annulene Model: Porphine



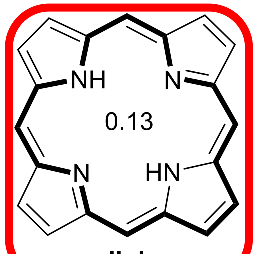
oioi



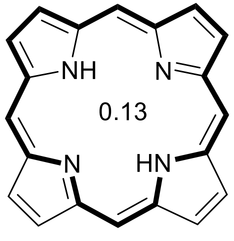
oooi



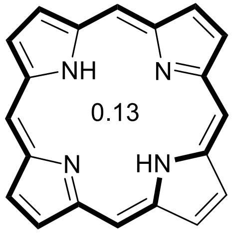
oooo



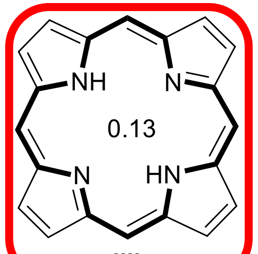
iioi



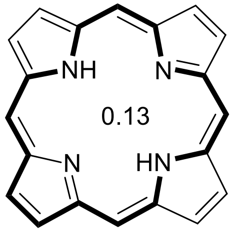
ooii



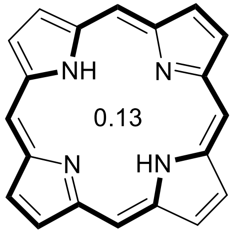
ooio



iiii



iiio

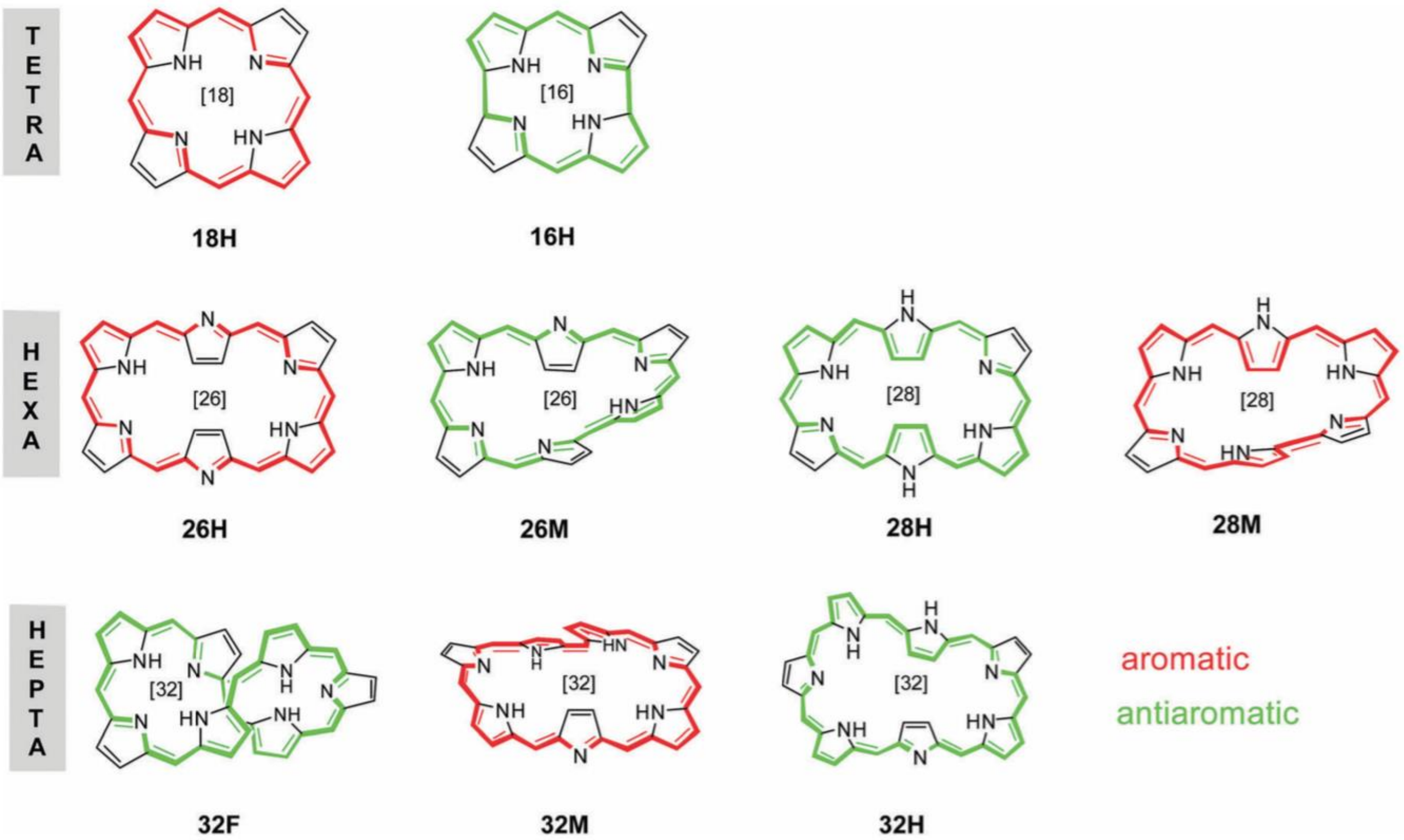


ioio

	✗	✗	✗	✗	✓	✓
Pathway	**FLU**	**BOA**	**HOMA**	**BLA**	**AV1245**	**AV_{min}**
oioi	0.010	0.000	0.872	0.000	2.16	1.28
oooi	0.016	0.309	0.734	0.288	1.91	0.49
oooo	0.022	0.041	0.610	0.011	1.70	0.49
iioi	0.008	0.367	0.917	0.313	1.57	0.13
ooii	0.015	0.023	0.769	0.006	1.36	0.13
ooio	0.021	0.372	0.637	0.270	1.17	0.13
iiii	0.006	0.000	0.968	0.000	0.91	0.13
iiio	0.013	0.388	0.808	0.307	0.73	0.13
ioio	0.019	0.000	0.666	0.000	0.57	0.13

Casademont-Reig, I., *et al*. *Phys. Chem. Chem. Phys.* **2018**, *20*, 2787

Annulene Model: Test Set



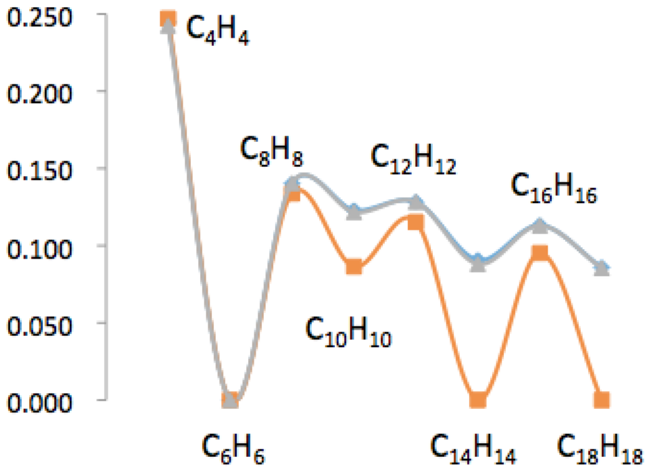
How many correct systems?

FLU	1
HOMA	1
BOA	1
BLA	1
AV1245	2
AV$_{min}$	9

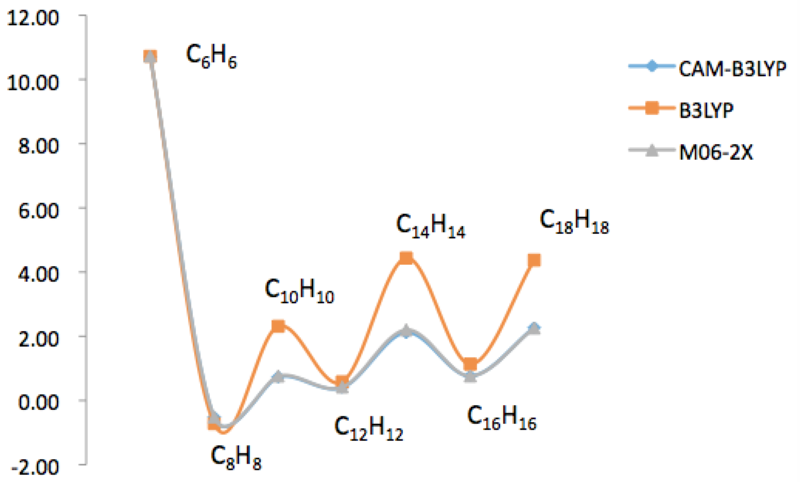
Only **AV$_{min}$** can detect the most conjugated pathway in ALL species

Casademont-Reig, I., *et al*. *Phys. Chem. Chem. Phys.* **2018**, *20*, 2787

Which Computational Level?



BLA



AV_{min}

B3LYP overestimates aromaticity of some species ($C_{14}H_{14}$ & $C_{18}H_{18}$)

A good (DFT) description of conjugation effects calls for long-range exact exchange

e.g., CAM-B3LYP, LC-PBE, *even* M06-2X

Casademont-Reig, I., *et al*. *Molecules* **2020**, *25*, 711
Wannere, C.S., *et al*. *Angew. Chem. Int. Ed.* **2004**, *43*, 4200

How we can compute them?

- **ESI-3D** developed by Dr. Eduard Matito – distributed freely under some conditions (ematito@gmail.com)
  - Needs other software to compute overlap matrices (e.g., AIMall)
    - AIMall needs wfn/wfx or fchk files produced by other programs

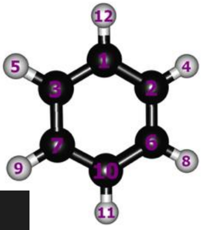
- **ESIpy** developed by Joan Grèbol-Tomàs under the supervision of Dr. Eduard Matito (DIPC) and Dr. Pedro Salvador (UdG)

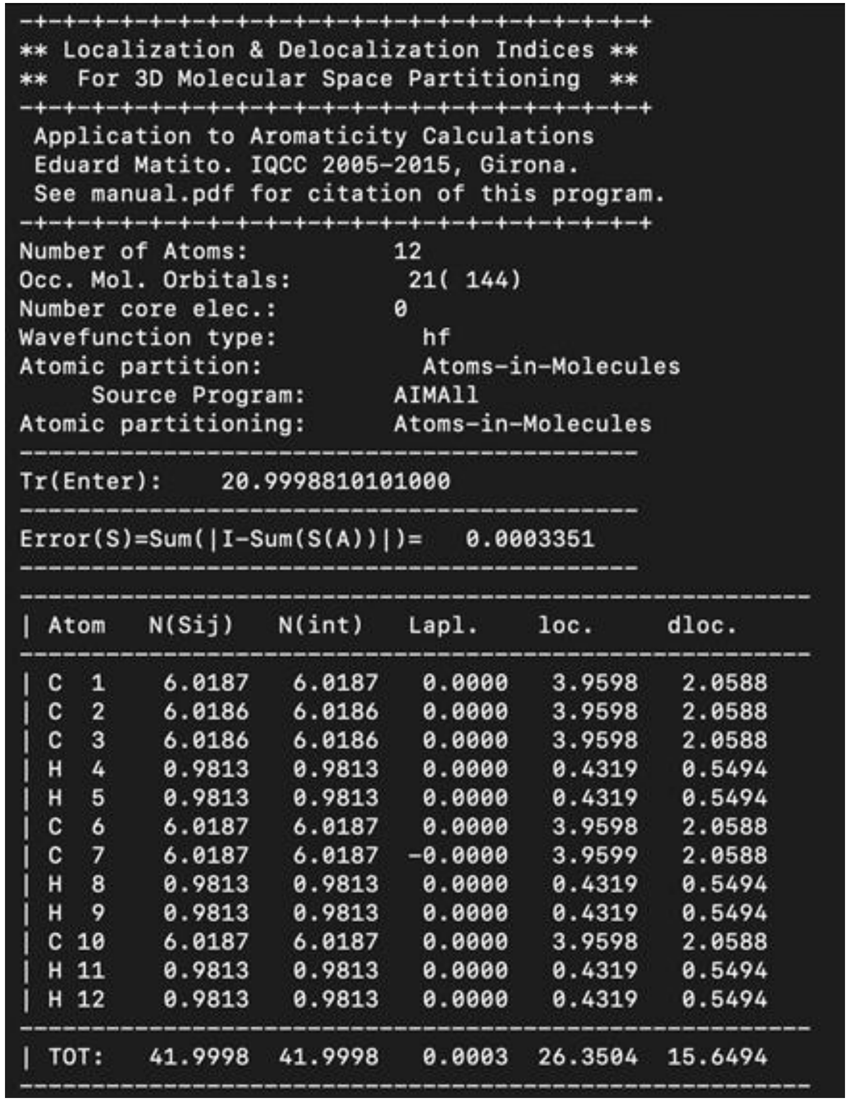
Grèbol-Tomàs J., Matito E., Salvador, P. *Chem. Eur. J.*, **2024**, *30*, e202401282

https://github.com/jgrebol/ESIpy

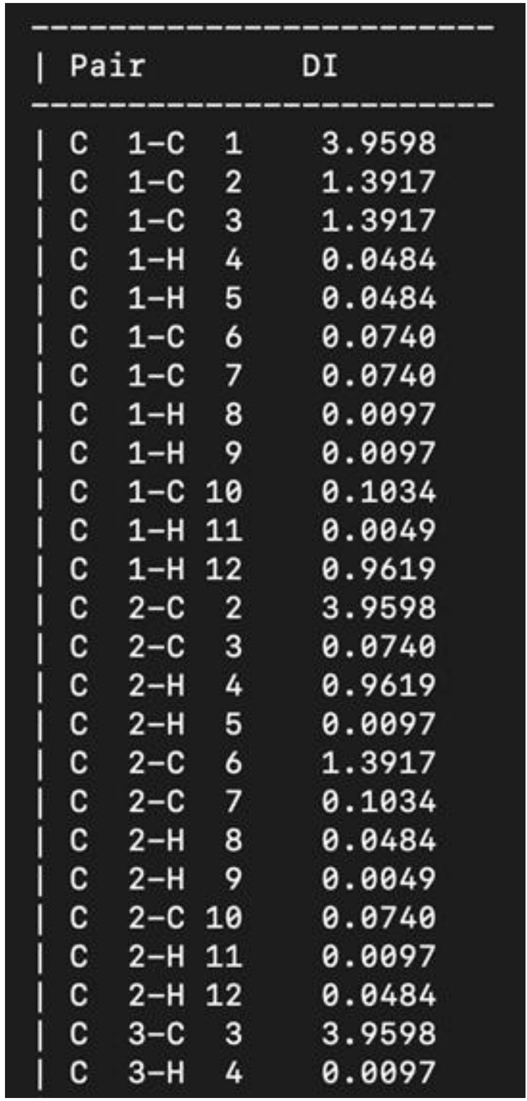
ESIpy

ESI-3D

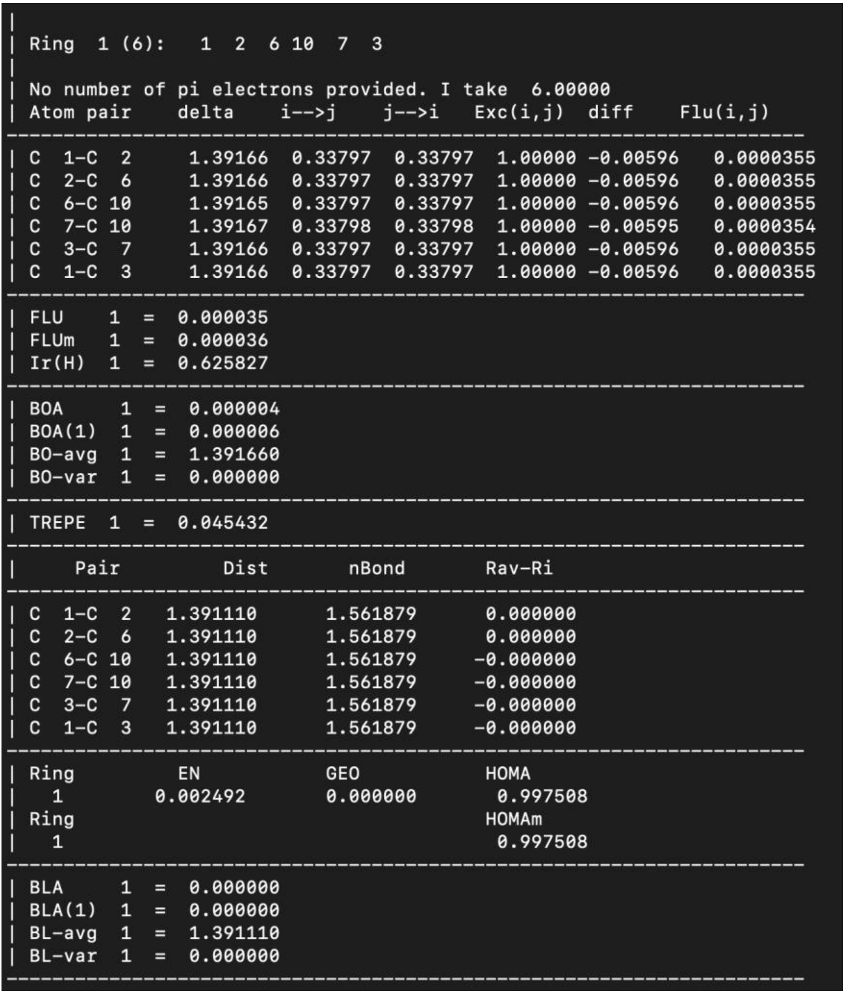




```
-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+
** Localization & Delocalization Indices **
**  For 3D Molecular Space Partitioning  **
-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+
 Application to Aromaticity Calculations
 Eduard Matito. IQCC 2005-2015, Girona.
 See manual.pdf for citation of this program.
-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+
Number of Atoms:          12
Occ. Mol. Orbitals:        21( 144)
Number core elec.:        0
Wavefunction type:          hf
Atomic partition:           Atoms-in-Molecules
     Source Program:      AIMAll
Atomic partitioning:      Atoms-in-Molecules
-------------------------------------------
Tr(Enter):    20.9998810101000
-------------------------------------------
Error(S)=Sum(|I-Sum(S(A))|)=   0.0003351
-------------------------------------------
-------------------------------------------------------
| Atom   N(Sij)   N(int)   Lapl.    loc.    dloc.
-------------------------------------------------------
| C  1    6.0187   6.0187   0.0000   3.9598   2.0588
| C  2    6.0186   6.0186   0.0000   3.9598   2.0588
| C  3    6.0186   6.0186   0.0000   3.9598   2.0588
| H  4    0.9813   0.9813   0.0000   0.4319   0.5494
| H  5    0.9813   0.9813   0.0000   0.4319   0.5494
| C  6    6.0187   6.0187   0.0000   3.9598   2.0588
| C  7    6.0187   6.0187  -0.0000   3.9599   2.0588
| H  8    0.9813   0.9813   0.0000   0.4319   0.5494
| H  9    0.9813   0.9813   0.0000   0.4319   0.5494
| C 10    6.0187   6.0187   0.0000   3.9598   2.0588
| H 11    0.9813   0.9813   0.0000   0.4319   0.5494
| H 12    0.9813   0.9813   0.0000   0.4319   0.5494
-------------------------------------------------------
| TOT:   41.9998  41.9998   0.0003  26.3504  15.6494
-------------------------------------------------------
```

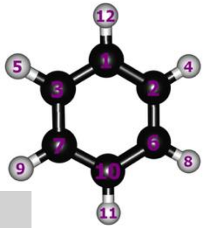


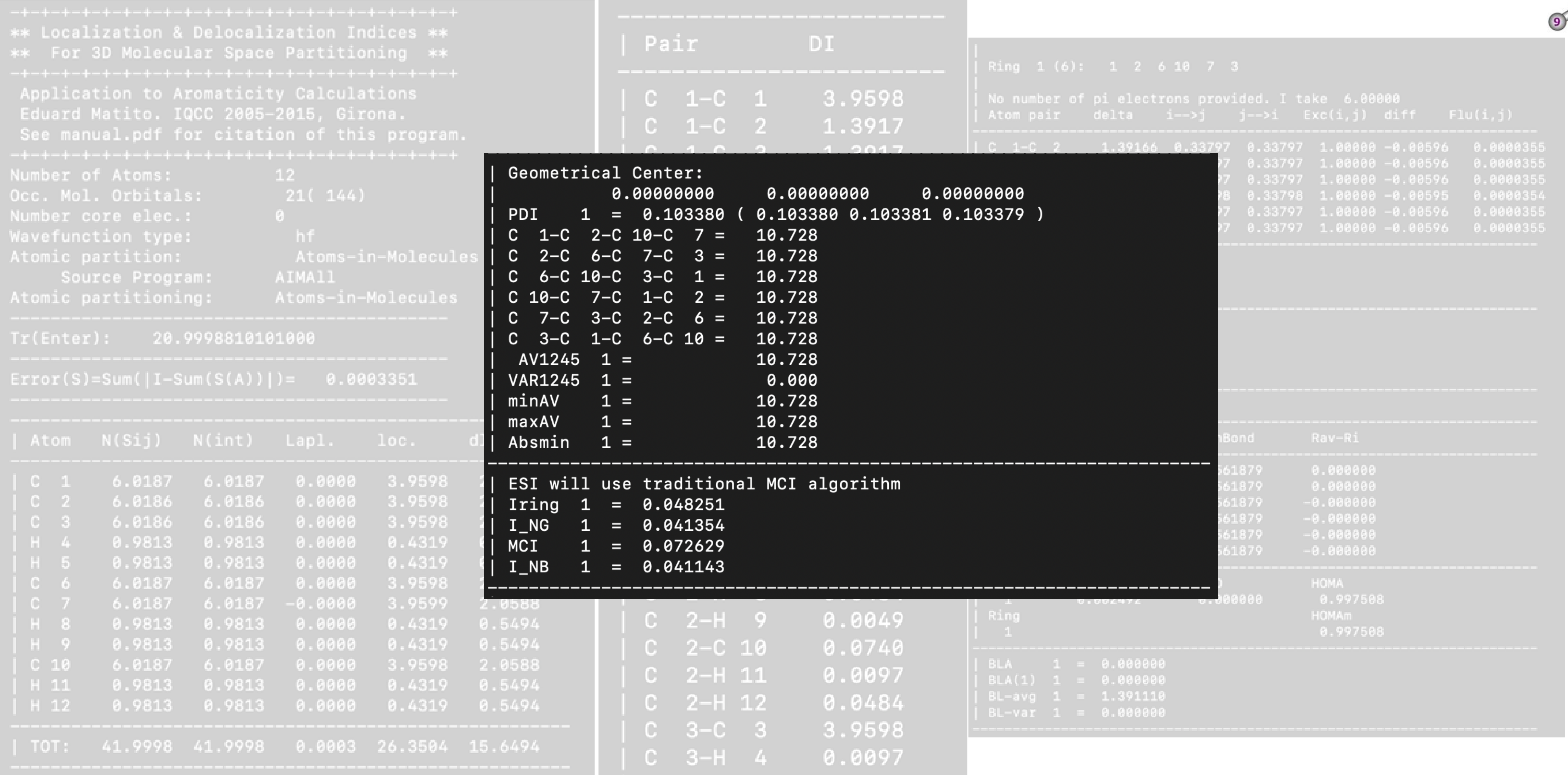
```
--------------------------
| Pair         DI
--------------------------
| C  1-C  1    3.9598
| C  1-C  2    1.3917
| C  1-C  3    1.3917
| C  1-H  4    0.0484
| C  1-H  5    0.0484
| C  1-C  6    0.0740
| C  1-C  7    0.0740
| C  1-H  8    0.0097
| C  1-H  9    0.0097
| C  1-C 10    0.1034
| C  1-H 11    0.0049
| C  1-H 12    0.9619
| C  2-C  2    3.9598
| C  2-C  3    0.0740
| C  2-H  4    0.9619
| C  2-H  5    0.0097
| C  2-C  6    1.3917
| C  2-C  7    0.1034
| C  2-H  8    0.0484
| C  2-H  9    0.0049
| C  2-C 10    0.0740
| C  2-H 11    0.0097
| C  2-H 12    0.0484
| C  3-C  3    3.9598
| C  3-H  4    0.0097
```



```
|
| Ring  1 (6):   1  2  6 10  7  3
|
| No number of pi electrons provided. I take  6.00000
| Atom pair    delta    i-->j    j-->i   Exc(i,j)  diff    Flu(i,j)
---------------------------------------------------------------------
| C  1-C  2     1.39166  0.33797  0.33797  1.00000 -0.00596   0.0000355
| C  2-C  6     1.39166  0.33797  0.33797  1.00000 -0.00596   0.0000355
| C  6-C 10     1.39165  0.33797  0.33797  1.00000 -0.00596   0.0000355
| C  7-C 10     1.39167  0.33798  0.33798  1.00000 -0.00595   0.0000354
| C  3-C  7     1.39166  0.33797  0.33797  1.00000 -0.00596   0.0000355
| C  1-C  3     1.39166  0.33797  0.33797  1.00000 -0.00596   0.0000355
---------------------------------------------------------------------
| FLU    1  =  0.000035
| FLUm   1  =  0.000036
| Ir(H)  1  =  0.625827
---------------------------------------------------------------------
| BOA     1  =  0.000004
| BOA(1)  1  =  0.000006
| BO-avg  1  =  1.391660
| BO-var  1  =  0.000000
---------------------------------------------------------------------
| TREPE  1  =  0.045432
---------------------------------------------------------------------
|     Pair          Dist       nBond       Rav-Ri
---------------------------------------------------------------------
| C  1-C  2   1.391110      1.561879      0.000000
| C  2-C  6   1.391110      1.561879      0.000000
| C  6-C 10   1.391110      1.561879     -0.000000
| C  7-C 10   1.391110      1.561879     -0.000000
| C  3-C  7   1.391110      1.561879     -0.000000
| C  1-C  3   1.391110      1.561879     -0.000000
---------------------------------------------------------------------
| Ring         EN          GEO          HOMA
|   1       0.002492     0.000000       0.997508
| Ring                                  HOMAm
|   1                                   0.997508
---------------------------------------------------------------------
| BLA     1  =  0.000000
| BLA(1)  1  =  0.000000
| BL-avg  1  =  1.391110
| BL-var  1  =  0.000000
---------------------------------------------------------------------
```

ESI-3D





```
-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+
** Localization & Delocalization Indices **
**  For 3D Molecular Space Partitioning  **
-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+
 Application to Aromaticity Calculations
 Eduard Matito. IQCC 2005-2015, Girona.
 See manual.pdf for citation of this program.
-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+
Number of Atoms:            12
Occ. Mol. Orbitals:          21( 144)
Number core elec.:          0
Wavefunction type:            hf
Atomic partition:             Atoms-in-Molecules
     Source Program:        AIMAll
Atomic partitioning:        Atoms-in-Molecules
-------------------------------------------
Tr(Enter):    20.9998810101000
-------------------------------------------
Error(S)=Sum(|I-Sum(S(A))|)=   0.0003351
-------------------------------------------

----------------------------------------------
| Atom   N(Sij)   N(int)   Lapl.    loc.     dI
----------------------------------------------
| C  1    6.0187   6.0187   0.0000   3.9598
| C  2    6.0186   6.0186   0.0000   3.9598
| C  3    6.0186   6.0186   0.0000   3.9598
| H  4    0.9813   0.9813   0.0000   0.4319
| H  5    0.9813   0.9813   0.0000   0.4319
| C  6    6.0187   6.0187   0.0000   3.9598
| C  7    6.0187   6.0187  -0.0000   3.9599   2.0588
| H  8    0.9813   0.9813   0.0000   0.4319   0.5494
| H  9    0.9813   0.9813   0.0000   0.4319   0.5494
| C 10    6.0187   6.0187   0.0000   3.9598   2.0588
| H 11    0.9813   0.9813   0.0000   0.4319   0.5494
| H 12    0.9813   0.9813   0.0000   0.4319   0.5494
-------------------------------------------------------
| TOT:   41.9998  41.9998   0.0003  26.3504  15.6494
-------------------------------------------------------
```

```
-------------------------
| Pair         DI
-------------------------
| C  1-C  1     3.9598
| C  1-C  2     1.3917

| C  2-H  9     0.0049
| C  2-C 10     0.0740
| C  2-H 11     0.0097
| C  2-H 12     0.0484
| C  3-C  3     3.9598
| C  3-H  4     0.0097
```

```
|
| Ring  1 (6):   1  2  6 10  7  3
|
| No number of pi electrons provided. I take  6.00000
| Atom pair    delta    i-->j    j-->i   Exc(i,j)  diff    Flu(i,j)
--------------------------------------------------------------------
| C  1-C  2     1.39166  0.33797  0.33797  1.00000 -0.00596   0.0000355
                            97  0.33797  1.00000 -0.00596   0.0000355
                            97  0.33797  1.00000 -0.00596   0.0000355
                            98  0.33798  1.00000 -0.00595   0.0000354
                            97  0.33797  1.00000 -0.00596   0.0000355
                            97  0.33797  1.00000 -0.00596   0.0000355
--------------------------------------------------------------------

                     nBond        Rav-Ri
                     561879        0.000000
                     561879        0.000000
                     561879       -0.000000
                     561879       -0.000000
                     561879       -0.000000
                     561879       -0.000000
--------------------------------------------------------------------
                                   HOMA
                                    0.997508
| Ring                             HOMAm
|   1                               0.997508
--------------------------------------------------------------------
| BLA      1  =  0.000000
| BLA(1)   1  =  0.000000
| BL-avg   1  =  1.391110
| BL-var   1  =  0.000000
--------------------------------------------------------------------
```

```
| Geometrical Center:
|           0.00000000     0.00000000     0.00000000
| PDI    1  =  0.103380 ( 0.103380 0.103381 0.103379 )
| C  1-C  2-C 10-C  7 =   10.728
| C  2-C  6-C  7-C  3 =   10.728
| C  6-C 10-C  3-C  1 =   10.728
| C 10-C  7-C  1-C  2 =   10.728
| C  7-C  3-C  2-C  6 =   10.728
| C  3-C  1-C  6-C 10 =   10.728
|  AV1245  1 =            10.728
| VAR1245  1 =             0.000
| minAV    1 =            10.728
| maxAV    1 =            10.728
| Absmin   1 =            10.728
-----------------------------------------------------------------------------
| ESI will use traditional MCI algorithm
| Iring  1  =  0.048251
| I_NG   1  =  0.041354
| MCI    1  =  0.072629
| I_NB   1  =  0.041143
-----------------------------------------------------------------------------
```

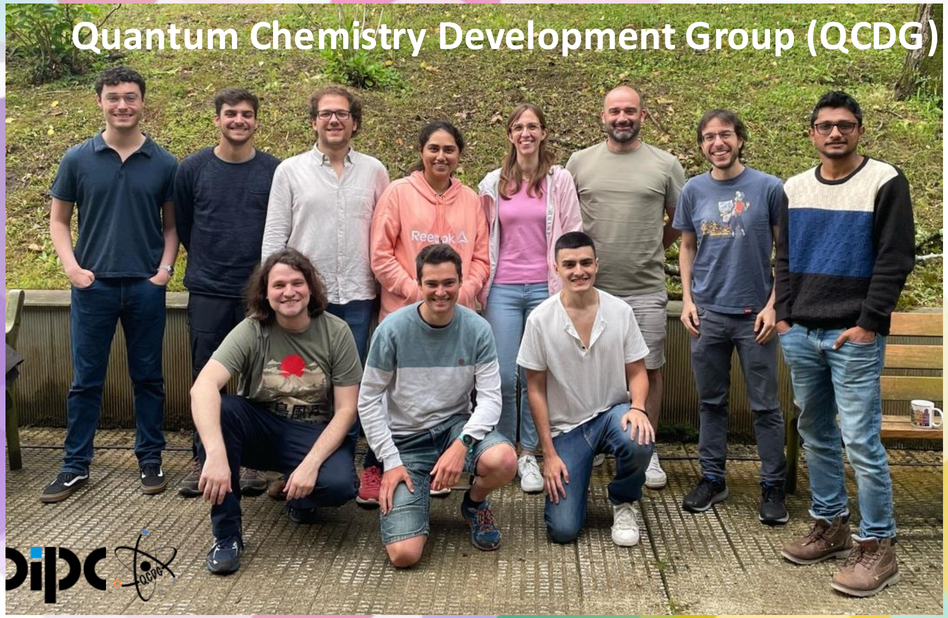
Summary

- MCI is the most reliable measure of aromaticity
- AV1245/AV$_{min}$ are a reliable, cost-efficient method to analyze the aromaticity of macrocycles
- AV$_{min}$ is the only index that can identify the most aromatic pathway in porphyrinoids
- A good (DFT) description of conjugation effects calls for long-range exact exchange

Aromaticity Review:	*Chem Soc Rev.* **2015**, *44*, 6434	**AV$_{min}$ aromaticity index:**	*JPCC* **2017**, *121*, 27118
AV1245 aromaticity index:	*PCCP* **2016**, *18*, 11839	**Tests on porphyrins:**	*PCCP* **2018**, *20*, 2787
ESI-3D:	available upon request (ematito@gmail.com)	**ESIpy:**	*CEJ* **2024**, *30*, e202401282

Acknowledgments


Algemene Chemie Group (ALGC)


Quantum Chemistry Development Group (QCDG)

MANCHESTER
1824
The University of Manchester

ICESAA-4
IISER TVM

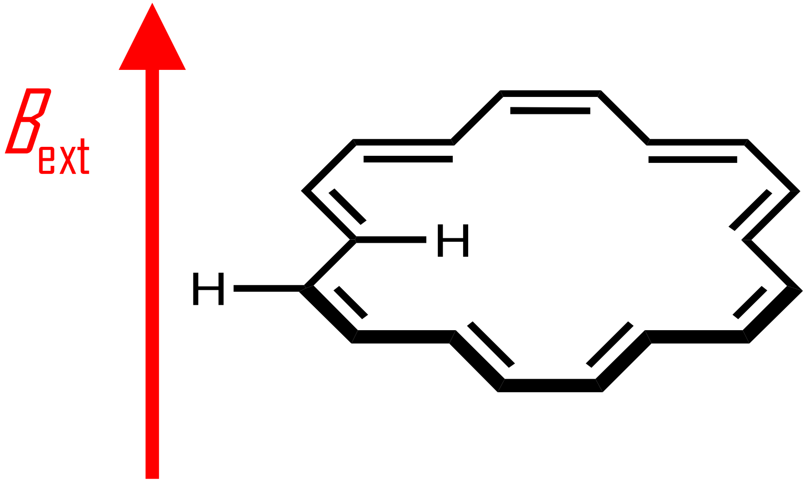
Magnetic aromaticity

Igor Roncevic

8 Jan 2026

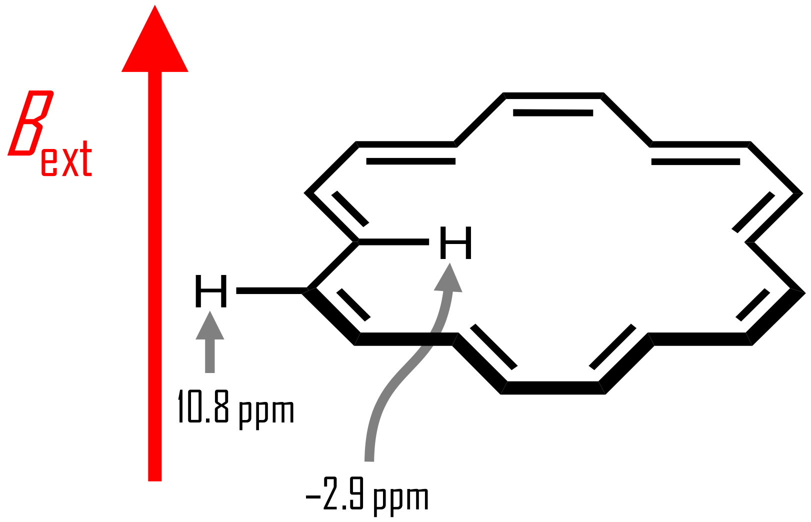
What is magnetic aromaticity?

Magnetically aromatic systems have ring currents.



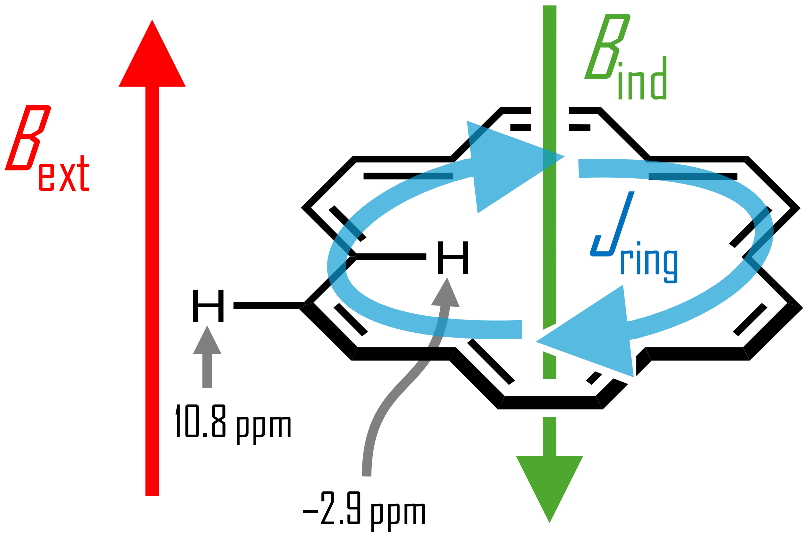
What is magnetic aromaticity?

Magnetically aromatic systems have ring currents.



What is magnetic aromaticity?

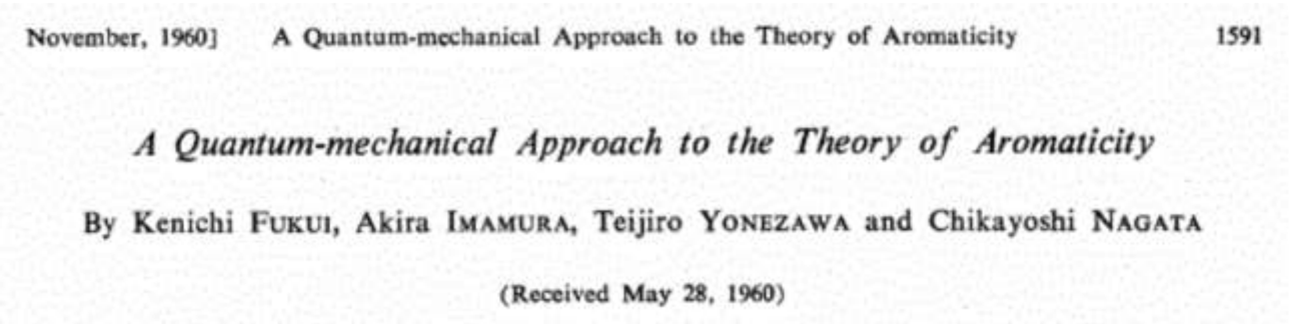
Magnetically aromatic systems have ring currents.



$J_{ring} > 0$ (diatropic, clockwise): aromatic
$J_{ring} < 0$ (paratropic, counter-clockwise): anti-aromatic

Why magnetic aromaticity?

Because aromaticity is quantum-mechanical.



November, 1960] A Quantum-mechanical Approach to the Theory of Aromaticity 1591

A Quantum-mechanical Approach to the Theory of Aromaticity

By Kenichi FUKUI, Akira IMAMURA, Teijiro YONEZAWA and Chikayoshi NAGATA

(Received May 28, 1960)

Molecular aromaticity: a quantum phenomenon

Miquel Solà and Dariusz W. Szczepanik

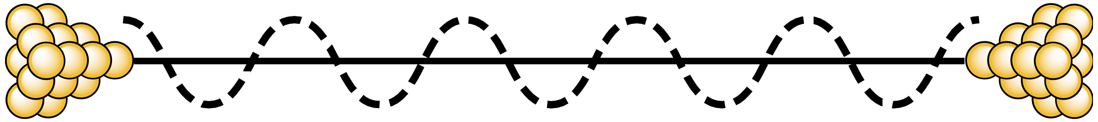
Published/Copyright: April 15, 2025

Why magnetic aromaticity?

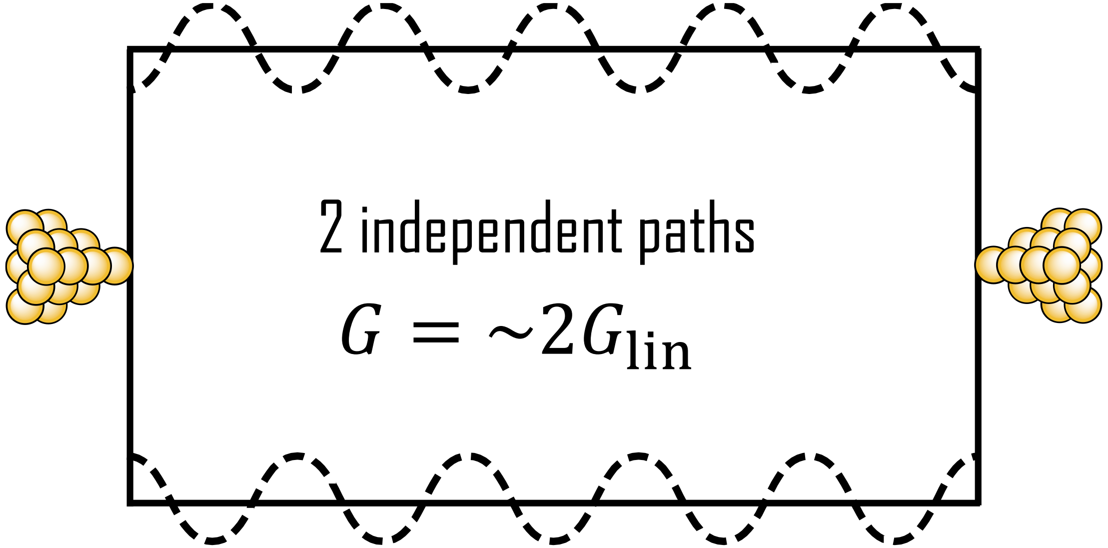
Because aromaticity is quantum-mechanical.

- Practical
  - Observable by NMR!
- Theoretical

Conductance

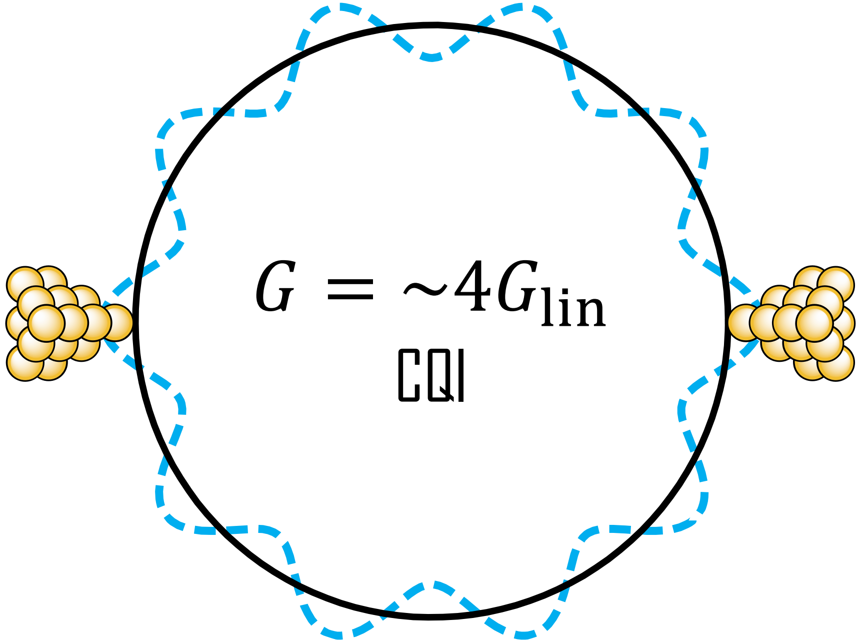


1 path $G = G_{\text{lin}}$



2 independent paths

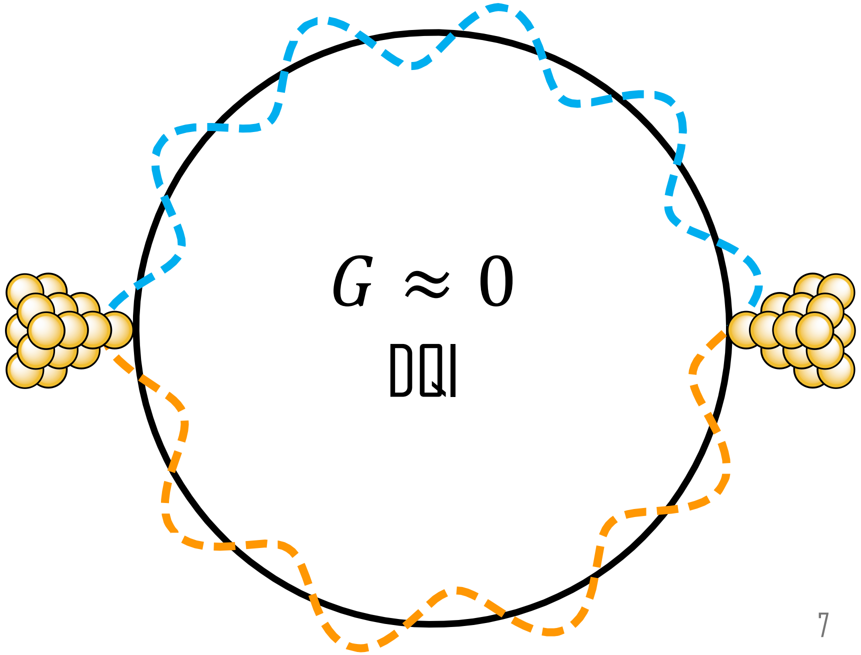
$G = \sim 2G_{\text{lin}}$



$G = \sim 4G_{\text{lin}}$

CQI

coherent ring



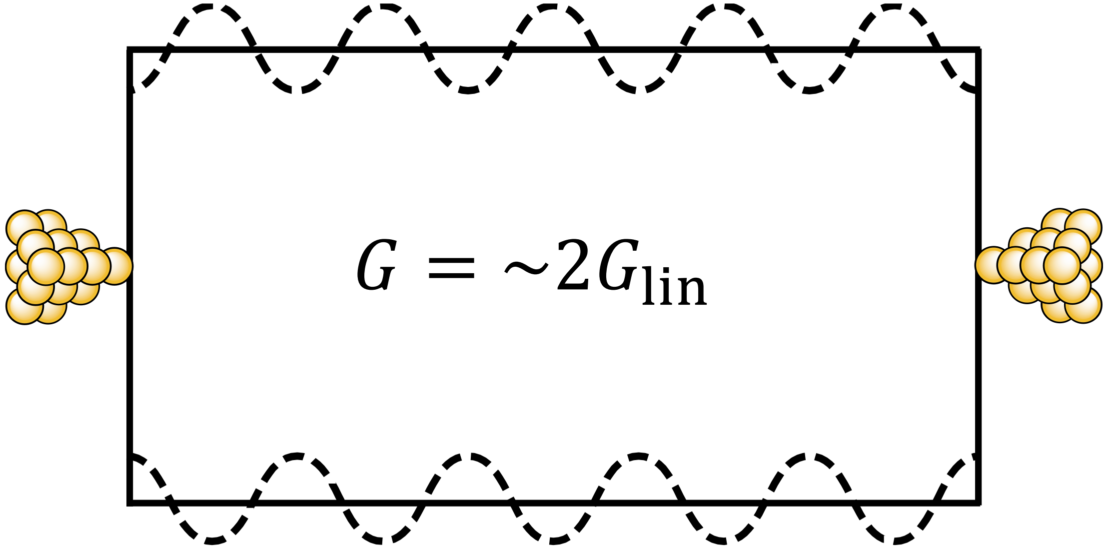
$G \approx 0$

DQI

Chem. Soc. Rev. **2015**, *44*, 875.
Chem. Sci. **2025**, *16*, 4392.

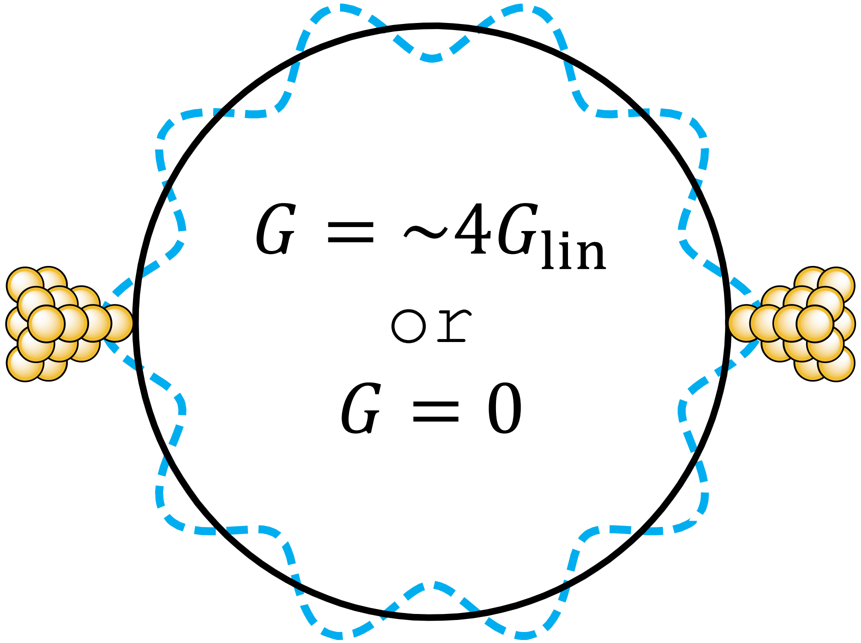
Conductance on a ring

Classical



$$G = \sim 2G_{\text{lin}}$$

Quantum



$$G = \sim 4G_{\text{lin}}$$

or

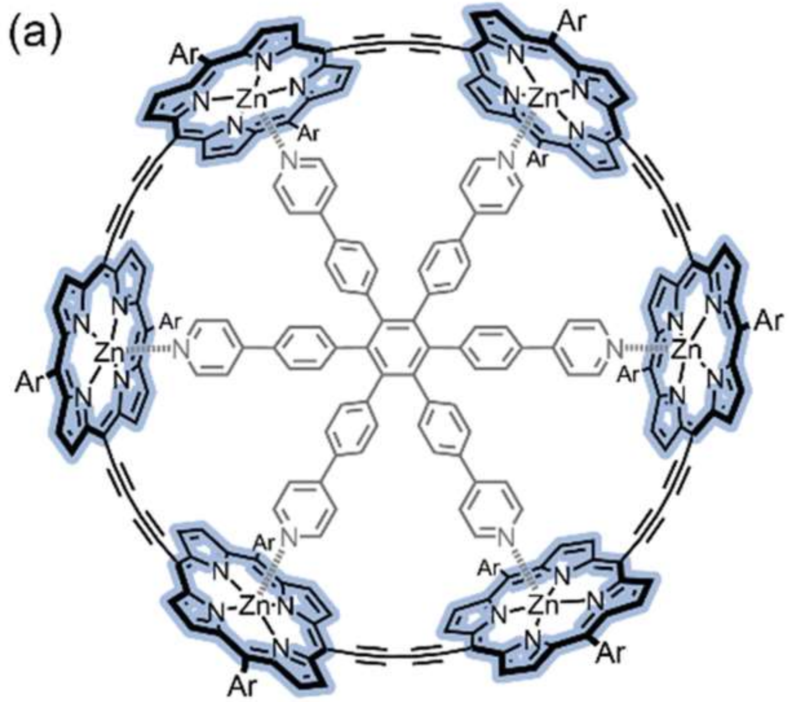
$$G = 0$$

Valid for a
quantum ring!

Chem. Soc. Rev. **2015**, *44*, 875.
Chem. Sci. **2025**, *16*, 4392.

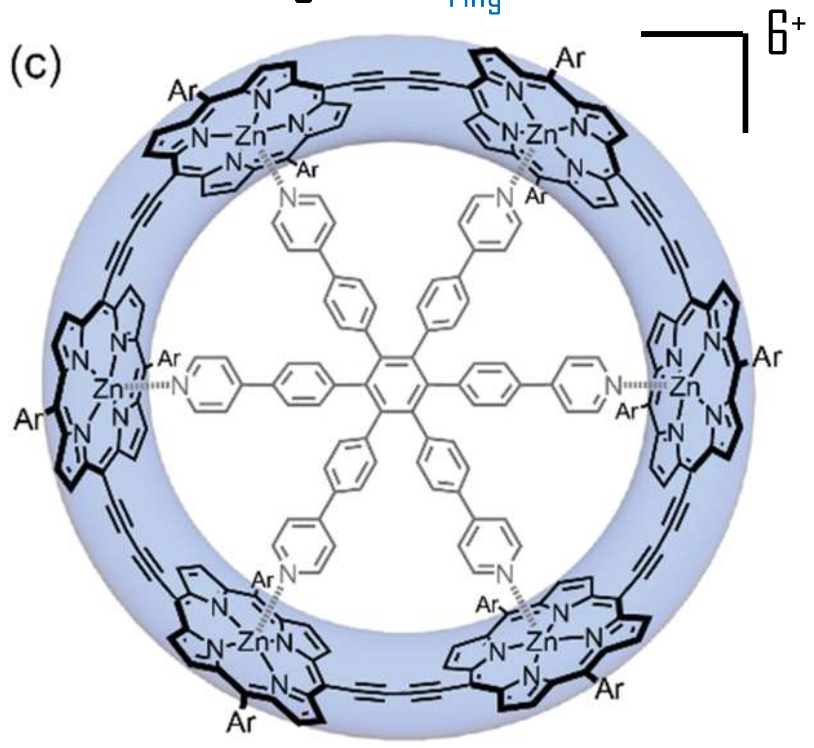
Classical and quantum objects

local J_{ring}



Classical

global J_{ring}



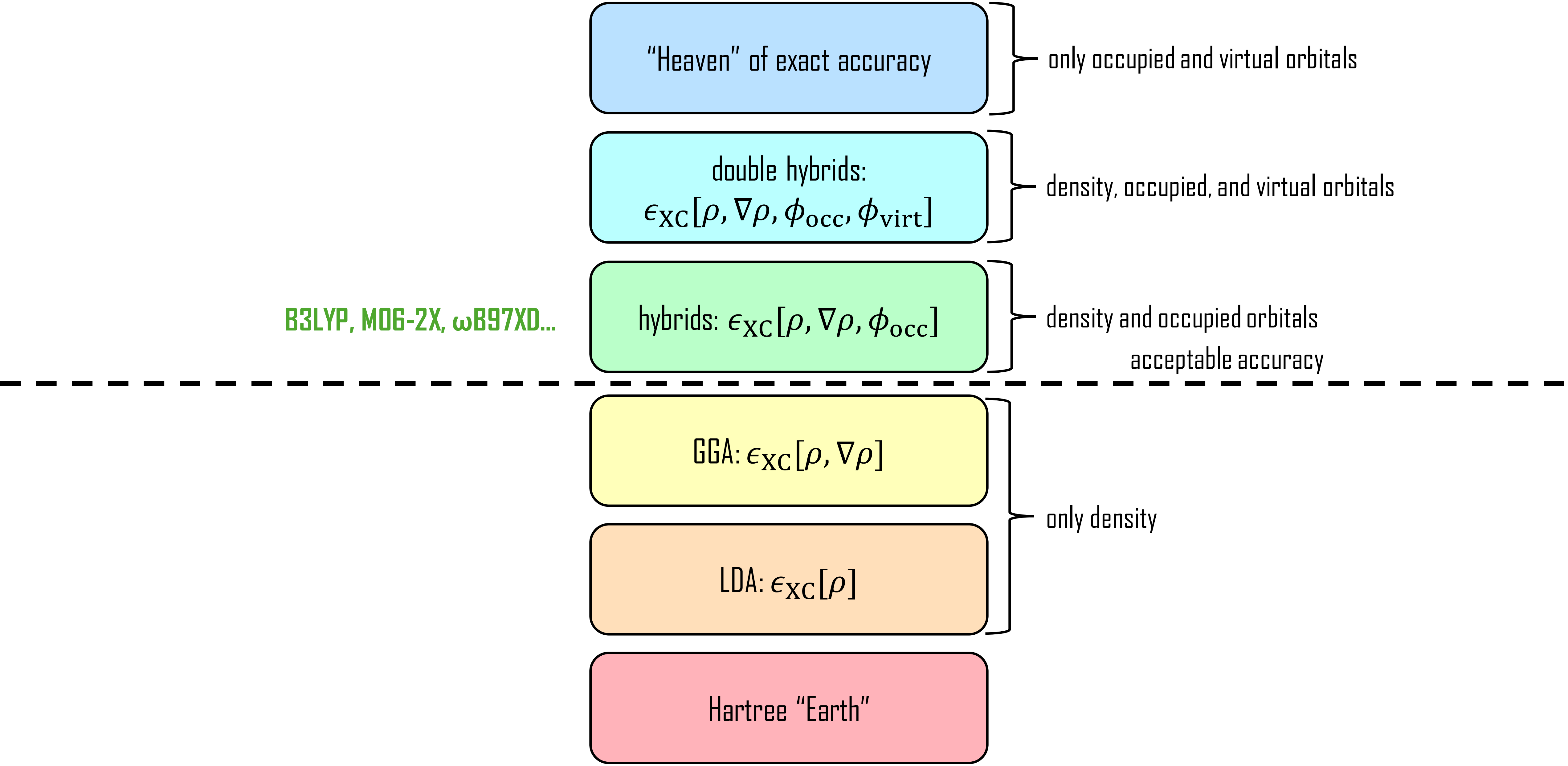
Quantum

Nature **2017**, *541*, 200.
Acc. Chem. Res. **2021**, *54*, 3241.
Chem Sci. **2023**, *14*, 1762.

Why magnetic aromaticity?

Because aromaticity is quantum-mechanical.

- Practical
    - Observable by NMR!
    - Identifies wavefunction coherence.
    - Affects optical properties, single-molecule conductance, spin-spin coupling...
- Theoretical



"Heaven" of exact accuracy

only occupied and virtual orbitals

double hybrids:
$\epsilon_{\mathrm{XC}}[\rho, \nabla\rho, \phi_{\mathrm{occ}}, \phi_{\mathrm{virt}}]$

density, occupied, and virtual orbitals

B3LYP, M06-2X, ωB97XD…

hybrids: $\epsilon_{\mathrm{XC}}[\rho, \nabla\rho, \phi_{\mathrm{occ}}]$

density and occupied orbitals

acceptable accuracy

GGA: $\epsilon_{\mathrm{XC}}[\rho, \nabla\rho]$

LDA: $\epsilon_{\mathrm{XC}}[\rho]$

only density

Hartree "Earth"

Why magnetic aromaticity?

Because aromaticity is quantum-mechanical.

- Practical
  - Observable by NMR!
  - Identifies wavefunction coherence.
  - Affects optical properties, single-molecule conductance, spin-spin coupling…
- Theoretical
  - Density is not enough to capture electronic structure.
  - Magnetic aromaticity is determined by orbitals, not density.

Response to a magnetic field

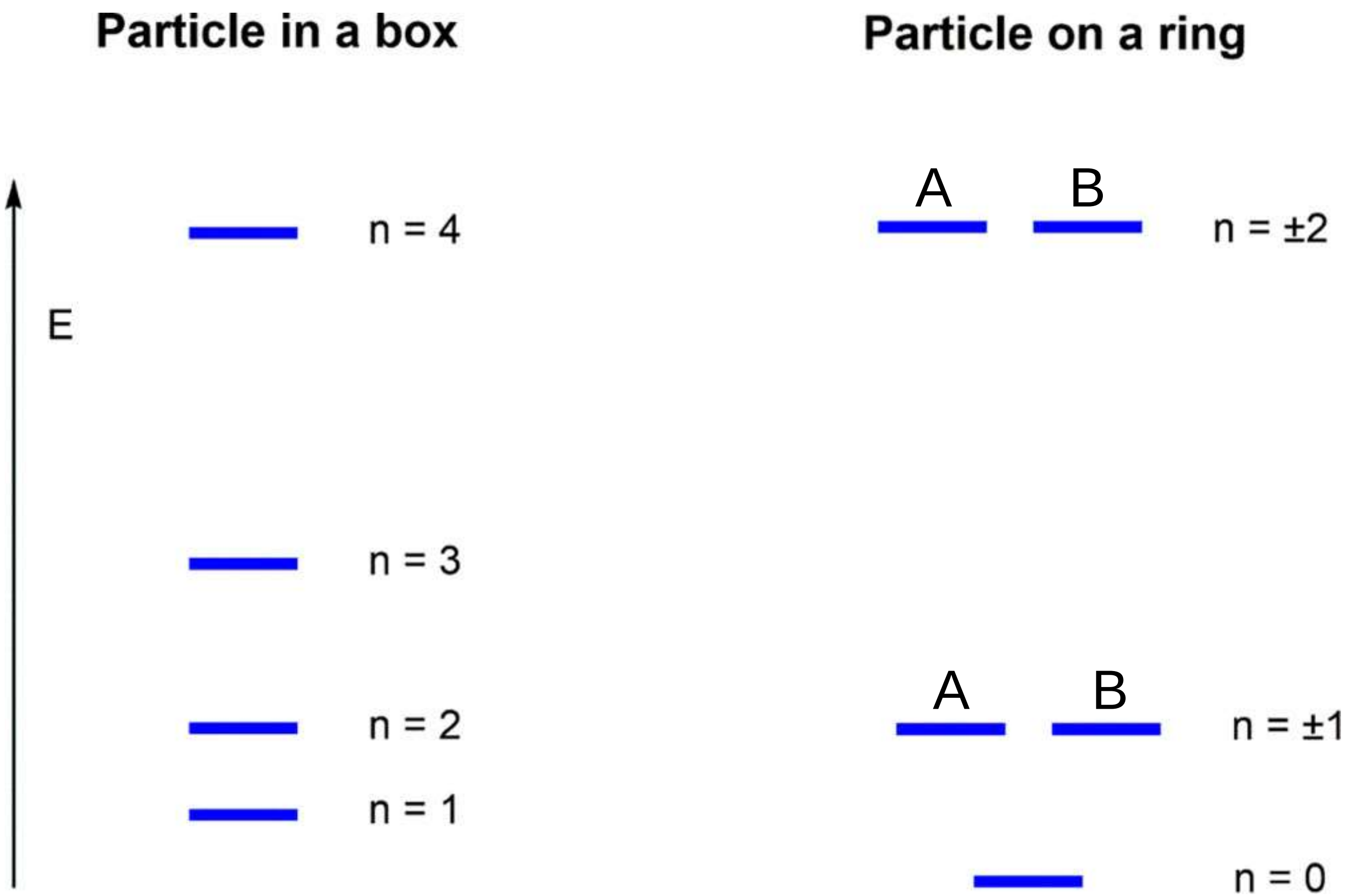
$$\psi_n^{(1)}(\boldsymbol{r}) = -\frac{e}{2m_{\mathrm{e}}}\left[\sum_{p>N/2}\psi_p(\boldsymbol{r})\frac{\left\langle\psi_p\middle|\hat{\boldsymbol{l}}(\mathbf{0})\middle|\psi_n\right\rangle}{\varepsilon_p-\varepsilon_n}\right]\cdot\boldsymbol{B}+\frac{e}{2m_{\mathrm{e}}}\left[\boldsymbol{d}\times\sum_{p>N/2}\psi_p(\boldsymbol{r})\frac{\left\langle\psi_p\middle|\hat{\boldsymbol{p}}\middle|\psi_n\right\rangle}{\varepsilon_p-\varepsilon_n}\right]\cdot\boldsymbol{B}$$

twisting
(paratropic)

linear momentum
(diatropic)

E. Steiner, P. W. Fowler,
Chem. Commun. **2001**, 2220.
J. Phys. Chem. A **2001**, *105*, 9553.
Phys. Chem. Chem. Phys. **2004**, *6*, 261.

Particle on a ring



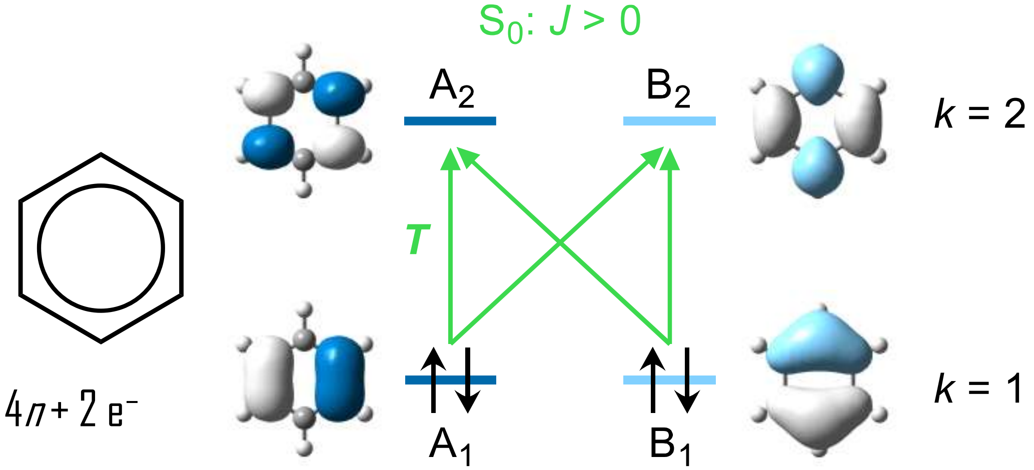
M. Sola, F. M. Bickelhaupt *J. Chem. Educ.* **2022**, *99*, 3497.

Magnetic aromaticity

Diatropic ring current:

- Orbitals coupled by translation

$$\boxed{J_{st}^{\mathrm{DIA}} \propto \frac{M_{st}^{\mathrm{T}}}{\Delta\varepsilon_{st}} = \frac{\langle \psi_t | \hat{p} | \psi_s \rangle}{\Delta\varepsilon_{st}}}$$



$\Delta k = 1$

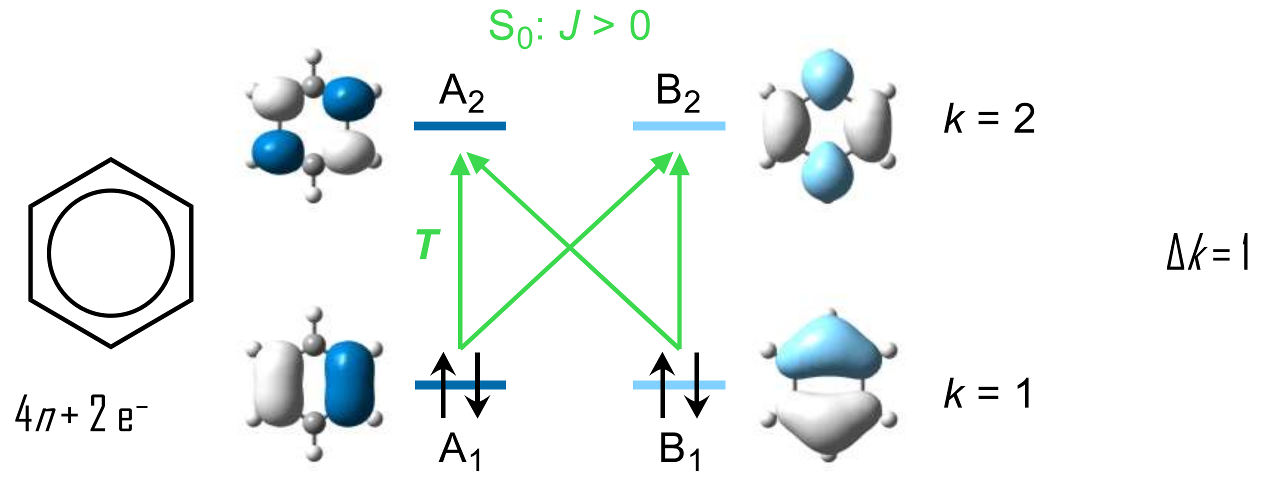
I. Roncevic* et al. *JACS* **2023**, *145*, 26962.

Magnetic aromaticity

Diatropic ring current:

- Orbitals coupled by translation

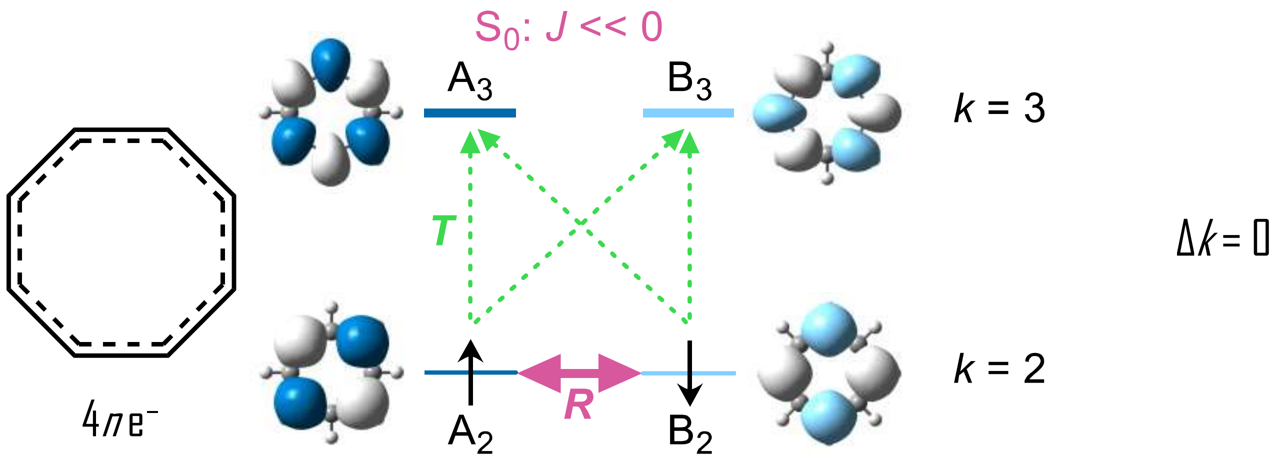
$$J_{st}^{\mathrm{DIA}} \propto \frac{M_{st}^{\mathrm{T}}}{\Delta\varepsilon_{st}} = \frac{\langle \psi_t | \hat{p} | \psi_s \rangle}{\Delta\varepsilon_{st}}$$



Paratropic ring current:

- Orbitals coupled by rotation

$$J_{st}^{\mathrm{PARA}} \propto \frac{M_{st}^{\mathrm{R}}}{\Delta\varepsilon_{st}} = \frac{\langle \psi_t | \hat{l} | \psi_s \rangle}{\Delta\varepsilon_{st}}$$



I. Roncevic* et al. *JACS* **2023**, *145*, 26962.

N.C. Baird, *J. Am. Chem. Soc.* **1972**, *94*, 4941.

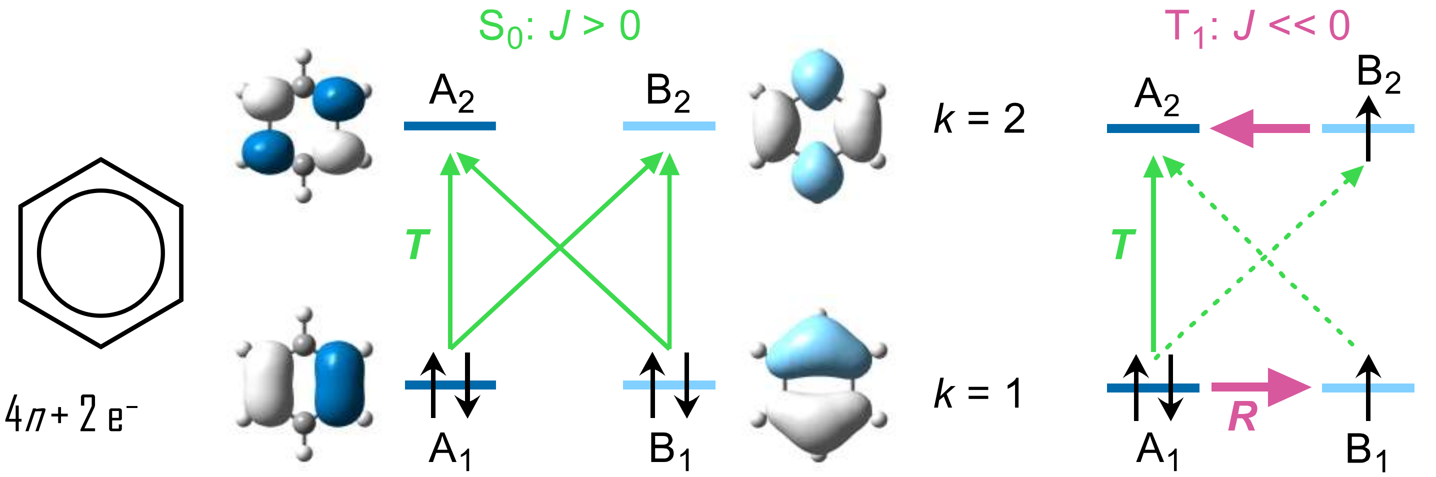
Magnetic aromaticity

Baird's rule!

Diatropic ring current:

- Orbitals coupled by translation

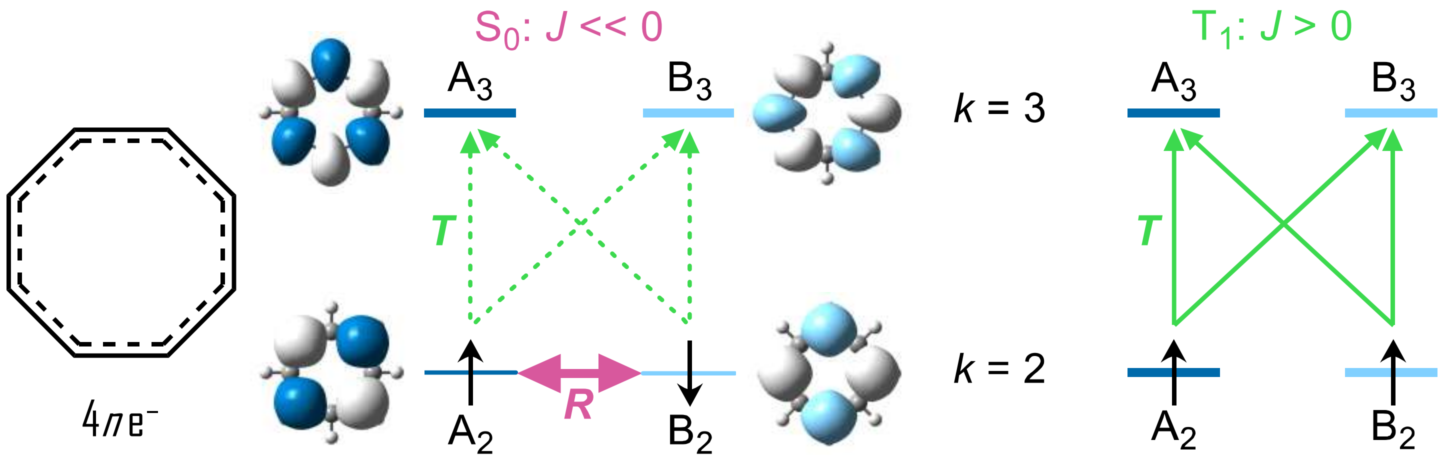
$$J_{st}^{\mathrm{DIA}} \propto \frac{M_{st}^{\mathrm{T}}}{\Delta\varepsilon_{st}} = \frac{\left\langle \psi_t \middle| \hat{p} \middle| \psi_s \right\rangle}{\Delta\varepsilon_{st}}$$



Paratropic ring current:

- Orbitals coupled by rotation

$$J_{st}^{\mathrm{PARA}} \propto \frac{M_{st}^{\mathrm{R}}}{\Delta\varepsilon_{st}} = \frac{\left\langle \psi_t \middle| \hat{l} \middle| \psi_s \right\rangle}{\Delta\varepsilon_{st}}$$

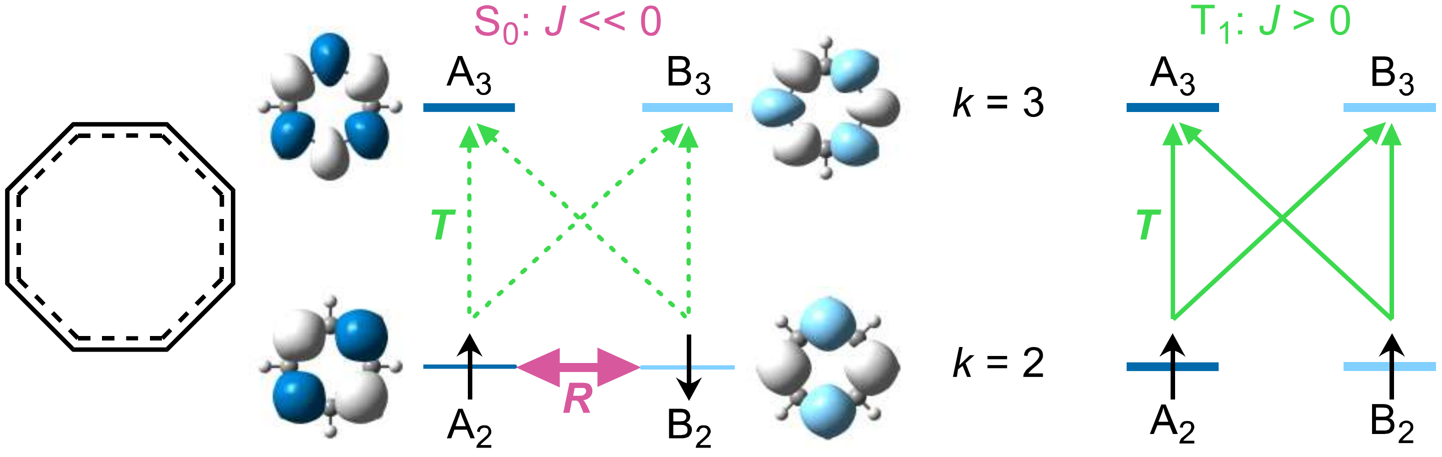


I. Roncevic* et al. *JACS* **2023**, *145*, 26962.

Anti-aromaticity relief (or Peierls distortion or JTE)

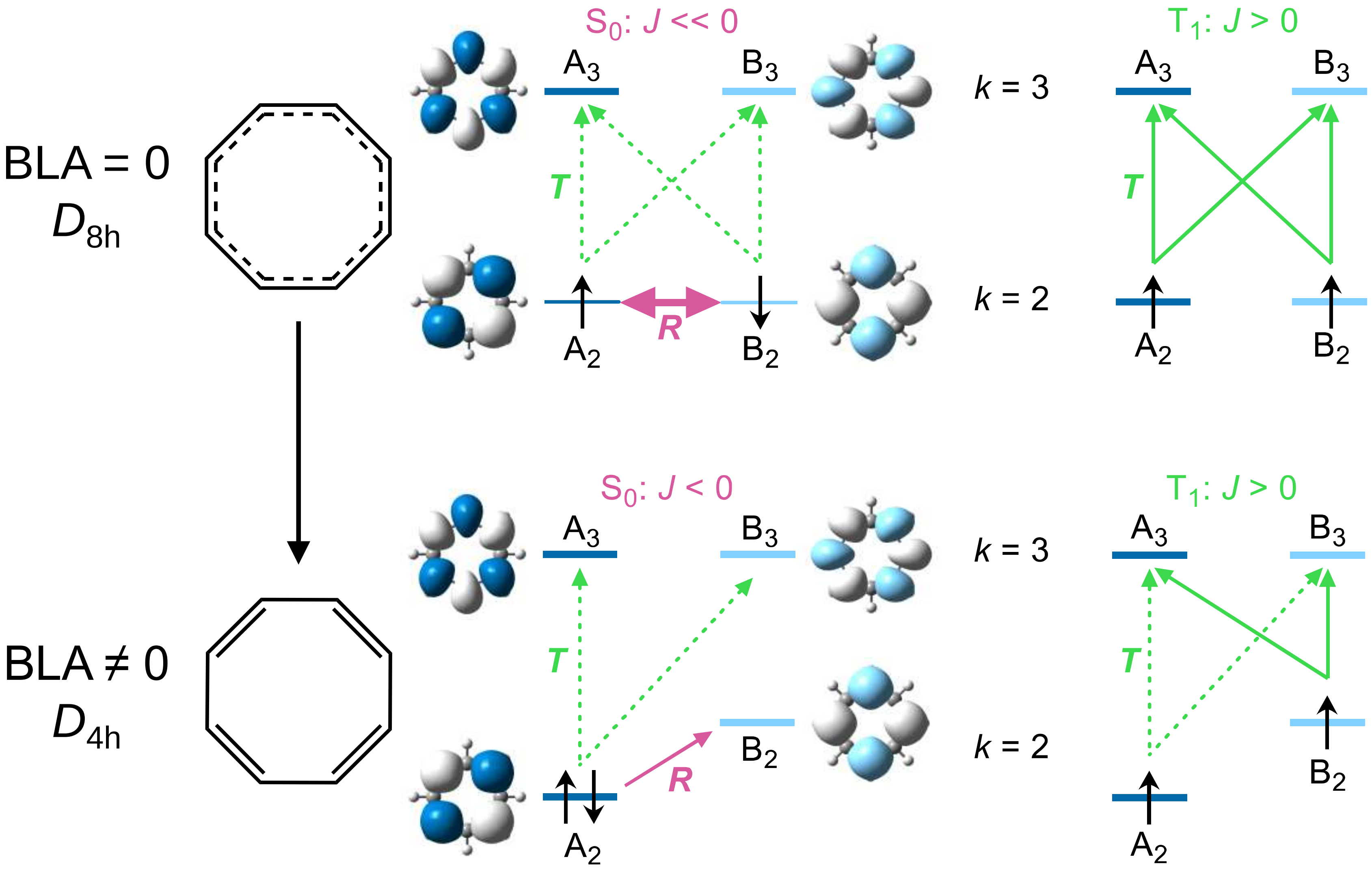
BLA = 0

D_{8h}



I. Roncevic* et al. *JACS* **2023**, *145*, 26962.

Anti-aromaticity relief (or Peierls distortion or JTE)



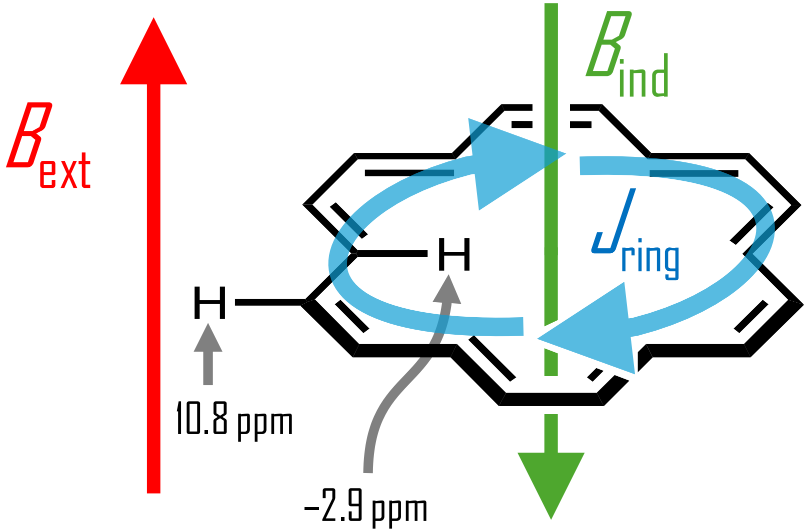
I. Roncevic* et al. *JACS* **2023**, *145*, 26962.

Why magnetic aromaticity?

- Practical
  - Observable by NMR!
  - Identifies wavefunction coherence.
  - Affects optical properties, single-molecule conductance, spin-spin coupling…
- Theoretical
  - Density is not enough to capture electronic structure.
  - Magnetic aromaticity is determined by orbitals, not density.
  - Explains the origin of Hückel (and Möbius), and Baird's rules.
  - Connects anti-aromaticity with electronic instabilities, which rationalises anti-aromaticity relief.

Determining magnetic aromaticity

- Ring current (J_{ring})
  - Accessible by theory
  - GIMIC and Sysmoic

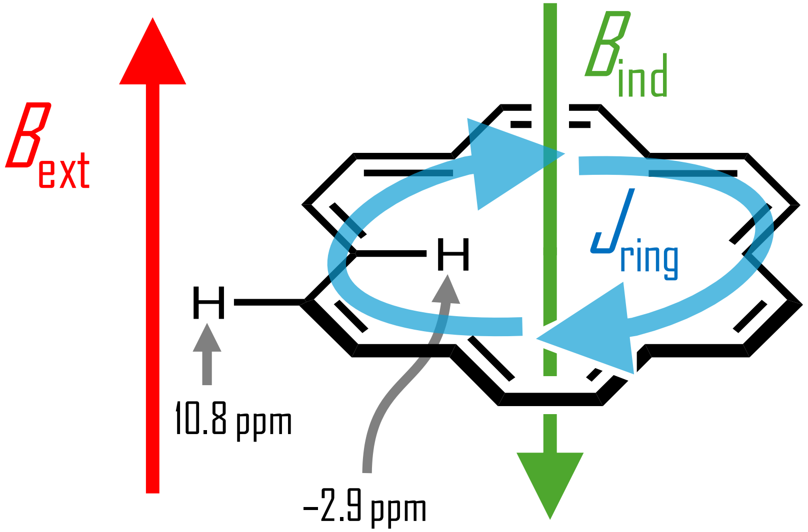


- Effect of J_{ring}
  - B_{ind} at atoms: chemical shielding σ (NMR and theory)
  - B_{ind} in space: NICS (theory)

GIMIC: D. Sundholm, H. Fliegl, R. J. Berger, *WIREs Comput. Mol. Sci.* **2016**, *6*, 639.
Sysmoic: G. Monaco, F. F. Summa, R. Zanasi, *J. Chem. Inf. Model.* **2021**, *61*, 270.
NICS: e.g. A. Stanger *Eur. J. Org. Chem.* **2020**, *2020*, 3120.

Determining magnetic aromaticity

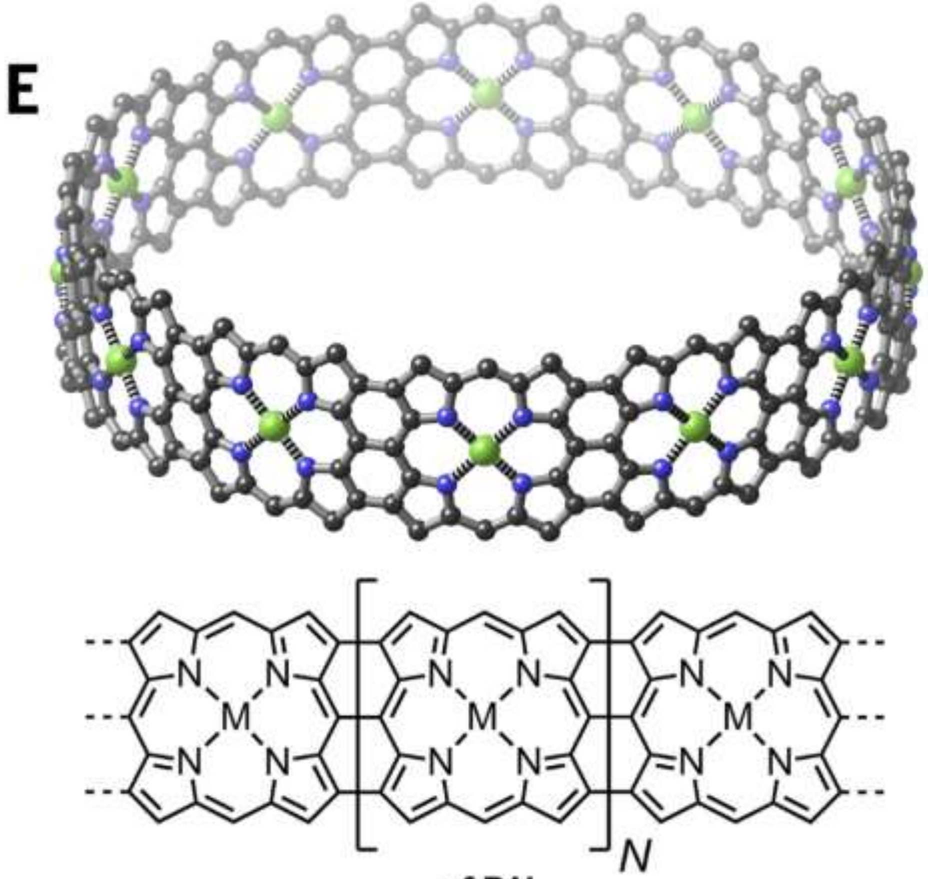
- Ring current (J_{ring})
  - Accessible by theory
  - GIMIC and Sysmoic



- **<u>Effect of J_{ring}</u>**
  - B_{ind} at atoms: chemical shielding σ (NMR and theory)
  - B_{ind} in space: NICS (theory)

GIMIC: D. Sundholm, H. Fliegl, R. J. Berger, *WIREs Comput. Mol. Sci.* **2016**, *6*, 639.
Sysmoic: G. Monaco, F. F. Summa, R. Zanasi, *J. Chem. Inf. Model.* **2021**, *61*, 270.
NICS: e.g. A. Stanger *Eur. J. Org. Chem.* **2020**, *2020*, 3120.

Evaluating chemical shielding



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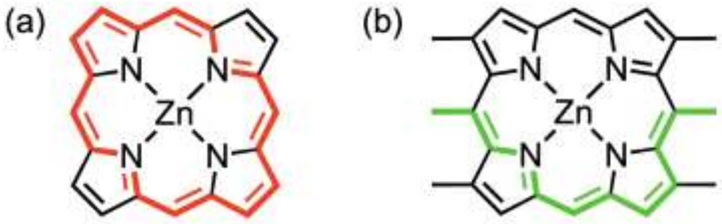


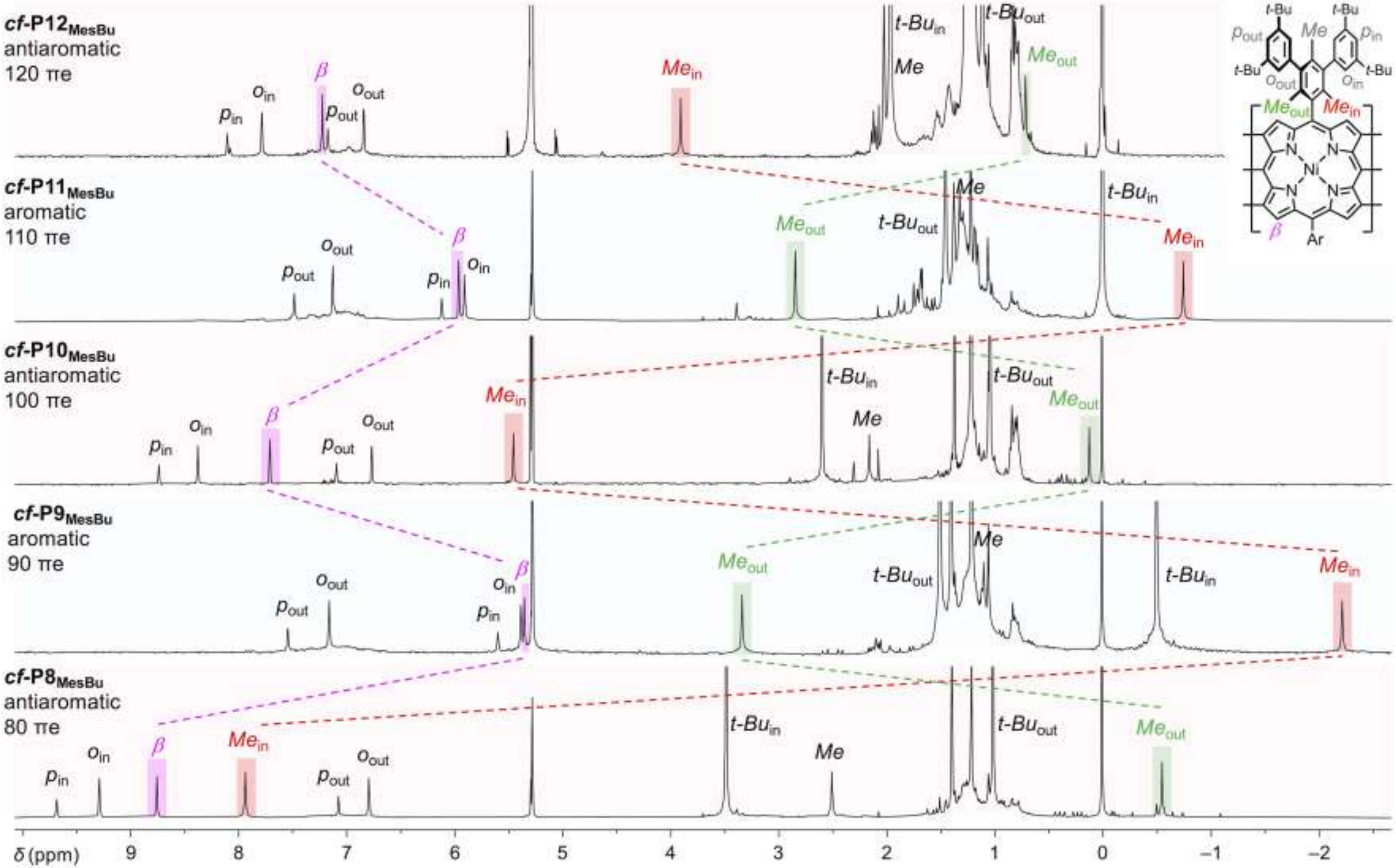
π-circuit in zinc porphyrin

meso-meso 10 electrons dominant pathway

Expectation:
N = 7, 9, 11, 13: aromatic
N = 8, 10, 12, 14: anti-aromatic

Theory: Roncevic and co-workers *ACS Nano* **2025**, *19*, 1405.
Experiment: Anderson and co-workers *Science* **2025**, *390*, 290.

Evaluating chemical shielding



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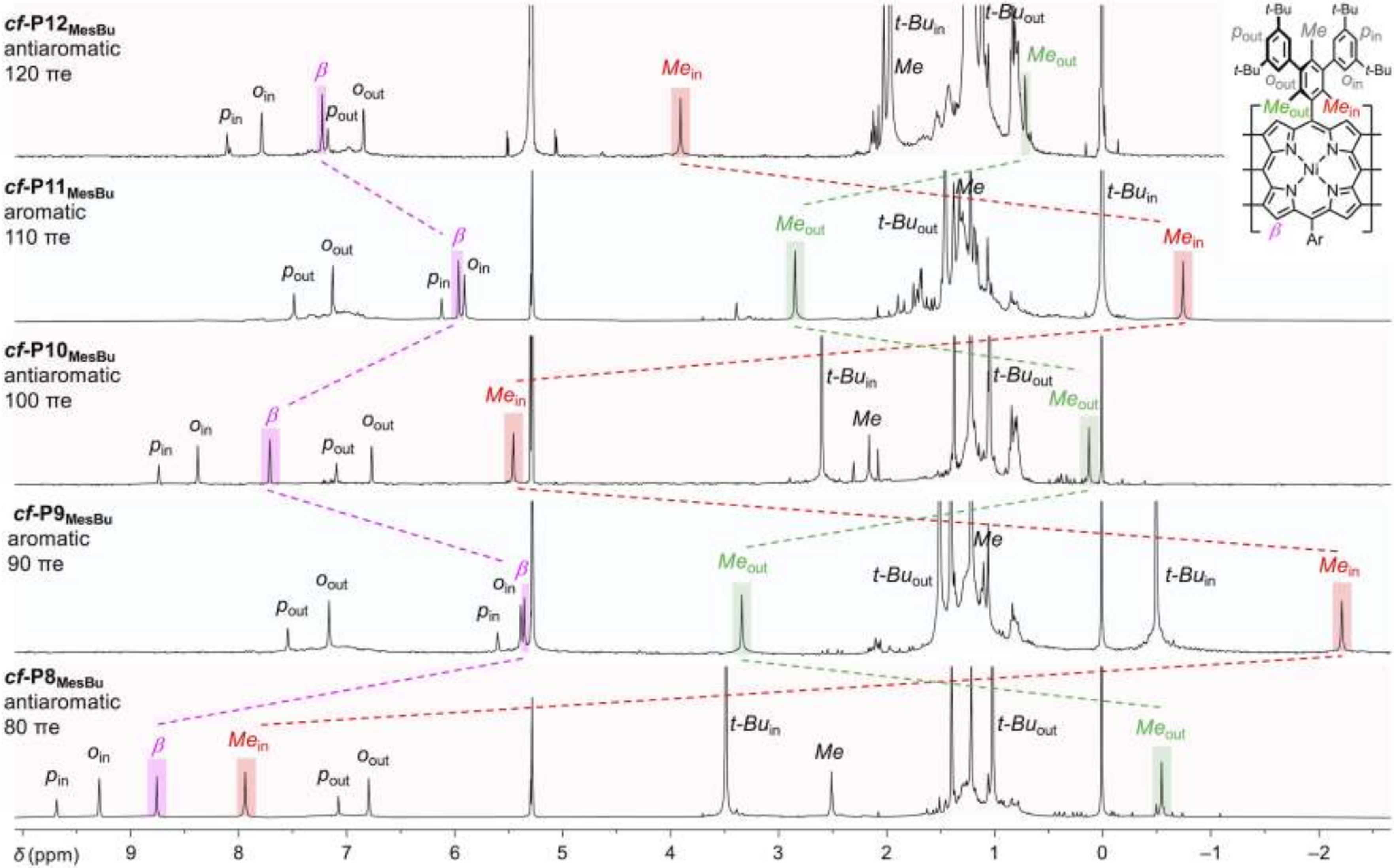
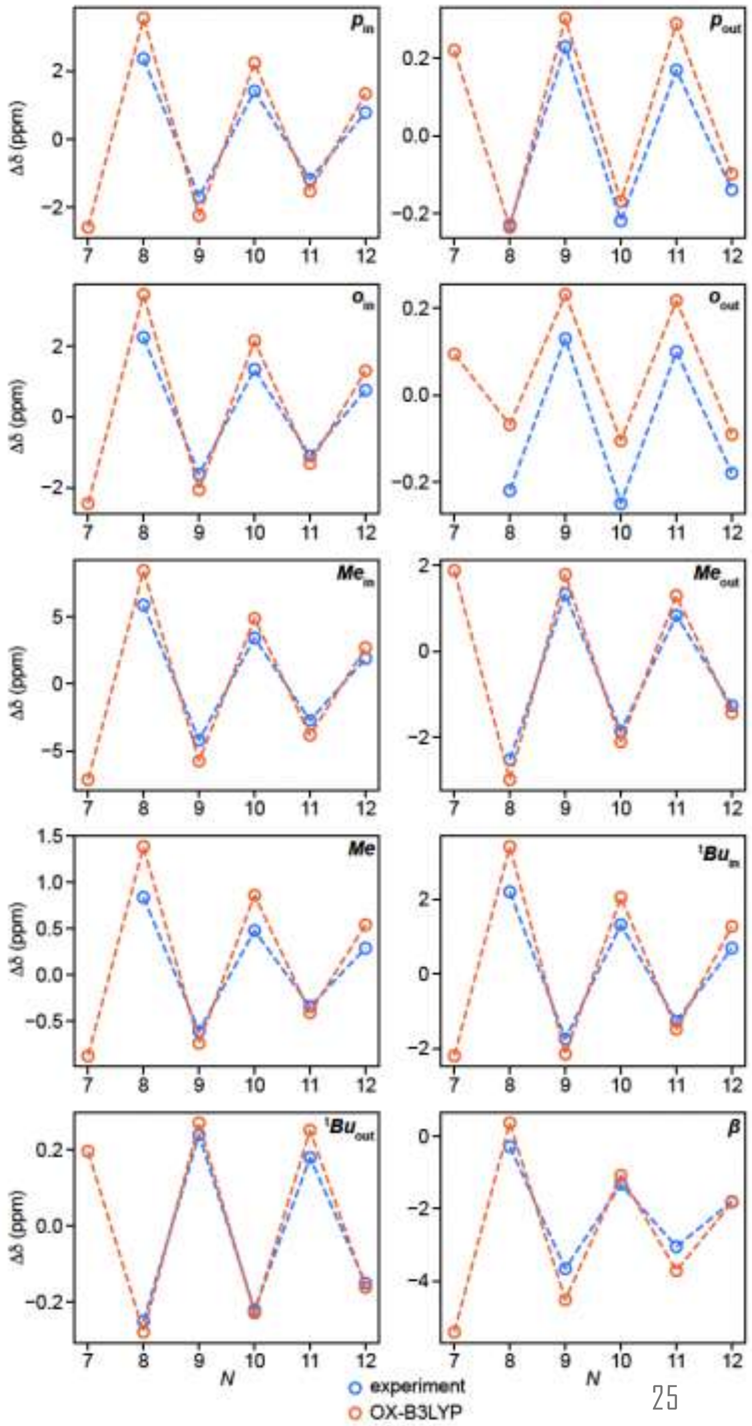
Evaluating chemical shielding





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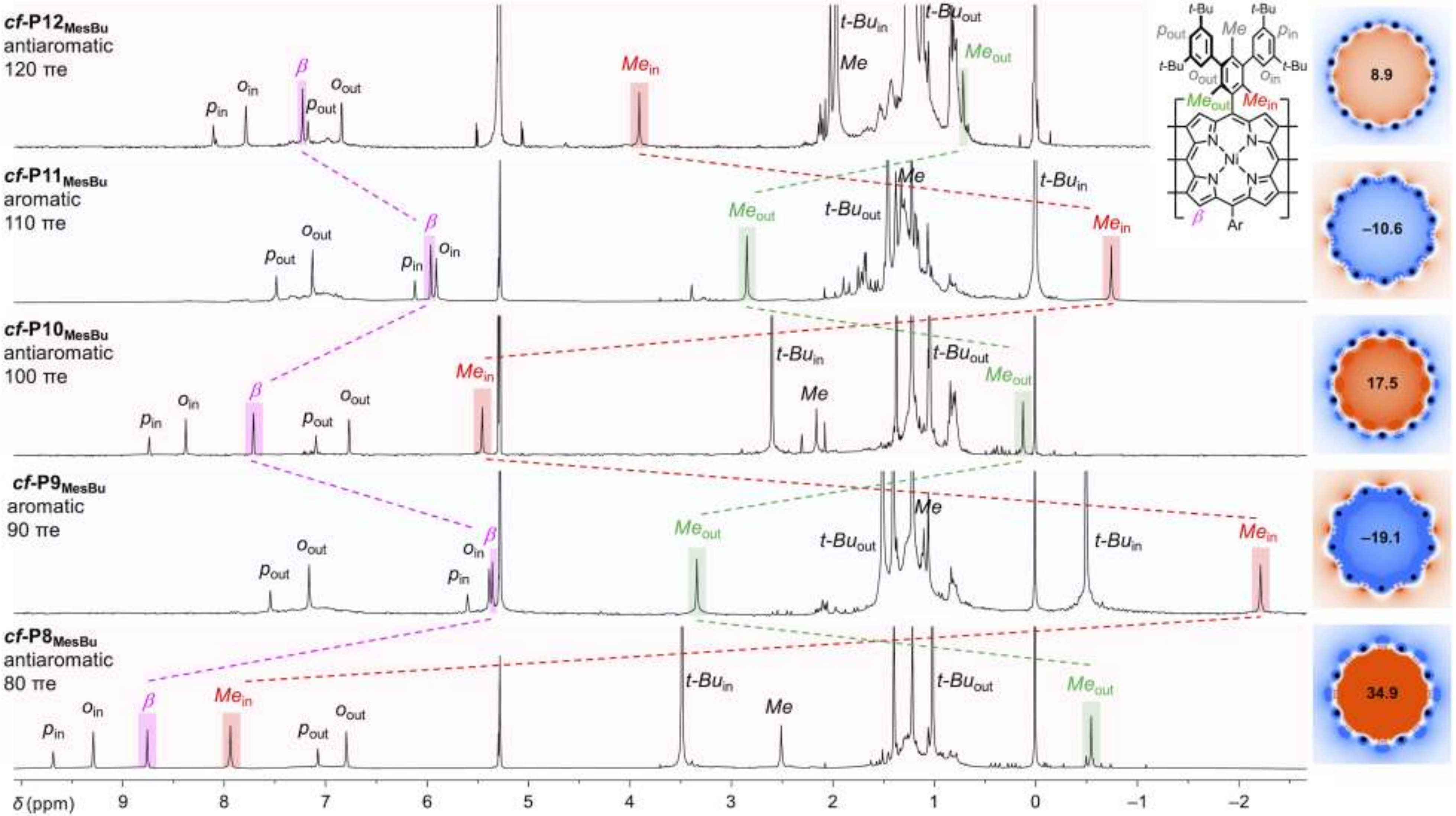
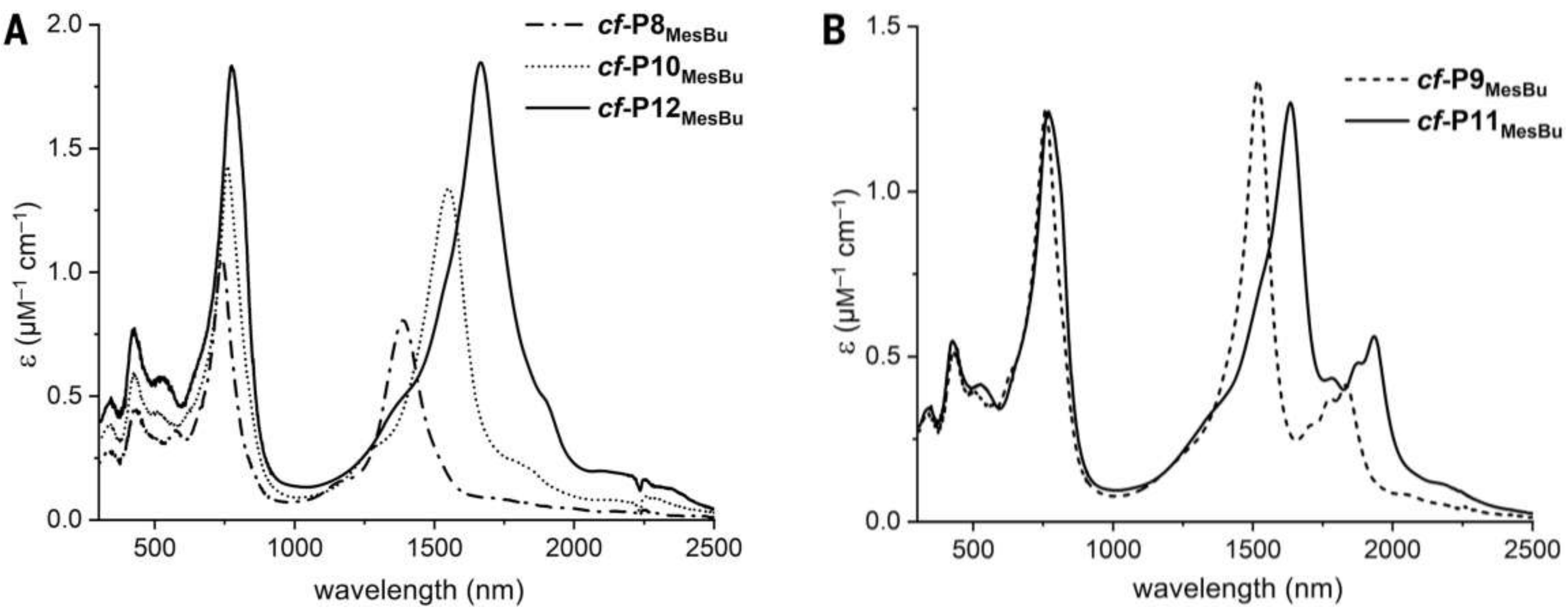
Evaluating chemical shielding



2D NICS plot
Blue: shielded
Red: deshielded
Number: NICS(0)$_{zz}$

Theory: Roncevic and co-workers *ACS Nano* **2025**, *19*, 1405.
Experiment: Anderson and co-workers *Science* **2025**, *390*, 290.

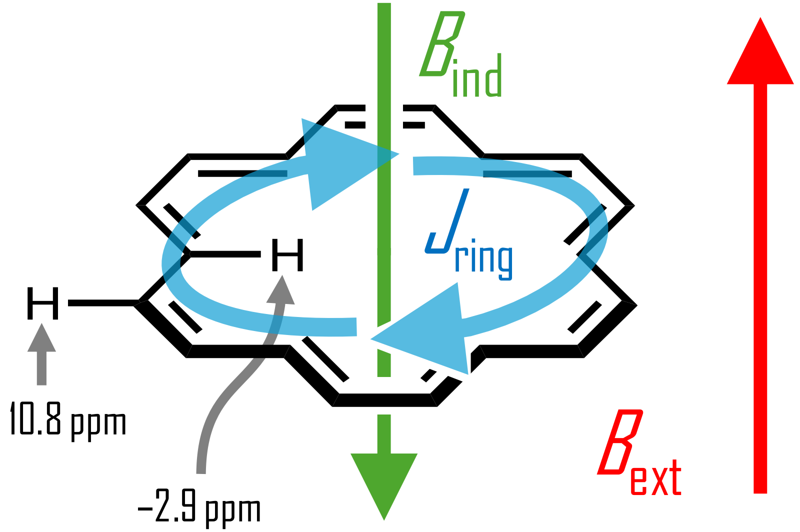
Connection with optical properties



As long as $J_{\mathrm{ring}} \neq 0$, the absorption maximum redshifts with increasing M!

Anderson and co-workers *Science* **2025**, *390*, 290.

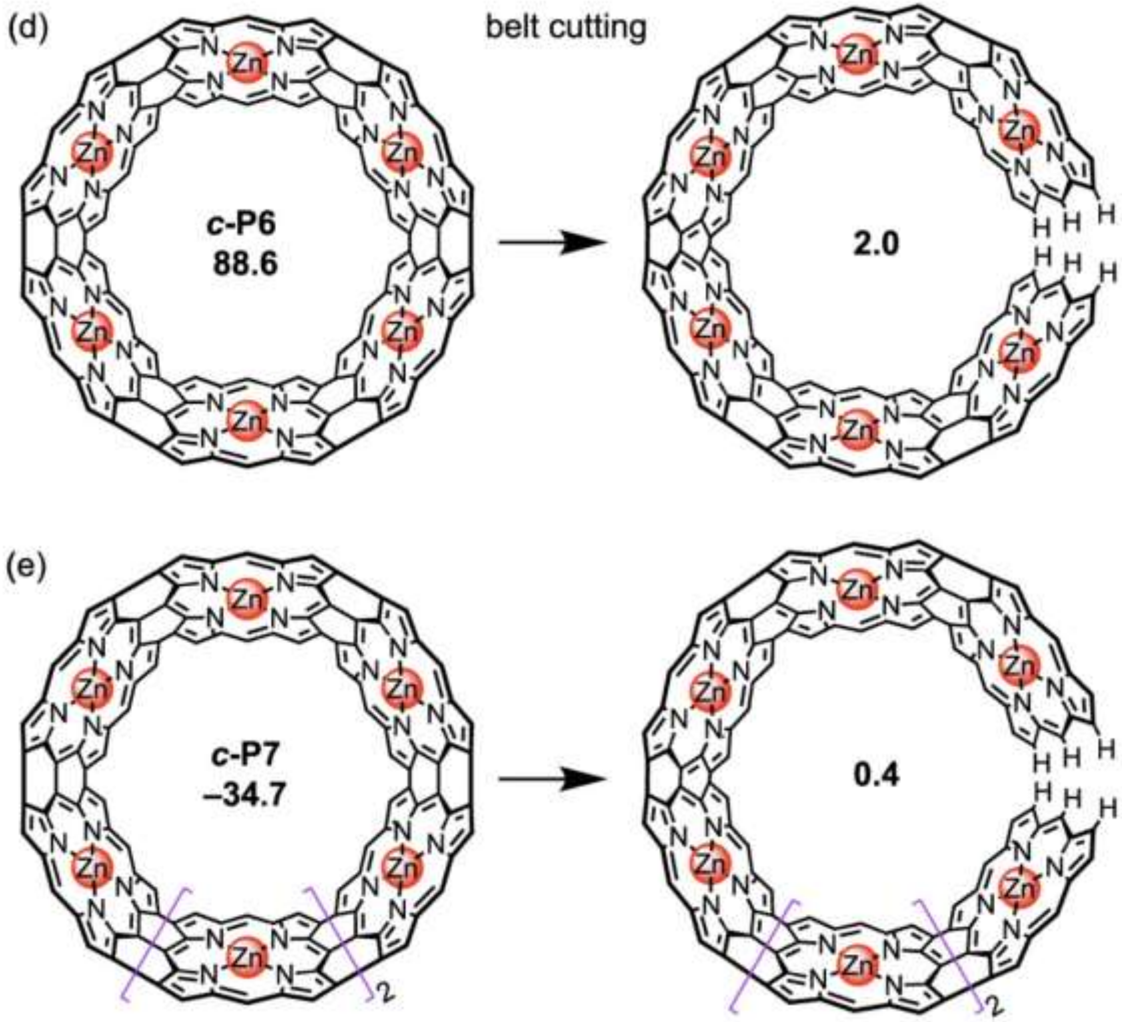
Practicalities of σ and NICS



- σ and NICS = $-\sigma$ are tensor fields
- Each position **r** ⟶ 3x3 matrix
- Planar systems: NICS_{zz} (field induced in z and applied in z)
- Non-planar systems: 1/3 Tr(NICS) = NICS_{iso}
- At ring centre: usually NICS(1)

- **σ_{iso} is useful for matching experiment and theory**
- **Remember: NICS is the response of the whole molecule at a point in space!**

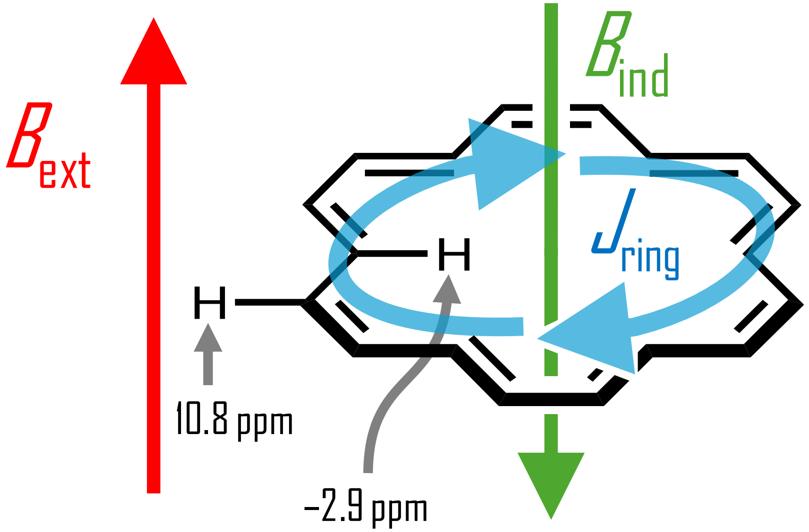
- **Remember: NICS is the response of the whole molecule at a point in space!**



Roncevic and co-workers *ACS Nano* **2025**, *19*, 1405.

Determining magnetic aromaticity

- **Ring current (J_{ring})**
  - Accessible by theory
  - GIMIC and Sysmoic

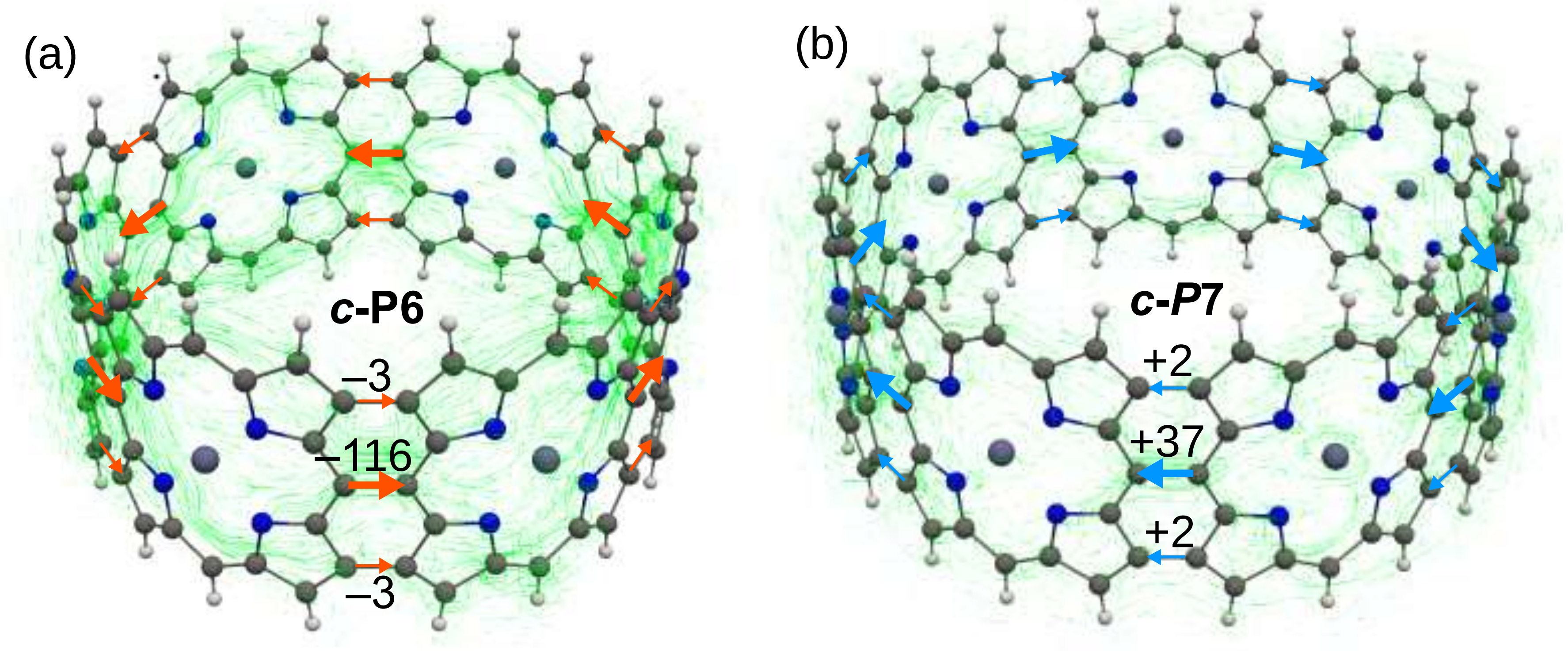


- Effect of J_{ring}
  - B_{ind} at atoms: chemical shielding σ (NMR and theory)
  - B_{ind} in space: NICS (theory)

GIMIC: D. Sundholm, H. Fliegl, R. J. Berger, *WIREs Comput. Mol. Sci.* **2016**, *6*, 639.
Sysmoic: G. Monaco, F. F. Summa, R. Zanasi, *J. Chem. Inf. Model.* **2021**, *61*, 270.
NICS: e.g. A. Stanger *Eur. J. Org. Chem.* **2020**, *2020*, 3120.

Ring current

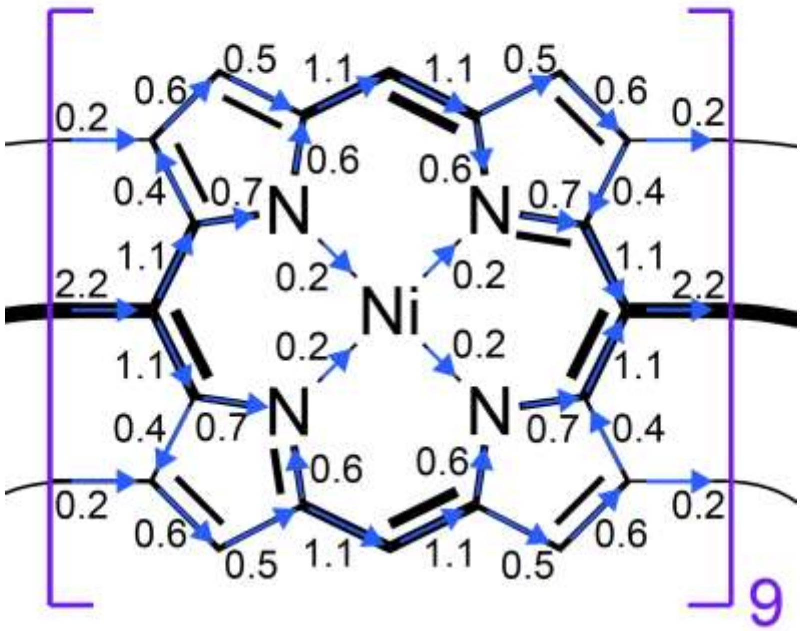
- Vector field: each **r** has $J_x(\mathbf{r})$, $J_y(\mathbf{r})$, $J_z(\mathbf{r})$
- Kirchhoff's law: J_{ring} forms closed loops
- Electrons are in bonds: we can i



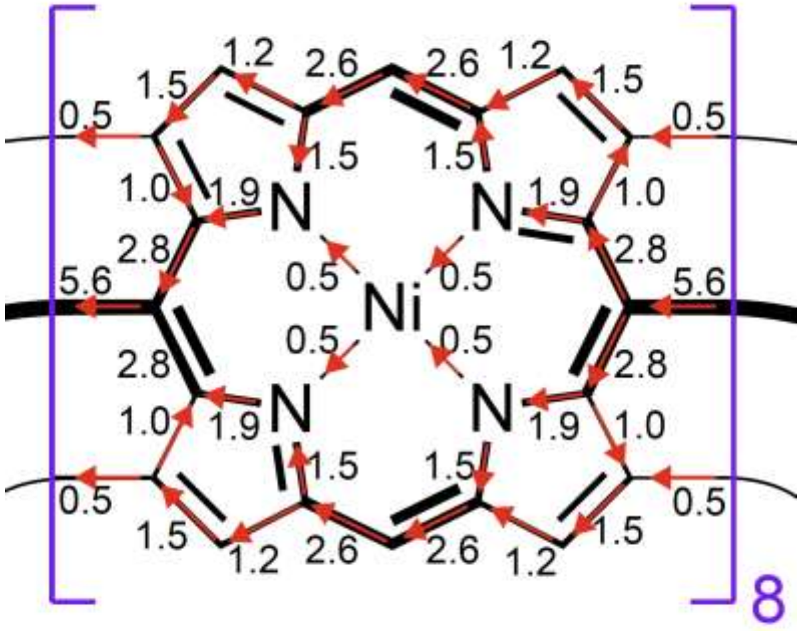
Roncevic and co-workers *ACS Nano* **2025**, *19*, 1405.

Ring current

- Vector field: each $\mathbf{r}$ has $J_x(\mathbf{r})$, $J_y(\mathbf{r})$, $J_z(\mathbf{r})$
- Kirchhoff's law: J_{ring} forms closed loops
- Electrons are in bonds: <u>we can integrate bond cross-sections</u>



aromatic



anti-aromatic

Science **2025**, *390*, 290.

Practicalities of J_{ring}

The good:

- Reveals electron delocalisation pathways
- Can be assigned to each bond
- Assigns magnetic aromaticity to each ring

The bad:

- Integration can be tedious – NICS is simpler.

The ugly:

- **J_{ring} is not an observable!**

It is sometimes possible to go
NICS → J_{ring}:
R. Poranne *Phys. Chem. Chem. Phys.* **2022**, *24*, 8631.
D. Sundholm *Phys. Chem. Chem. Phys.* **2022**, *24*, 624.

Magnetic aromaticity

- Wavefunction response to a magnetic field
  - Strong paratropic current → near-degeneracies → relief
  - Strong diatropic current → exalted magnetic susceptibility

- **Characterises the coherence of a (quantum) ring**

- **Experimentally observable: σ (and NICS)**

- Somewhat limited to main group elements

Geometric Aromaticity Descriptors

Bo Durbeej
Linköping University
Sweden

Outline

– Introduction: Geometric aromaticity descriptors

- The harmonic oscillator model of aromaticity (HOMA)
- The performance of HOMA for ground-state aromaticity and antiaromaticity (GSAA) and excited-state aromaticity and antiaromaticity (ESAA)

– New parameterizations of HOMA for ground and excited states

- Ground/S_0 HOMAc (“c” denotes “computational”)
- Excited/T_1 HOMER (“E” denotes “excited”)
- Parameters derived directly from the actual bond lengths of pertinent reference compounds
- Parameters derived from model aromatic and **antiaromatic** compounds
- Based on high-level ab initio calculations

– Assessment of HOMER and HOMAc

EM Arpa & B Durbeej, *PCCP* 25 (2023) 16763
EM Arpa, S Stafström & B Durbeej, *JOC* 90 (2025) 1297

Geometric aromaticity descriptors

– Aromatic systems tend to show equalization of bond lengths

– Easy to calculate once bond lengths are known from experiments or modeling

– Early model: The Julg index

A Julg & P François, *Theor Chim Acta* 7 (1967) 249

- Carbocyclic systems

$$A = 1 - \frac{225}{n}\sum_i \left(1 - \frac{R_i}{R_{\mathrm{av}}}\right)^2$$

- *n* CC bonds with lengths R_i
- R_{av} is the average of these lengths
- 225 is a normalization parameter introduced to ensure that a model non-aromatic compound (Kekule's benzene) assumes an *A* value of **0** when its bond lengths equal those of 1,3-butadiene
- A model aromatic compound with all R_i equal has an *A* value of **1**
- But any carbocycle with all R_i equal has an *A* value of **1**

⇒ cyclohexane just as aromatic as benzene!

Geometric aromaticity descriptors

– HOMA

J Kruszewski & TM Krygowski, *Tetrahedron Lett* 13 (1972) 3839

- At first for carbocycles only
- Uses an optimal CC bond length R_{opt} achieved by a model aromatic system

$$R_{\text{opt}} = \frac{R_{\text{S}} + 2R_{\text{D}}}{3}$$

$$\text{HOMA} = 1 - \frac{\alpha}{n}\sum_i (R_i - R_{\text{opt}})^2$$

$$\frac{\alpha}{n}\sum_i (R_i - R_{\text{opt}})^2 = 1$$

- R_{opt} is the length of a CC bond at which the energy needed to extend it to a pure single bond with length R_{S} equals the energy needed to compress it to a pure double bond with length R_{D}
- $E = k\Delta x^2$ and $k(\text{S})/k(\text{D}) = 1/2$
- Exp. R_{S} (ethane) and R_{D} (ethylene) ⇒ $R_{\text{opt}} = 1.397$ Å $\approx R_{\text{benzene}}$
- A model aromatic compound with all R_i equal to R_{opt} has a HOMA value of **1**
- α is a normalization parameter determined in such a way that a model non-aromatic compound (Kekule's benzene) shows a HOMA value of **0** when its bond lengths equal those of ethane and ethylene ⇒ $\alpha = 98.89$ Å^{-2}

Geometric aromaticity descriptors

– HOMA, some later developments

- Heterocyclic compounds TM Krygowski, *J Chem Inf Comput Sci* 33 (1993) 70

$R_{XY,opt}$ and α_{XY} values specific for each type of bond XY considered (CC, CN, NN, CO, CP, CS and NO)

CC: Exp. R_S and R_D values from 1,3-butadiene instead of ethane and ethylene

$\Rightarrow R_{CC,opt} = 1.388$ Å and $\alpha_{CC} = 257.70$ Å^{-2}

Other bonds parameterized based on exp. R_S and R_D values taken from other suitable reference systems

$$\begin{aligned}\mathrm{HOMA} = 1 - \frac{1}{n}\Big\{&\alpha_{\mathrm{CC}}\sum_{\mathrm{CC}}(R_{\mathrm{CC},i}-R_{\mathrm{CC,opt}})^2 + \alpha_{\mathrm{CN}}\sum_{\mathrm{CN}}(R_{\mathrm{CN},i}-R_{\mathrm{CN,opt}})^2 + \alpha_{\mathrm{NN}}\sum_{\mathrm{NN}}(R_{\mathrm{NN},i}-R_{\mathrm{NN,opt}})^2\\ &+ \alpha_{\mathrm{CO}}\sum_{\mathrm{CO}}(R_{\mathrm{CO},i}-R_{\mathrm{CO,opt}})^2 + \alpha_{\mathrm{CP}}\sum_{\mathrm{CP}}(R_{\mathrm{CP},i}-R_{\mathrm{CP,opt}})^2 + \alpha_{\mathrm{CS}}\sum_{\mathrm{CS}}(R_{\mathrm{CS},i}-R_{\mathrm{CS,opt}})^2\\ &+ \alpha_{\mathrm{NO}}\sum_{\mathrm{NO}}(R_{\mathrm{NO},i}-R_{\mathrm{NO,opt}})^2\Big\}\end{aligned}$$

Geometric aromaticity descriptors

– HOMA, some later developments

- Harmonic oscillator model of electron delocalization (HOMED)

ED Raczyńska et al, *Symmetry* 2 (2010) 1485

Goal: To improve the description of electron delocalization in heterocycles

Parameterization strategy: $R_{XY,opt}$ derived directly from the actual bond lengths of aromatic reference systems, rather than from R_S and R_D values

But α_{XY} derived from R_S and R_D values in the "usual" HOMA way

All parameterization based on DFT-calculated bond lengths

Similar ideas: CP Frizzo & MAP Martins, *Struct Chem* 23 (2012) 375

All parameterization based on experimental bond lengths

- Parameterization of/for more "unusual" bonds (eg, COs) or systems (eg, radicals)

Q Ye & J Zhu, *Organometallics* 42 (2023) 2369
A Mischie et al, *Comput Theor Chem* 1230 (2023) 114370

Geometric aromaticity descriptors

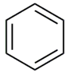
– Performance of HOMA: GSAA

- **Many observations** that HOMA-based indices agree quite well with different versions of the nucleus-independent chemical shift (NICS) index

Studies by Krygowski, Schleyer, Solà, … and their co-workers

- **Own recent tests**

EM Arpa & B Durbeej, *PCCP* 25 (2023) 16763
EM Arpa, S Stafström & B Durbeej,
JOC 90 (2025) 1297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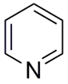

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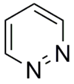

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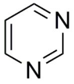

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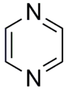

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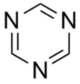

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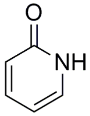

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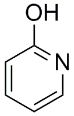

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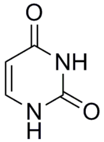

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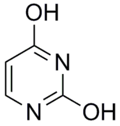

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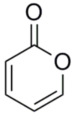

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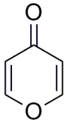

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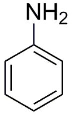

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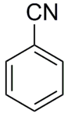

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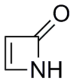

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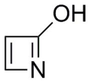

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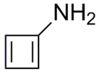

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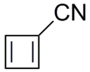

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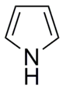

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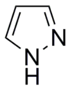

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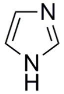

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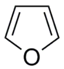

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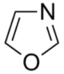

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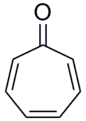

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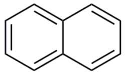
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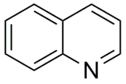

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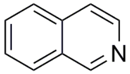

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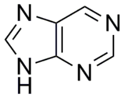

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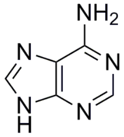

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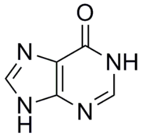

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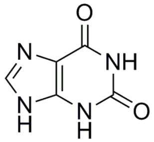

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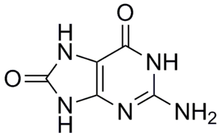

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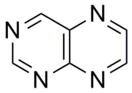

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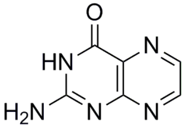

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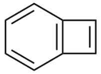
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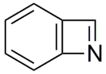

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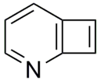

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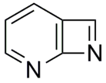

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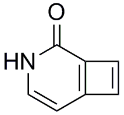

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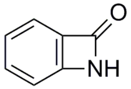

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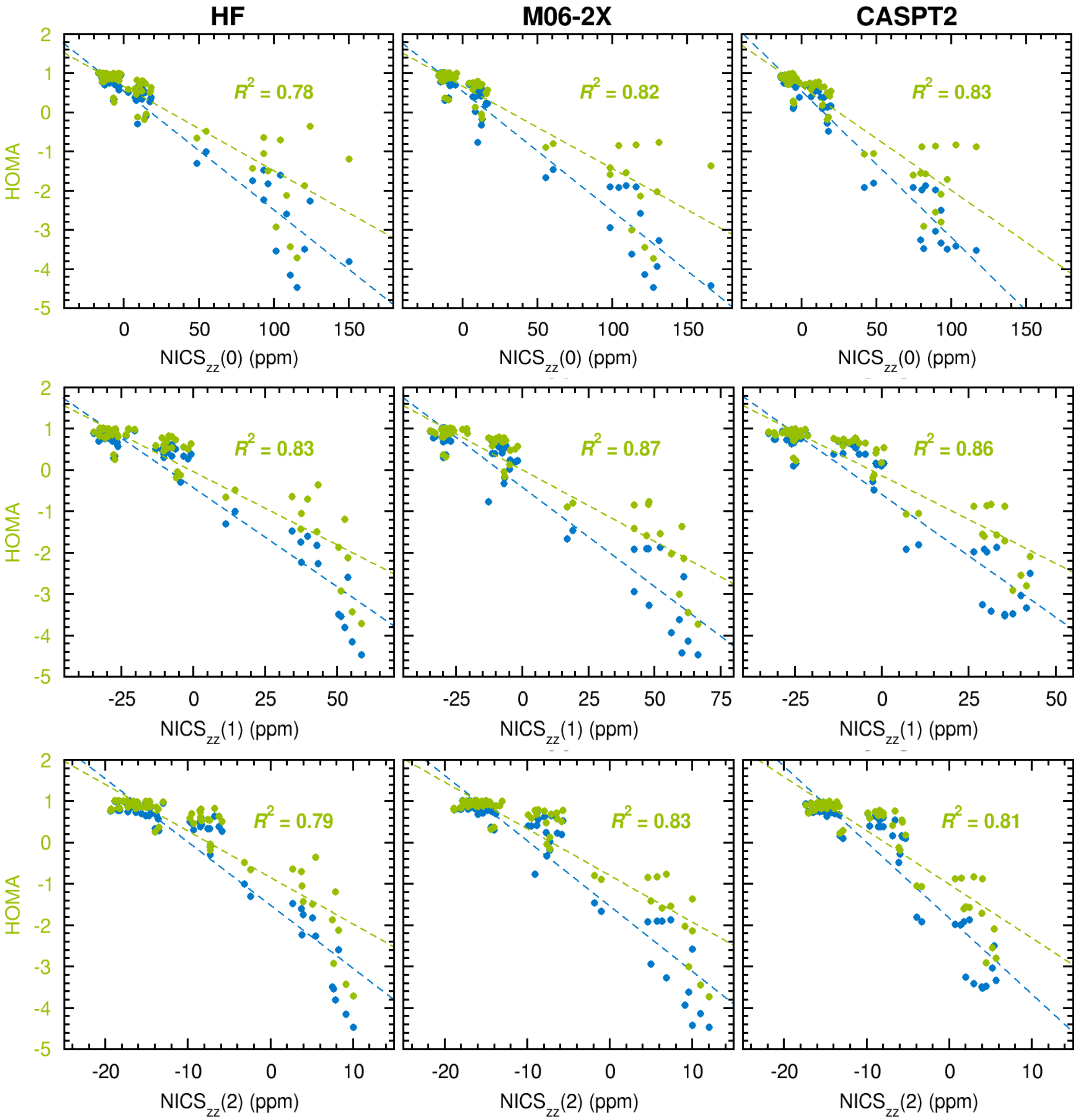
Geometric aromaticity descriptors

HOMA93	**NICS(0/1/2)$_{zz}$**
HF	HF
M06-2X	M06-2X
CASPT2	CASSCF

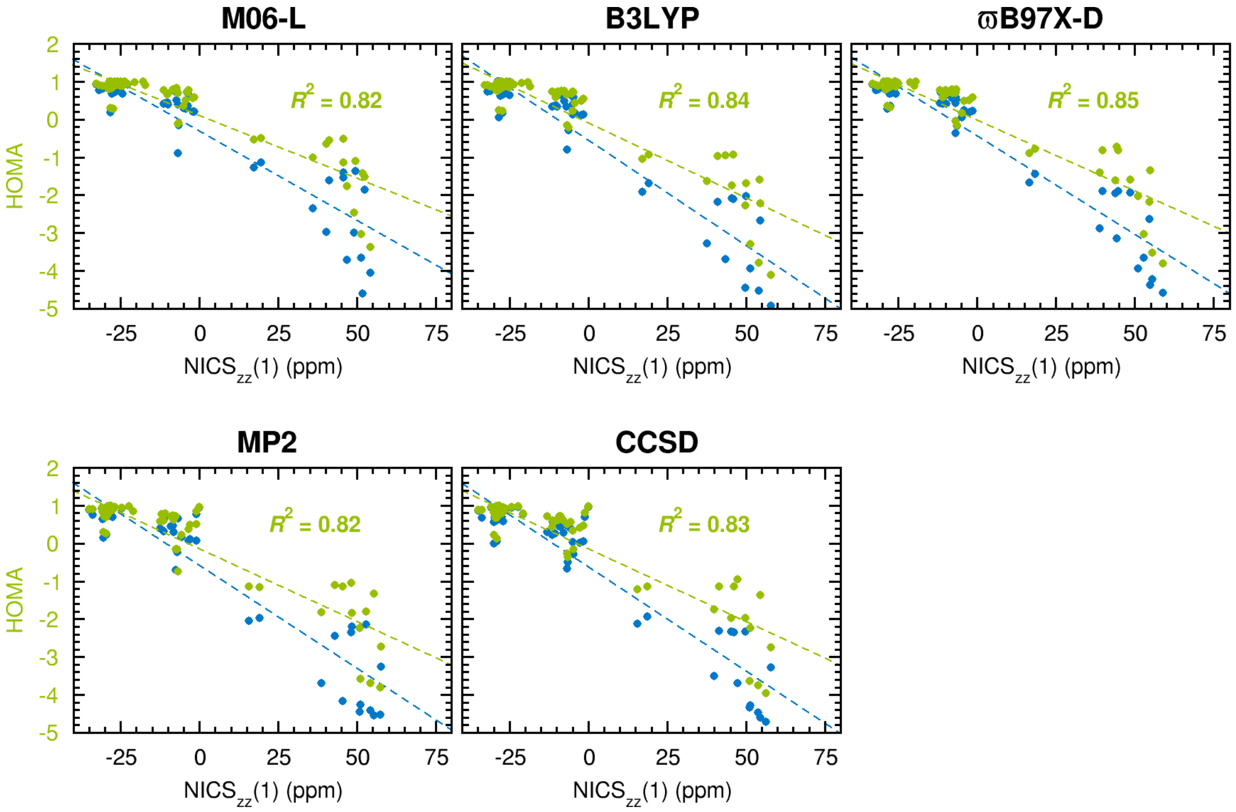
cc-pVDZ basis set



Geometric aromaticity descriptors

HOMA93	**NICS(1)$_{zz}$**
M06-L	M06-L
B3LYP	B3LYP
ωB97X-D	ωB97X-D
MP2	MP2
CCSD	MP2

cc-pVDZ basis set



Geometric aromaticity descriptors

HOMA93	**SA**	**MCI**
HF	HF	HF
M06-2X	M06-2X	M06-2X
CASPT2	CASSCF	CASSCF

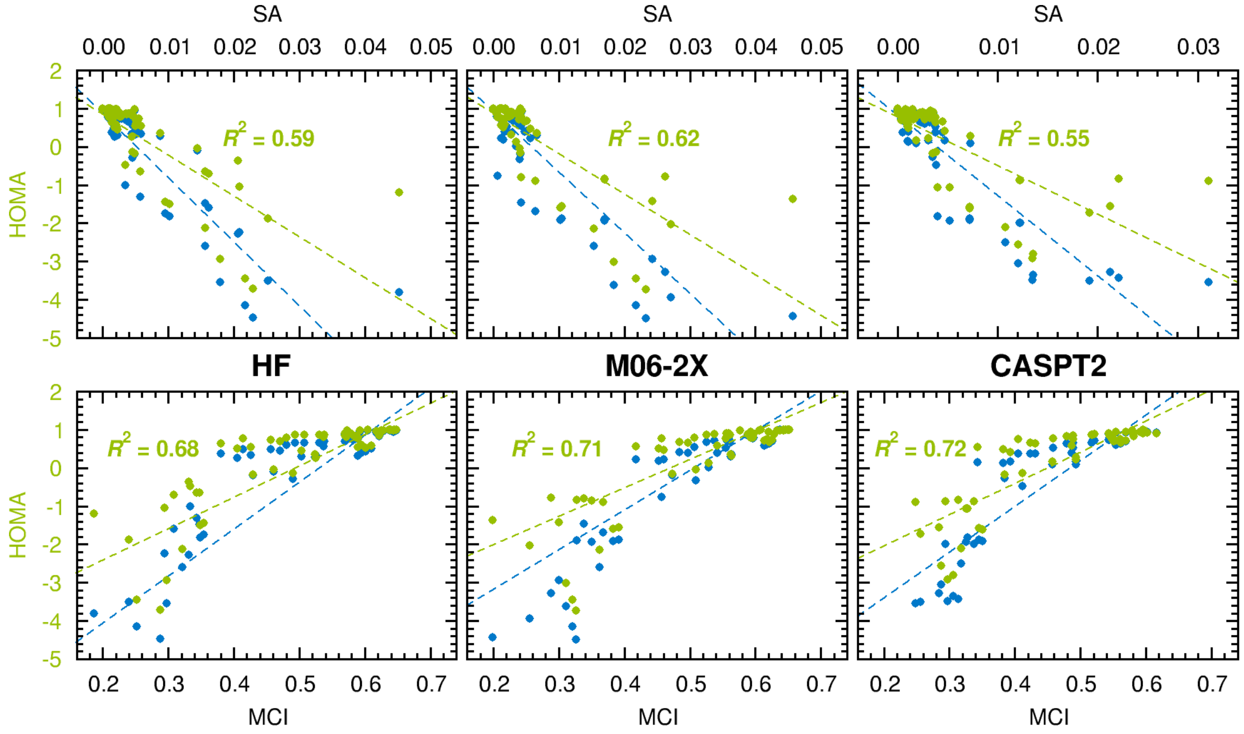
cc-pVDZ basis set

SA – Shannon aromaticity index

S Noorizadeh & E Shakerzadeh,
PCCP 12 (2010) 4742

MCI – Multicenter index

P Bultinck, R Ponec & S Van Damme,
JPOC 18 (2005) 706



Conclusion

Overall, HOMA performs rather well for GSAA

Geometric aromaticity descriptors

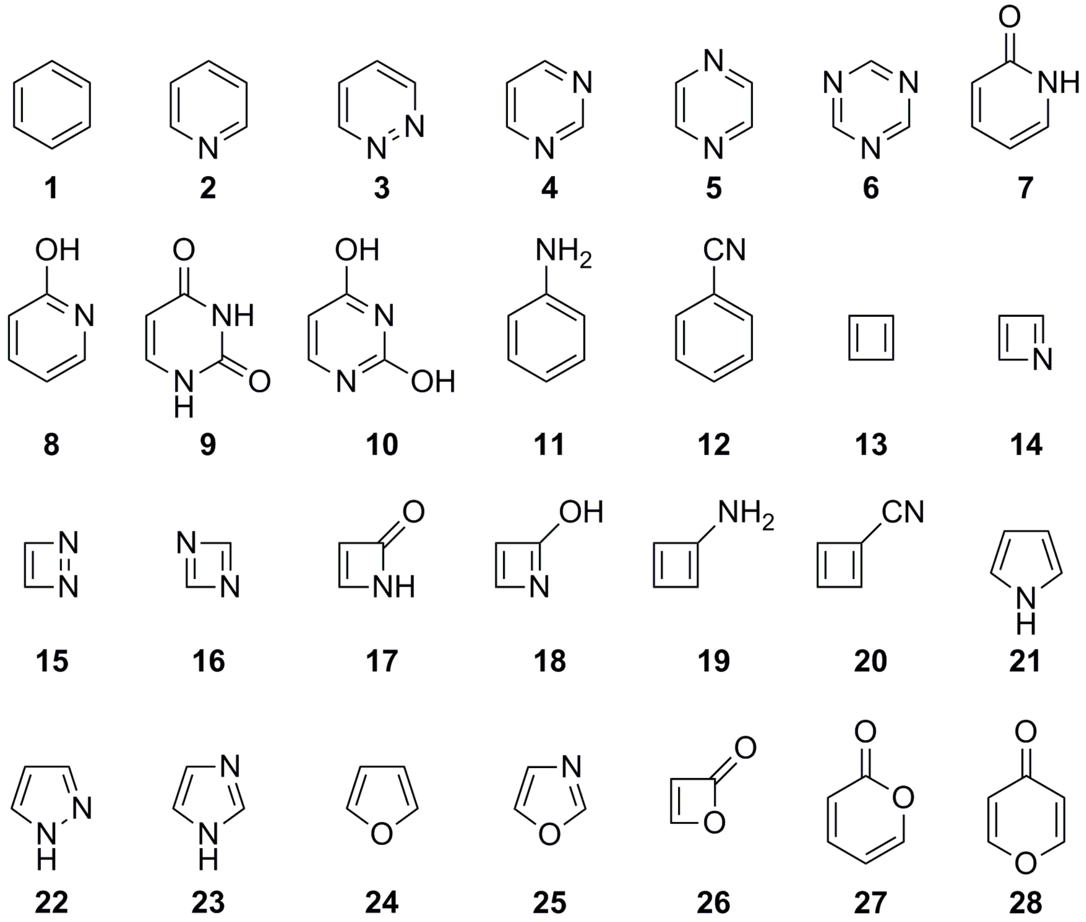
– Performance of HOMA: ESAA

- **Fewer benchmarks** than for GSAA

J Pedersen & KV Mikkelsen, *JPCA* 127 (2023) 122

- **Own recent tests**

EM Arpa & B Durbeej, *PCCP* 25 (2023) 16763
EM Arpa, S Stafström & B Durbeej,
JOC 90 (2025) 1297



Geometric aromaticity descriptors

HOMA93 **$\text{NICS}(0/1/2)_{zz}$**

CASPT2 CASSCF

cc-pVDZ basis set

Panel A

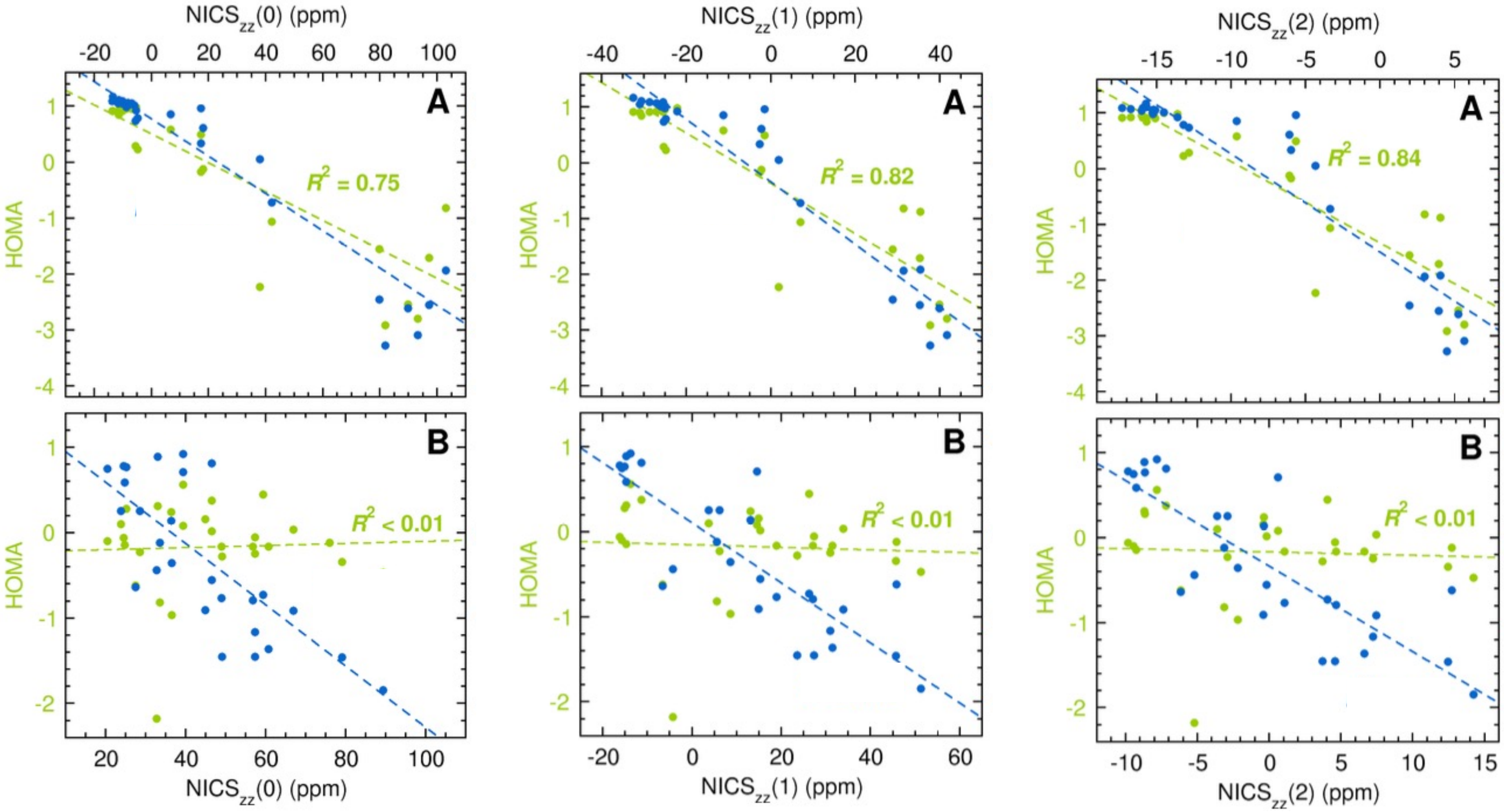
GSAA

(S_0)

Panel B

ESAA

(T_1)



Geometric aromaticity descriptors

HOMA93

M06-2X
CAM-B3LYP

NICS(1)$_{zz}$

M06-2X
CAM-B3LYP

cc-pVDZ basis set

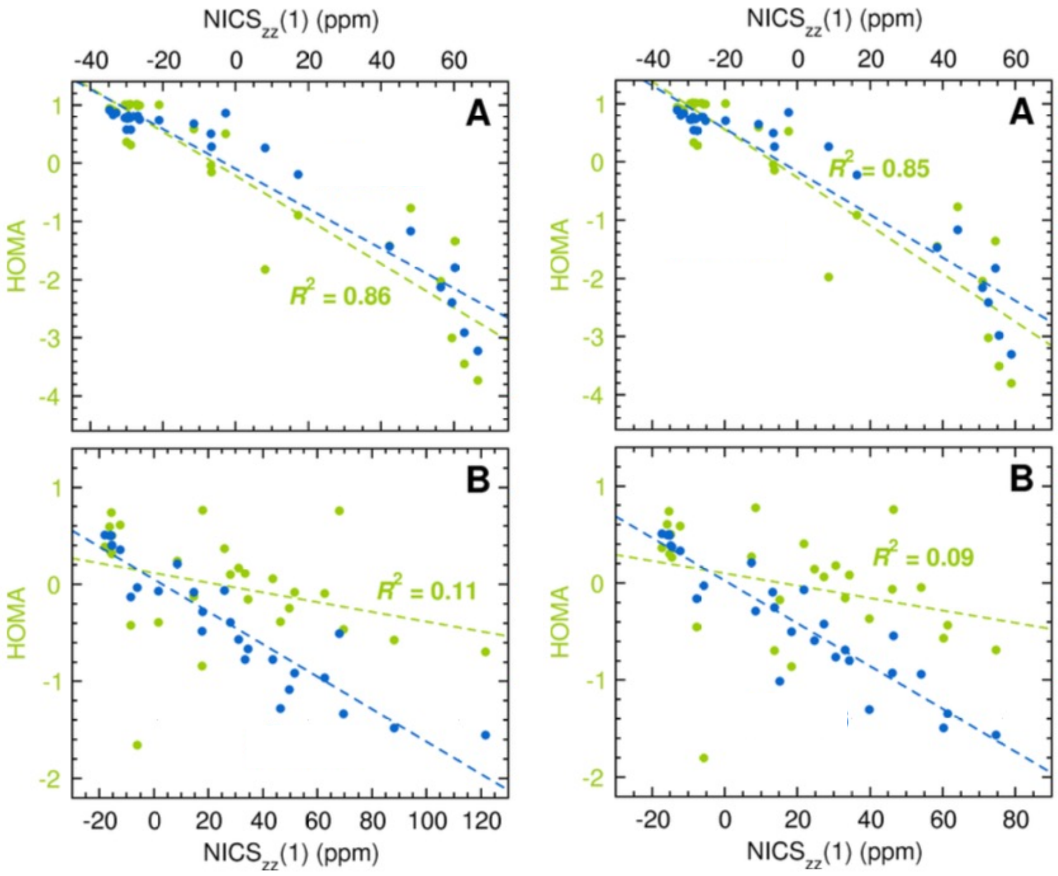
M06-2X **CAM-B3LYP**

Panel A

GSAA
(S_0)

Panel B

ESAA
(T_1)



Conclusion

- **HOMA performs poorly** in probing differences in ESAA between **different molecules**

- Still, many studies have found that **HOMA-based indices are useful probes** of changes in ESAA along photochemical reaction paths between **different molecular isomers**

- ***E*/*Z* photoisomerizations**

B Oruganti et al, *Org Lett* 19 (2017) 4818
J Wang et al, *ChemPhotoChem* 3 (2019) 450

- **Photoplanarization processes**

J Toldo et al, *ChemPlusChem* 84 (2019) 712
R Kotani et al, *JACS* 142 (2020) 14985

- **Photocyclization reactions**

B Oruganti et al, *JACS* 142 (2020) 13941

- **Excited-state proton transfer reactions**

LJ Karas et al, *Chem Sci* 11 (2020) 10071

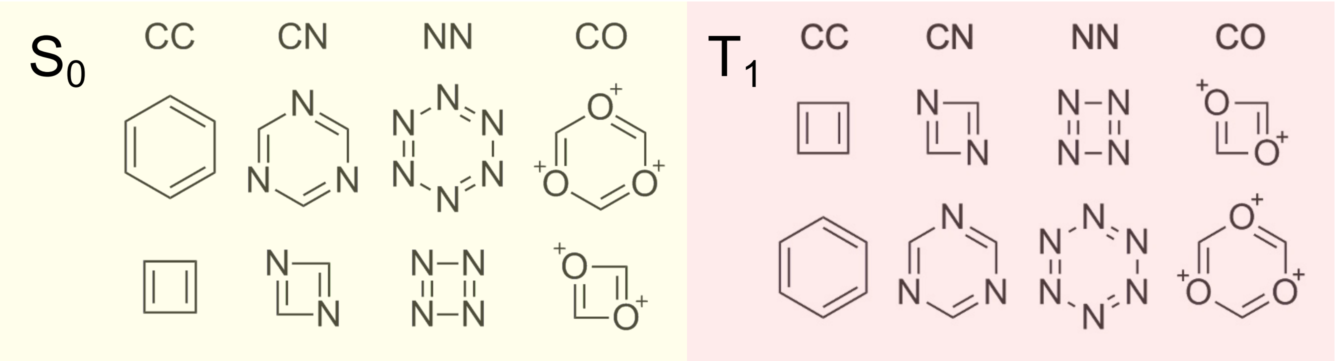
New parameterizations of HOMA

– Parameterization details

- **State-specific** parameterizations for ground **(S_0, HOMAc)** and excited **(T_1, HOMER)** states
- CC, CN, NN and CO bonds
- **Both** $R_{XY,opt}$ and α_{XY} parameters derived directly from **the actual bond lengths** of suitable ref. compounds

$R_{XY,opt}$ Model aromatic compounds

α_{XY} Model **antiaromatic** compounds



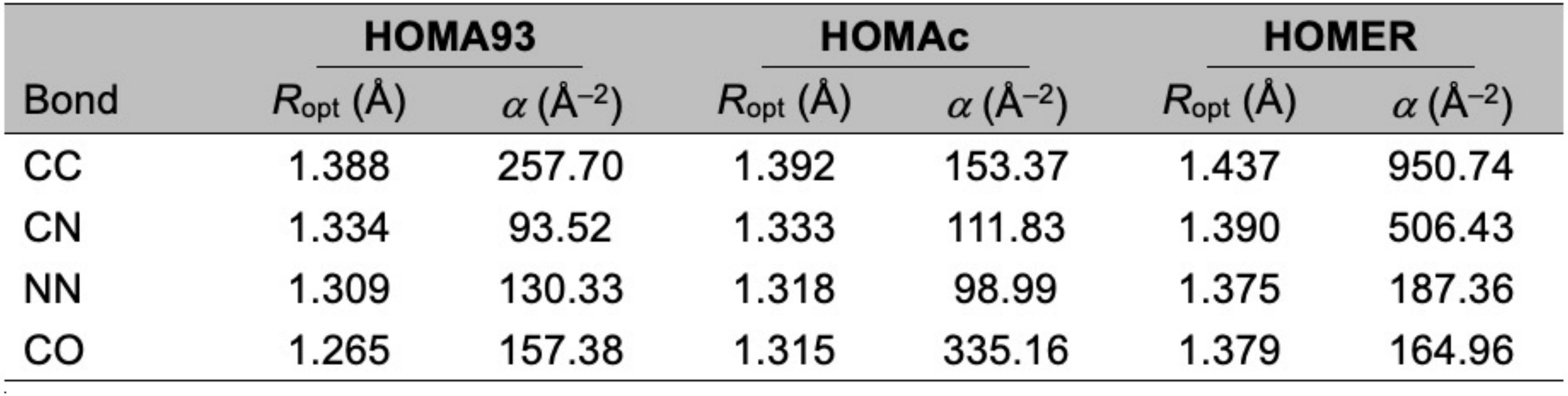
- Parameterization based on bond lengths calculated at the **CASPT2/cc-pVQZ** level of theory
- α_{XY} parameters determined using the condition that $\frac{\alpha_{XY}}{n}\sum_i (R_{XY,i} - R_{XY,opt})^2 = 2$

All HOMA-based indices	Model **aromatic** compounds ⇒ Values around 1
HOMA-based indices except HOMAc and HOMER	Model **non-aromatic** compounds ⇒ Values around 0
HOMAc and HOMER	Model **antiaromatic** compounds ⇒ Values around –1

EM Arpa & B Durbeej, *PCCP* 25 (2023) 16763
EM Arpa, S Stafström & B Durbeej, *JOC* 90 (2025) 1297

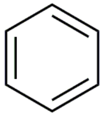
New parameterizations of HOMA

– Parameterization results



Bond	HOMA93		HOMAc		HOMER	
	R_{opt} (Å)	α (Å^{-2})	R_{opt} (Å)	α (Å^{-2})	R_{opt} (Å)	α (Å^{-2})
CC	1.388	257.70	1.392	153.37	1.437	950.74
CN	1.334	93.52	1.333	111.83	1.390	506.43
NN	1.309	130.33	1.318	98.99	1.375	187.36
CO	1.265	157.38	1.315	335.16	1.379	164.96

Assessment of HOMER for ESAA



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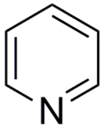

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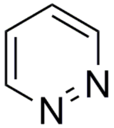

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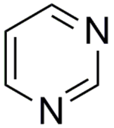

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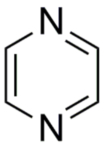

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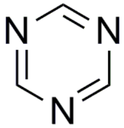

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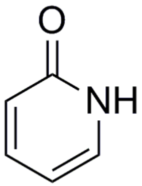

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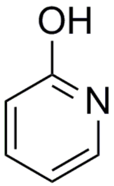

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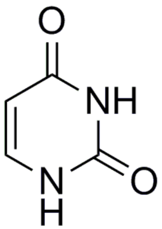

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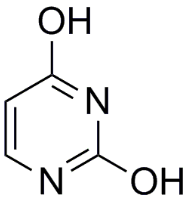

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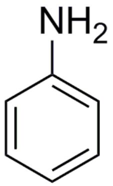

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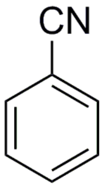

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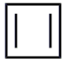

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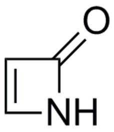

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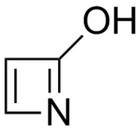

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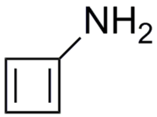

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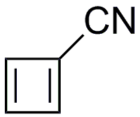

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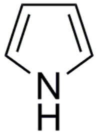

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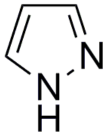

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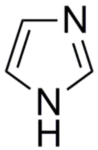

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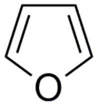

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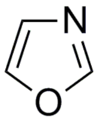

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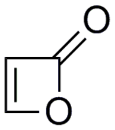

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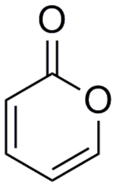

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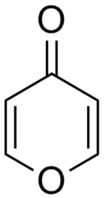

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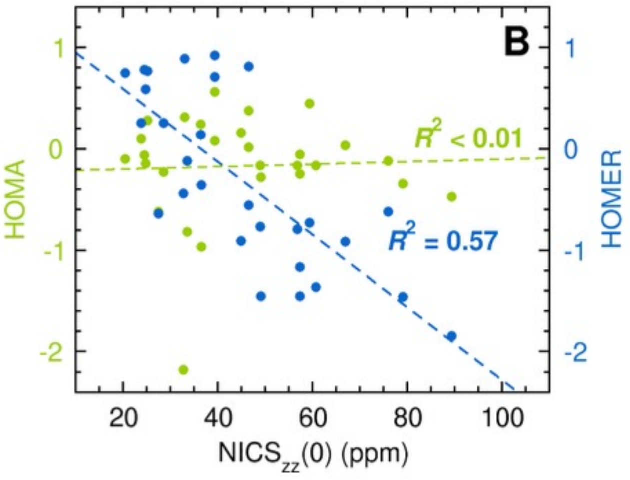
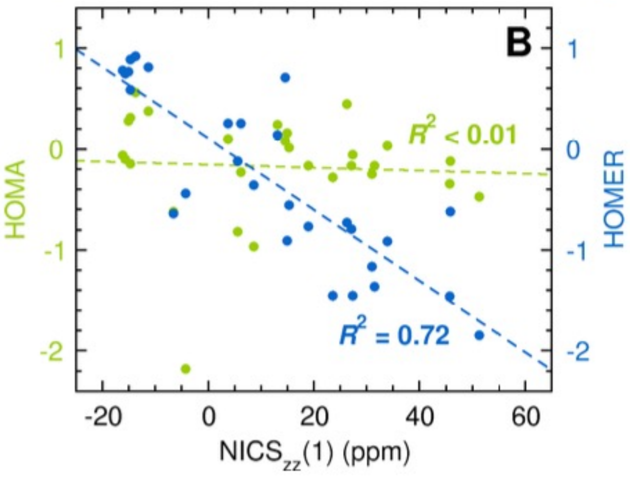
Assessment of HOMER for ESAA

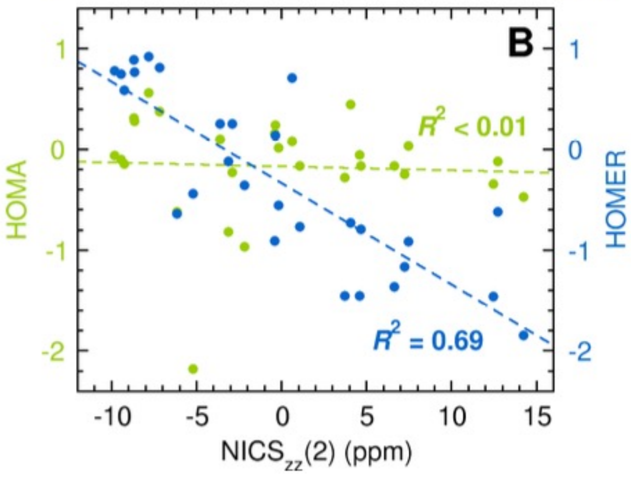
HOMA93 **HOMER** **NICS(0/1/2)$_{zz}$**

CASPT2 CASPT2 CASSCF

cc-pVDZ basis set







Assessment of HOMER for ESAA

HOMA93

M06-2X
CAM-B3LYP

HOMER

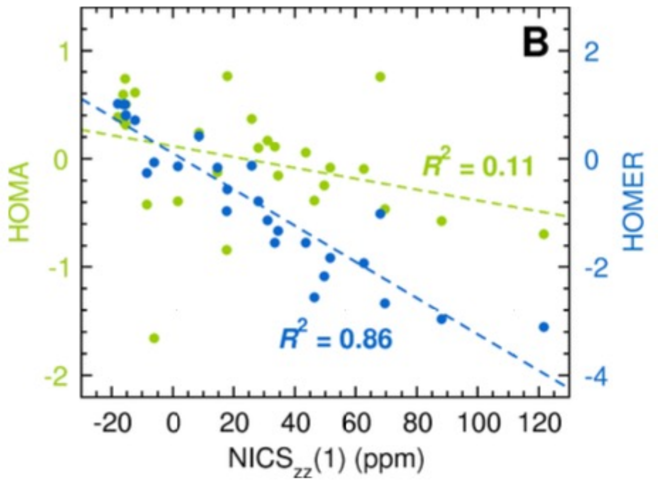
M06-2X
CAM-B3LYP

$NICS(1)_{zz}$

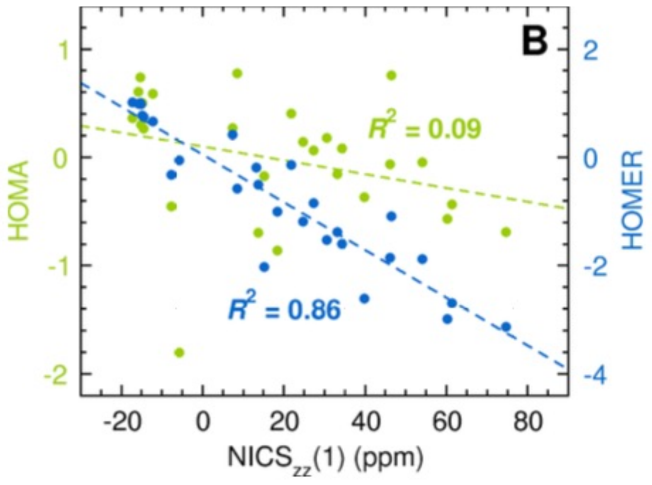
M06-2X
CAM-B3LYP

cc-pVDZ basis set

M06-2X



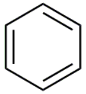
CAM-B3LYP



Conclusions

- HOMER is a clear improvement over HOMA93
- HOMER parameters transferable to other methods than CASPT2

Assessment of HOMAc for GSAA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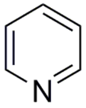

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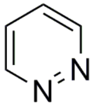

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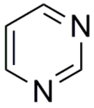

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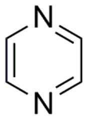

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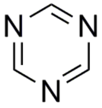

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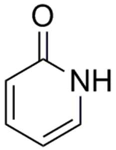

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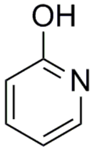

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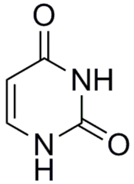

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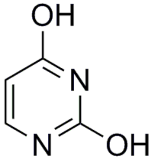

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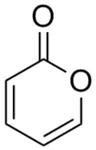

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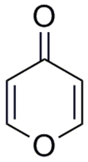

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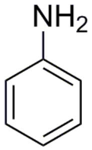

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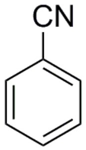

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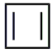
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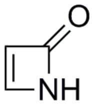

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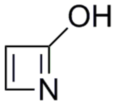

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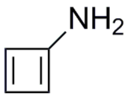

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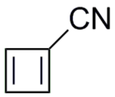

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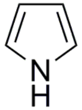

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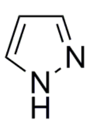

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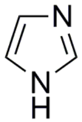

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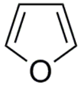

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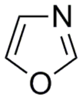

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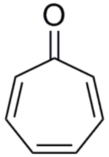

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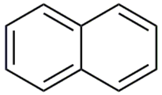
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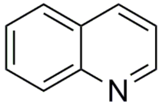

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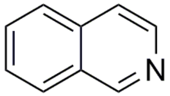

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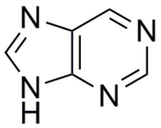

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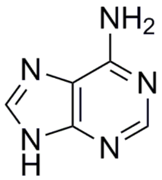

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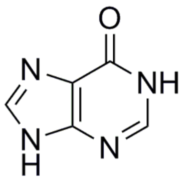

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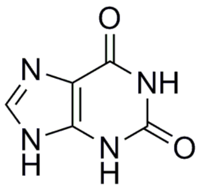

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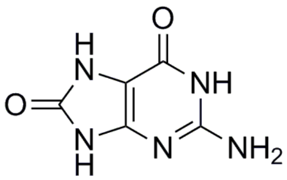

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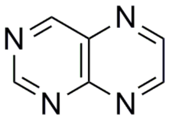

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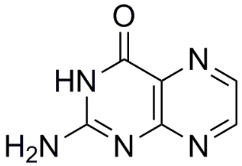

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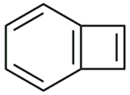
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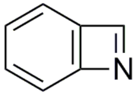

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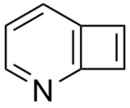

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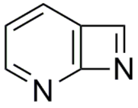

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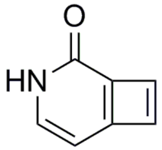

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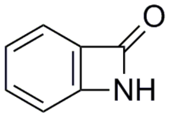
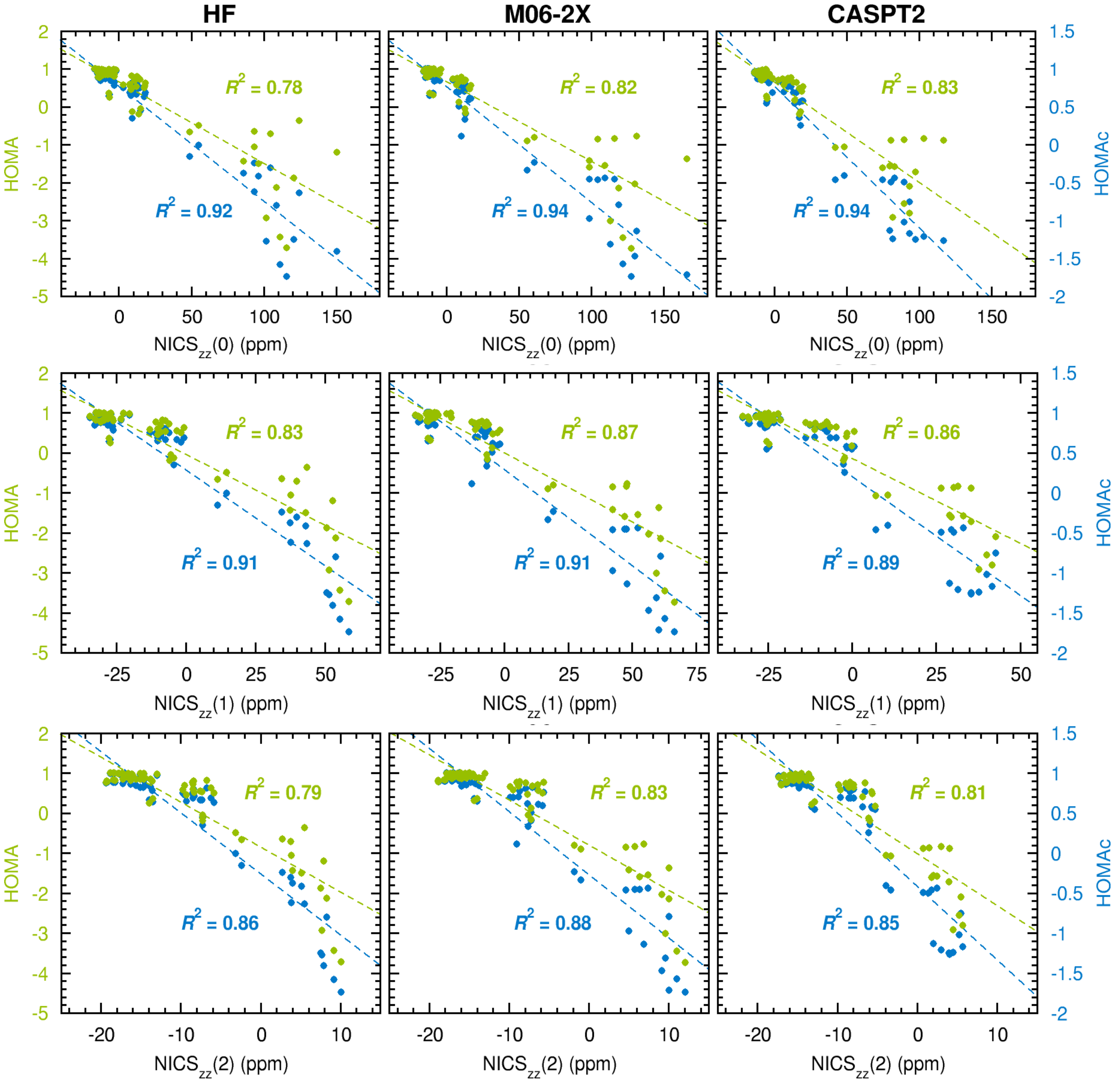


45

Assessment of HOMAc for GSAA

HOMA93	**HOMAc**	**NICS(0/1/2)$_{zz}$**
HF	HF	HF
M06-2X	M06-2X	M06-2X
CASPT2	CASPT2	CASSCF

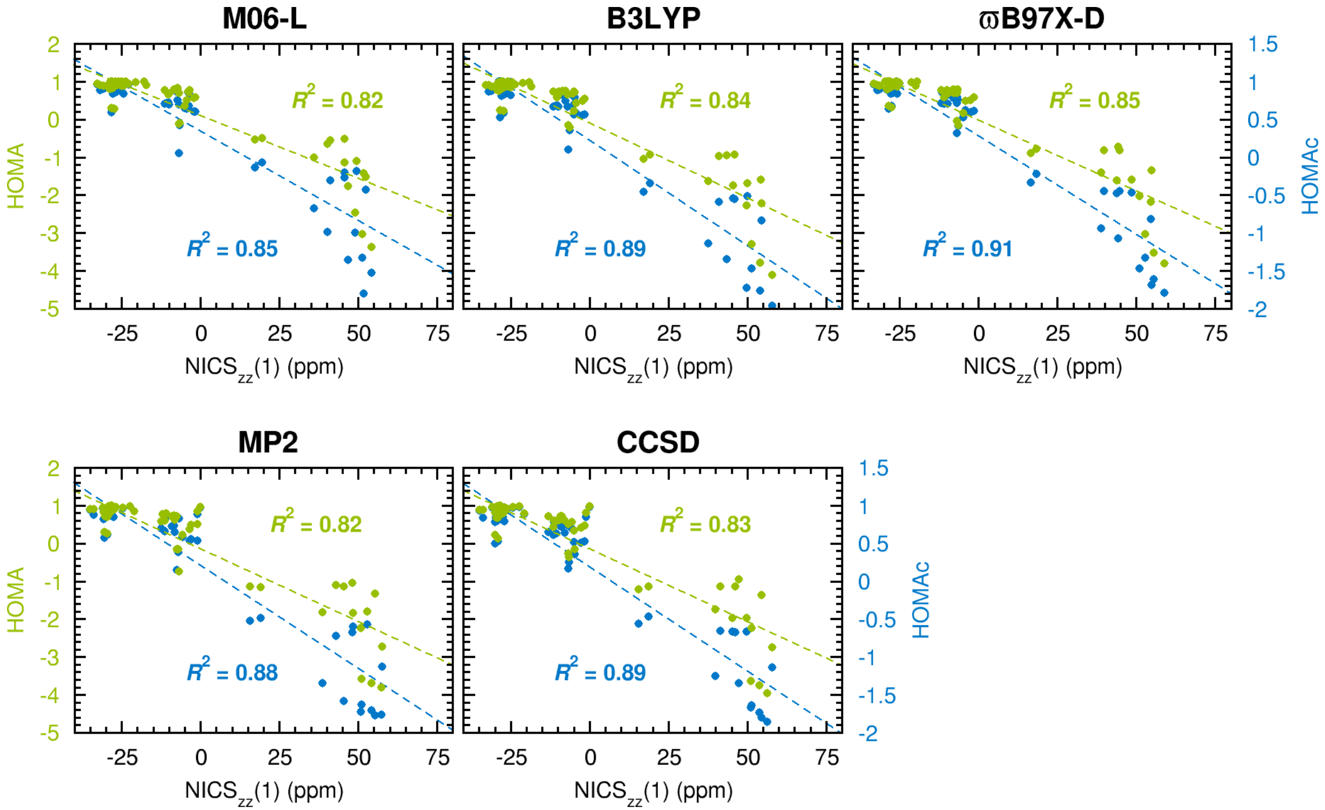
cc-pVDZ basis set



Assessment of HOMAc for GSAA

HOMA93	**HOMAc**	**NICS(1)$_{zz}$**
M06-L	M06-L	M06-L
B3LYP	B3LYP	B3LYP
ωB97X-D	ωB97X-D	ωB97X-D
MP2	MP2	MP2
CCSD	CCSD	MP2

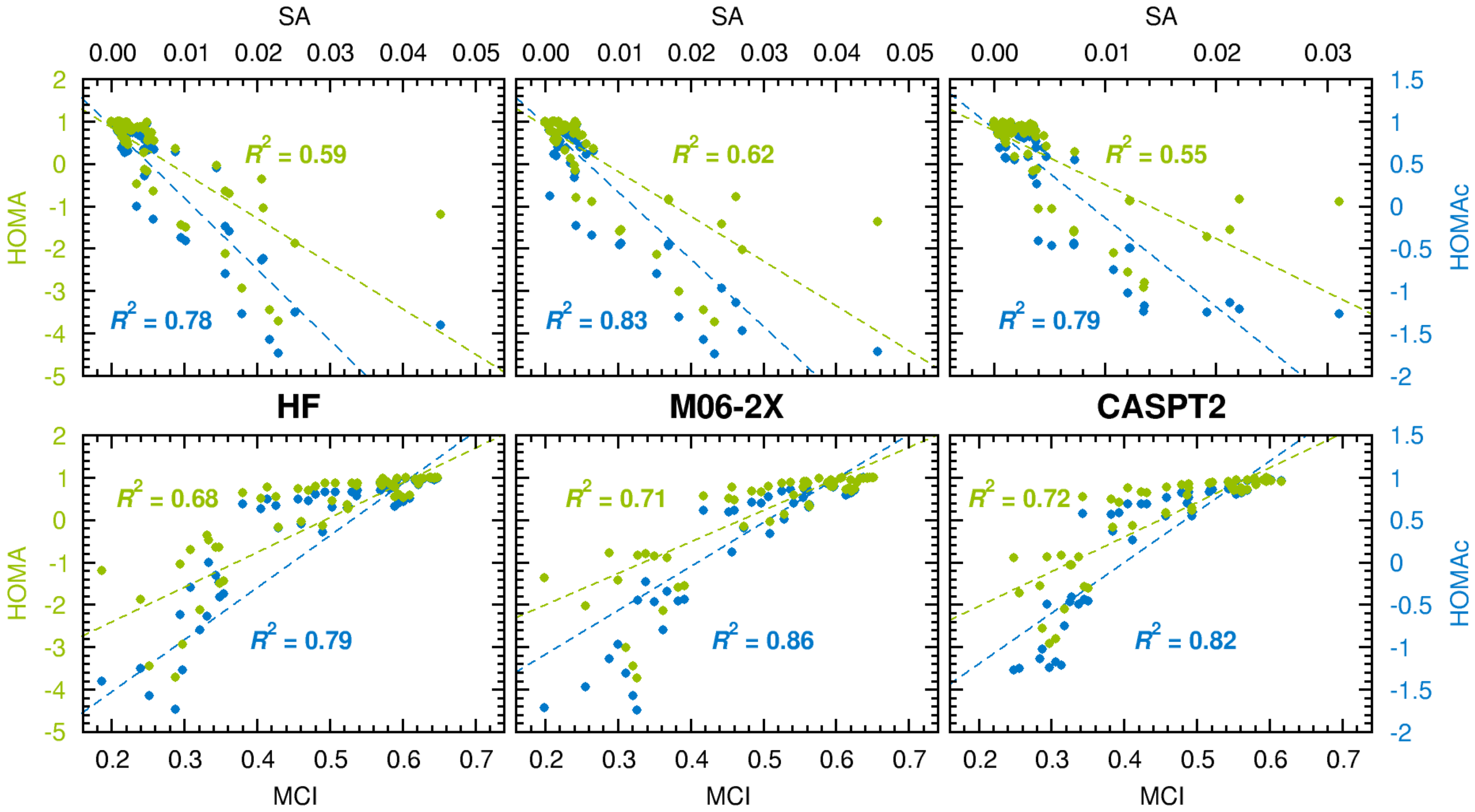
cc-pVDZ basis set



Assessment of HOMAc for GSAA

HOMA93	**HOMAc**	**SA**	**MCI**
HF	HF	HF	HF
M06-2X	M06-2X	M06-2X	M06-2X
CASPT2	CASPT2	CASSCF	CASSCF

cc-pVDZ basis set

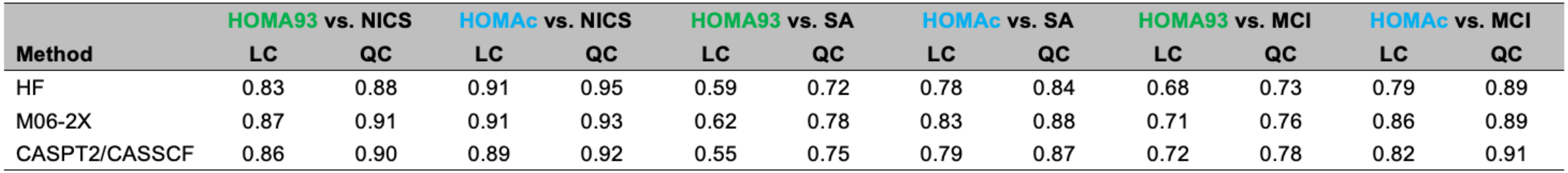


Assessment of HOMAc for GSAA

HOMA93	**HOMAc**	**NICS(1)$_{zz}$**	**SA**	**MCI**
HF	HF	HF	HF	HF
M06-2X	M06-2X	M06-2X	M06-2X	M06-2X
CASPT2	CASPT2	CASSCF	CASSCF	CASSCF

cc-pVDZ basis set

Comparison of R^2 values for linear and quadric correlations (LC and QC)



	HOMA93 vs. NICS		HOMAc vs. NICS		HOMA93 vs. SA		HOMAc vs. SA		HOMA93 vs. MCI		HOMAc vs. MCI	
Method	**LC**	**QC**	**LC**	**QC**	**LC**	**QC**	**LC**	**QC**	**LC**	**QC**	**LC**	**QC**
HF	0.83	0.88	0.91	0.95	0.59	0.72	0.78	0.84	0.68	0.73	0.79	0.89
M06-2X	0.87	0.91	0.91	0.93	0.62	0.78	0.83	0.88	0.71	0.76	0.86	0.89
CASPT2/CASSCF	0.86	0.90	0.89	0.92	0.55	0.75	0.79	0.87	0.72	0.78	0.82	0.91

Assessment of HOMAc for GSAA

HOMA93	**HOMAc**	**ISE**
M06-2X	M06-2X	M06-2X

cc-pVDZ basis set

ISE – Isomerization stabilization energy index

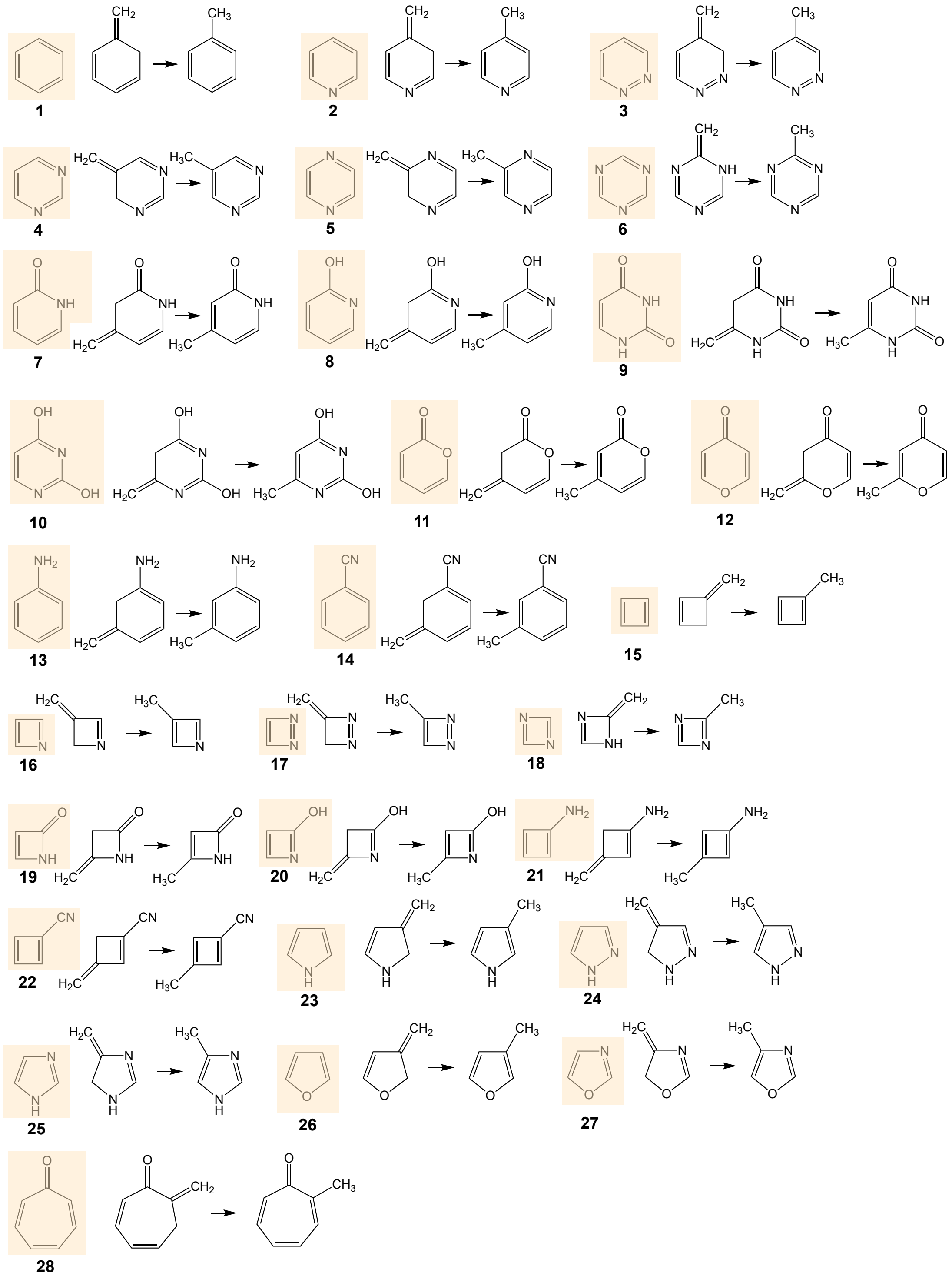
P v R Schleyer & F Pühlhofer,
Org Lett 4 (2002) 2873

$$\text{ISE} = E_{\text{elec}}(\text{CH}_3\text{ derivative}) - E_{\text{elec}}(\text{CH}_2\text{ isomer})$$

Methylated derivative of the species of interest

Its methylene isomer

ISE << 0	Aromatic
ISE >> 0	Antiaromatic



Assessment of HOMAc for GSAA

HOMA93	**HOMAc**	**ISE**
M06-2X	M06-2X	M06-2X

cc-pVDZ basis set

ISE – Isomerization stabilization energy index

P v R Schleyer & F Pühlhofer,
Org Lett 4 (2002) 2873

$$\mathrm{ISE} = E_{\mathrm{elec}}(\mathrm{CH_3\ derivative}) - E_{\mathrm{elec}}(\mathrm{CH_2\ isomer})$$

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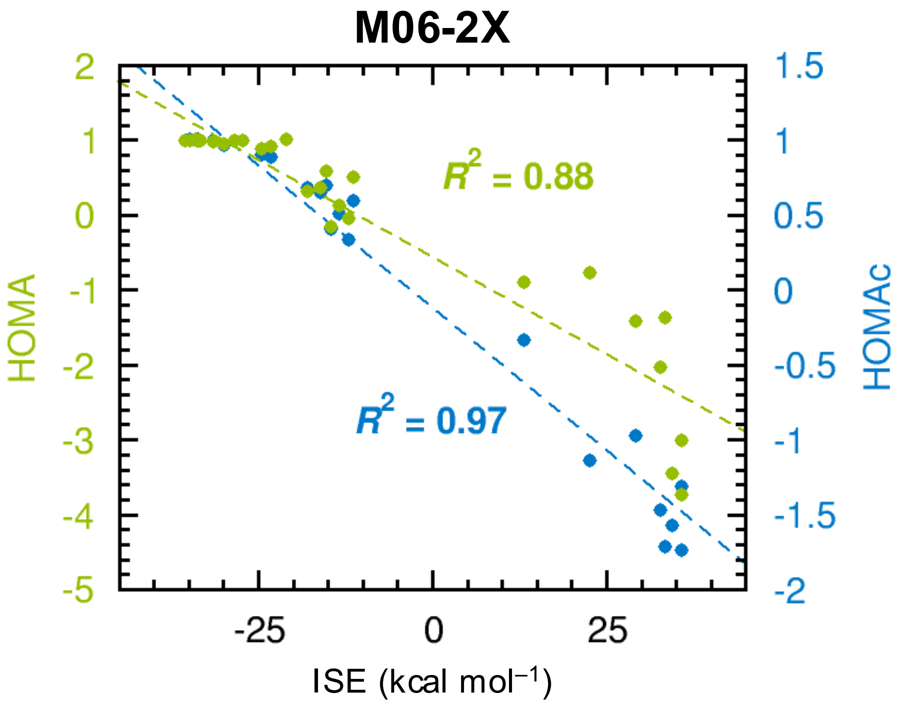


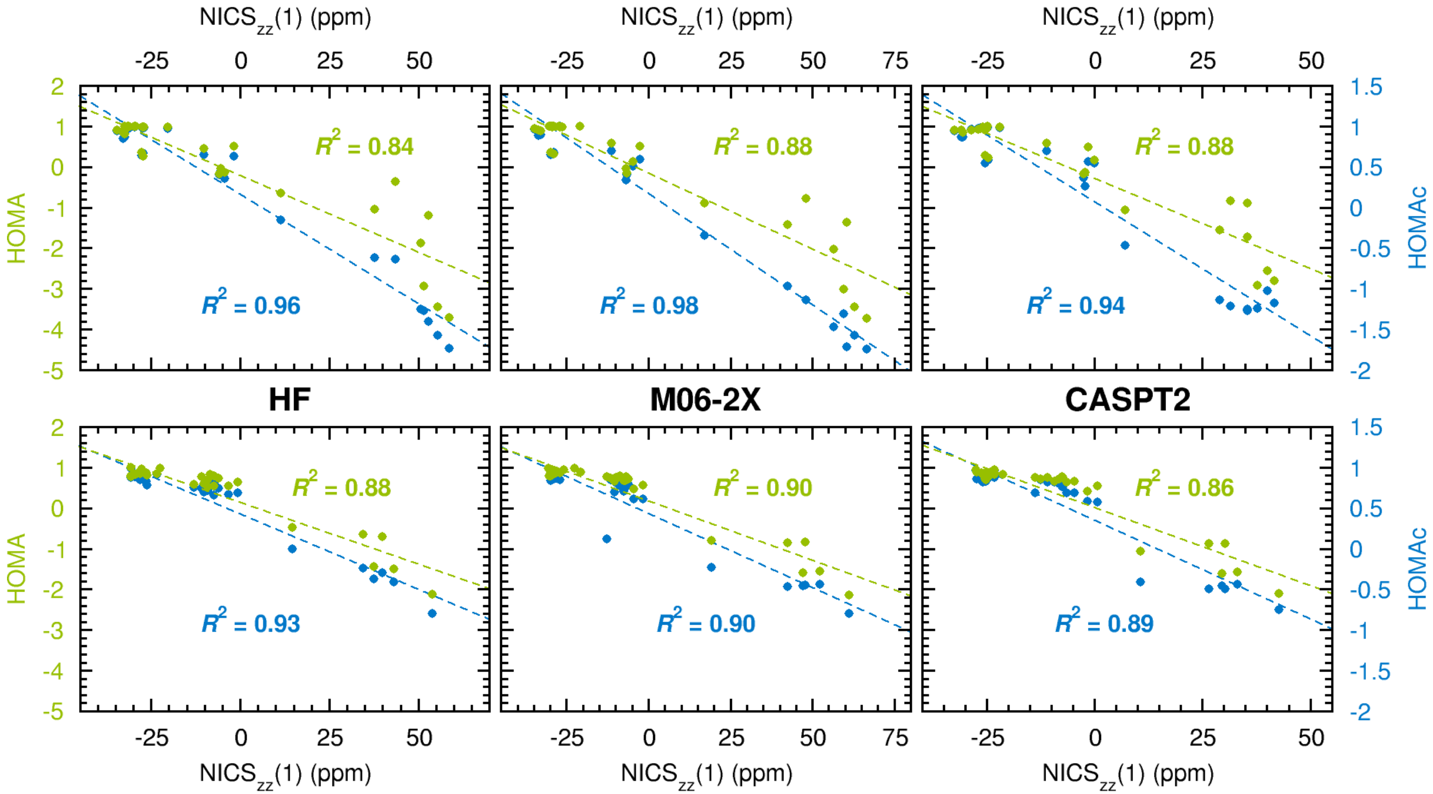
Assessment of HOMAc for GSAA

HOMA93	**HOMAc**	**NICS(1)$_{zz}$**
HF	HF	HF
M06-2X	M06-2X	M06-2X
CASPT2	CASPT2	CASSCF

cc-pVDZ basis set

Monocyclic systems only

Polycyclic systems only

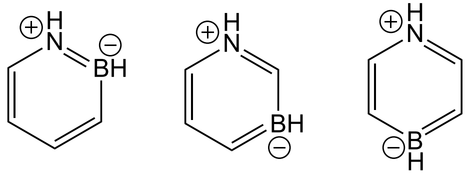


Conclusions

- HOMAc is an improvement over HOMA93, especially for monocyclic systems
- HOMAc parameters transferable to other methods than CASPT2

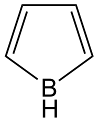
Some ongoing research

- **Deriving and testing HOMAc and HOMER parameters for other bonds than CC, CN, NN and CO**
  - CB, CS, CP, PP, NO and BN



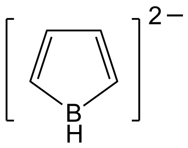
azaborines

S_0 aromatic



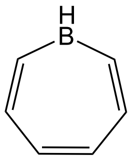
boroles

S_0 antiaromatic



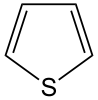
borole dianions

S_0 aromatic



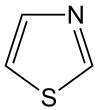
borepins

weakly S_0 aromatic



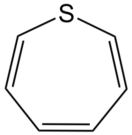
thiophenes

S_0 aromatic



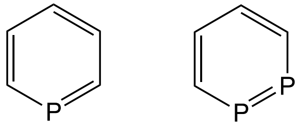
thiazoles

S_0 aromatic



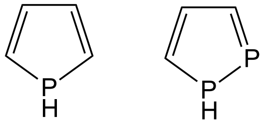
thiepines

S_0 antiaromatic



phosphorines

S_0 aromatic



phospholes

weakly S_0 aromatic

  - Poster by Sravan Perumalla, Sasi Institute of Technology & Engineering (CB, CS and CP)

- **Testing HOMER for other excited states than T_1**

ACKNOWLEDGMENTS


Baswanth Oruganti


Jun Wang


Michał Kochman


Enrique Arpa


Sravan Perumalla


Rafail Lingas

OTHER WORK IN THE FIELD

Gábor London, HUN-REN Research Centre for Natural Sciences, Budapest


Moumita Banerjee

COMPUTATIONAL RESOURCES AND FUNDING

NAISS

ÅFORSK

Wenner-Gren Foundations

Vetenskapsrådet

Stiftelsen Olle Engkvist Byggmästare
Signhild Engkvists Stiftelse

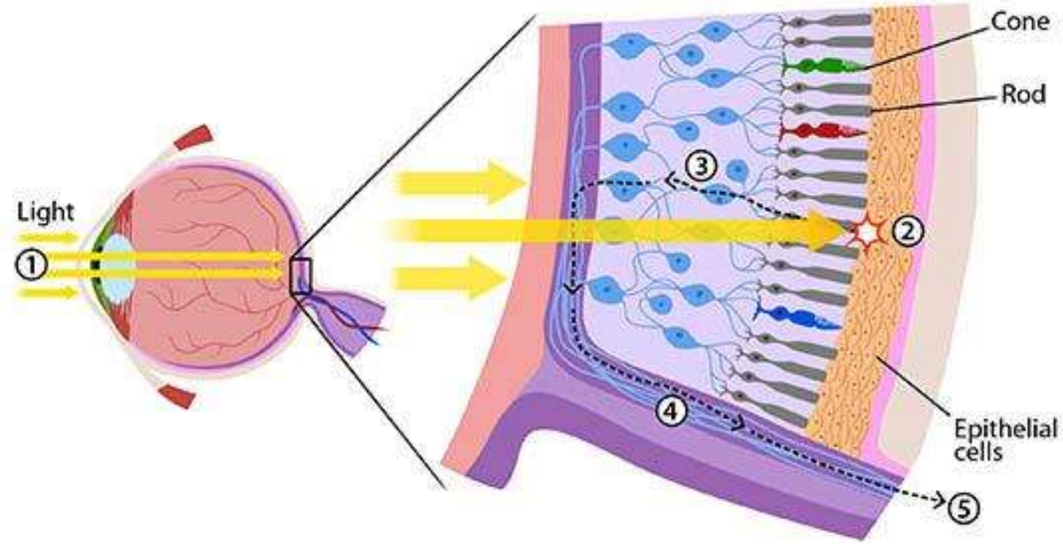

Carl Tryggers Stiftelse

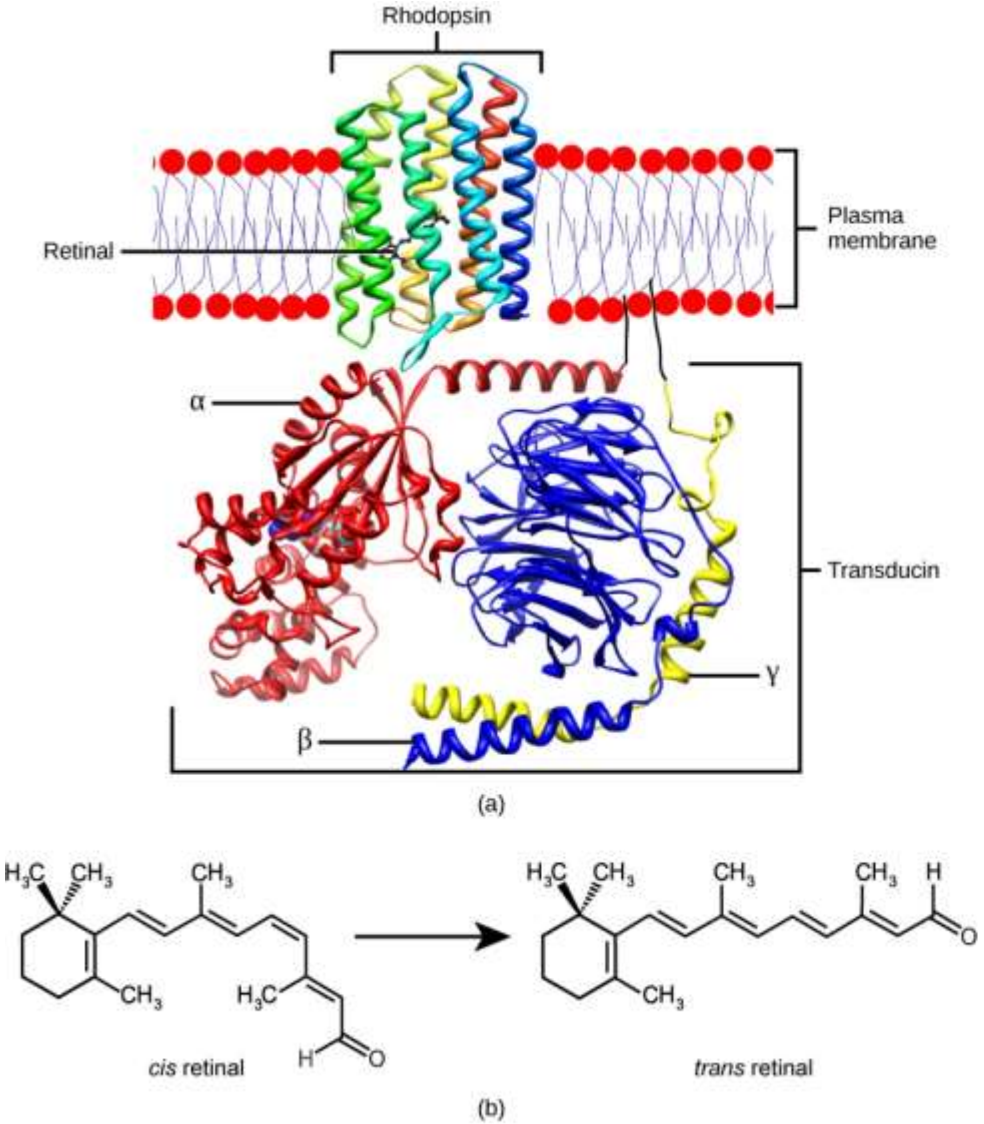
Excited state methods and photophysics

Debashree Ghosh

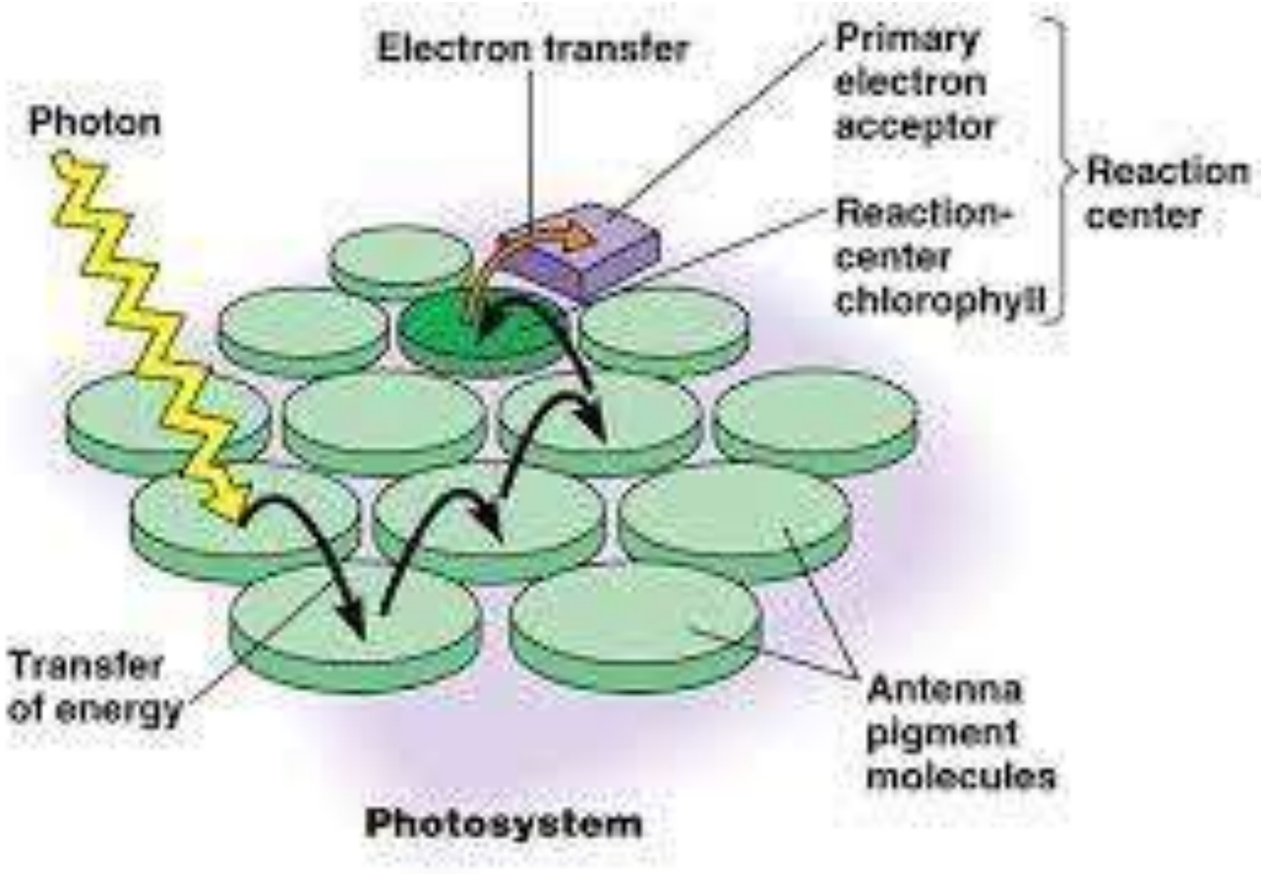
School of Chemical Sciences
Indian Association for the Cultivation of Science

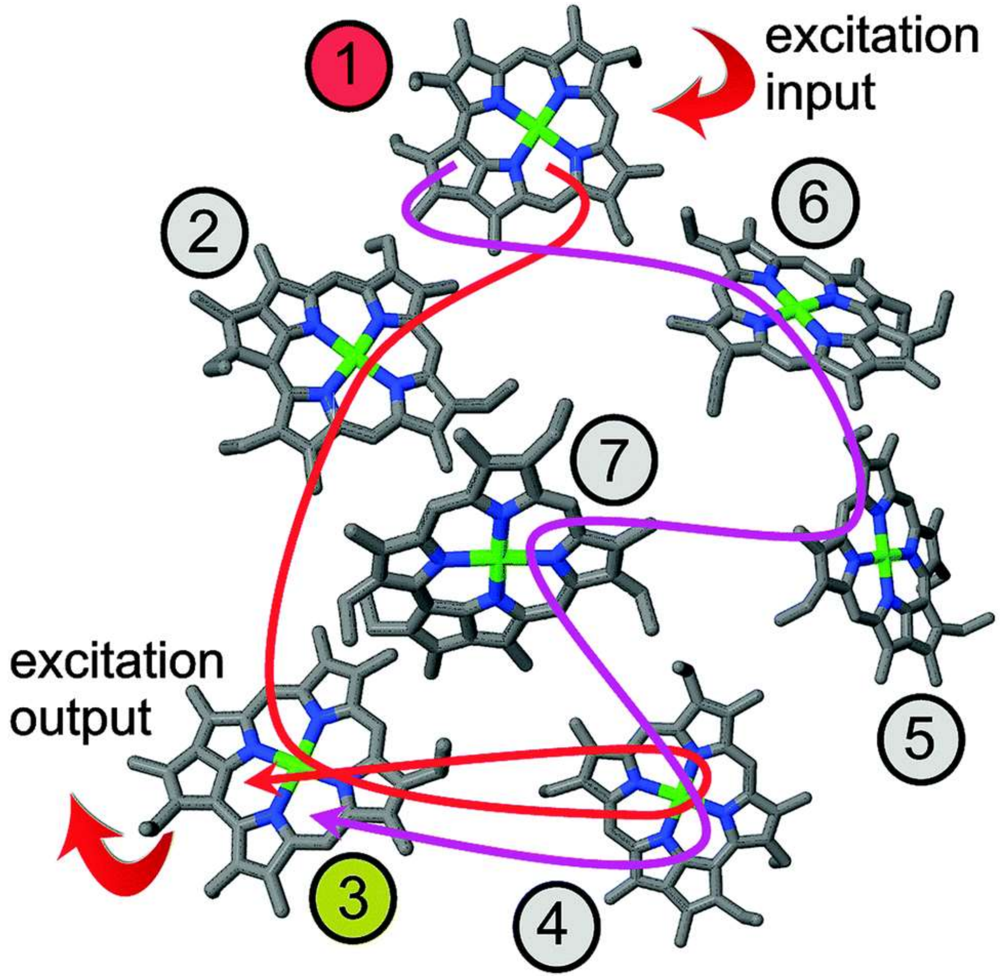
Vision


Light
①
Cone
Rod
③
②
④
Epithelial cells
⑤

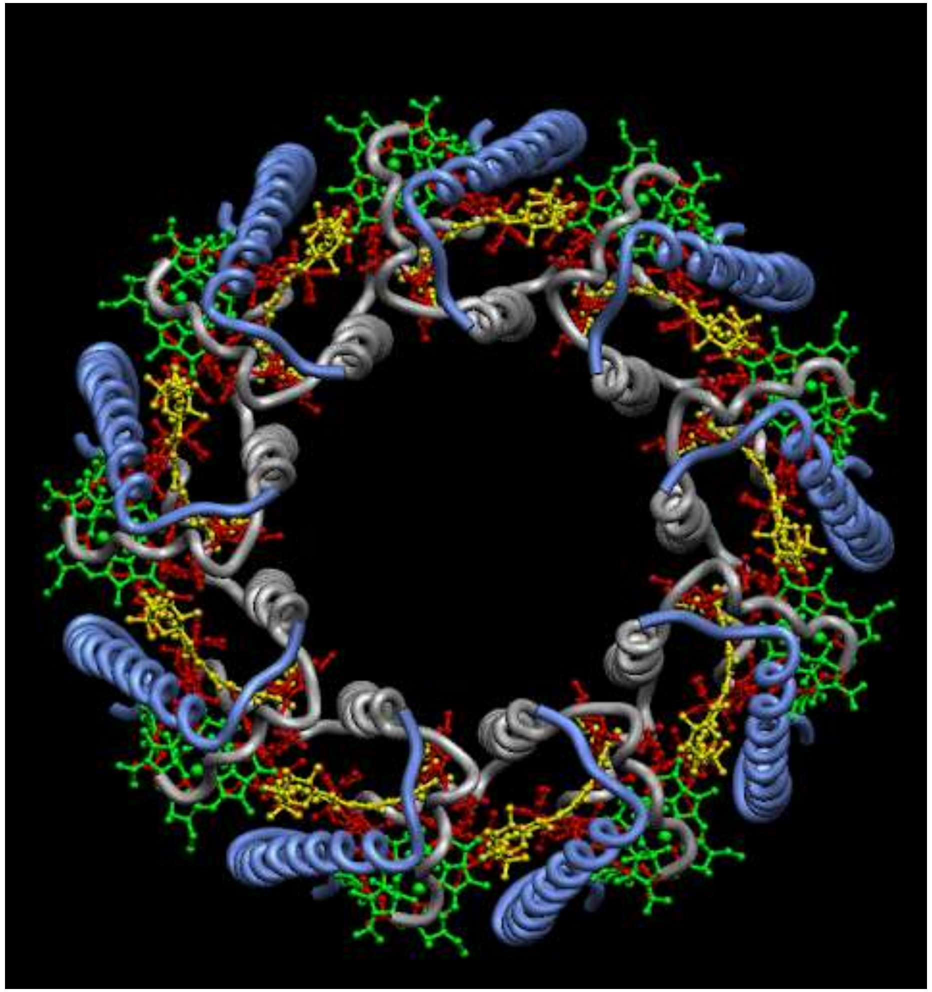

Rhodopsin
Retinal
Plasma membrane
α
Transducin
γ
β
(a)
H3C CH3
CH3
CH3
H3C
H
O
cis retinal
H3C CH3
CH3
CH3
H
O
CH3
trans retinal
(b)

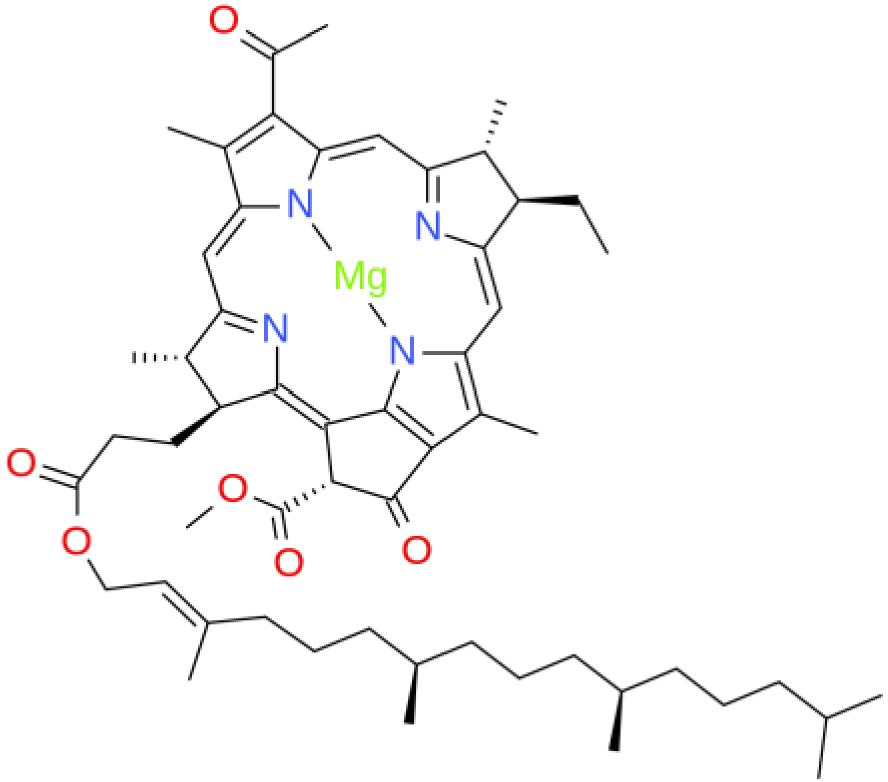
Light harvesting

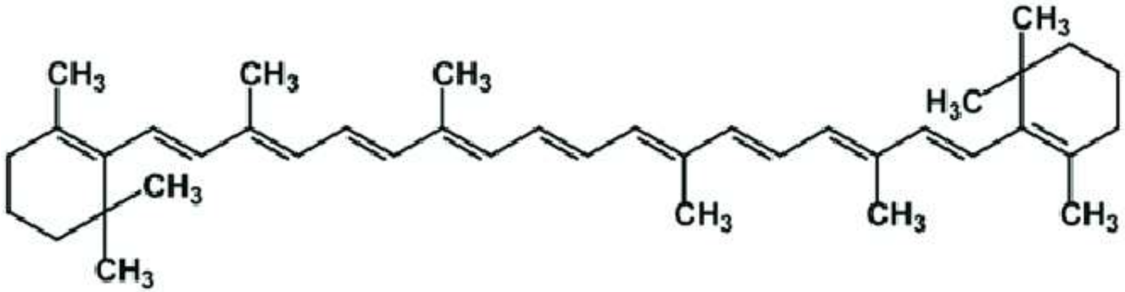




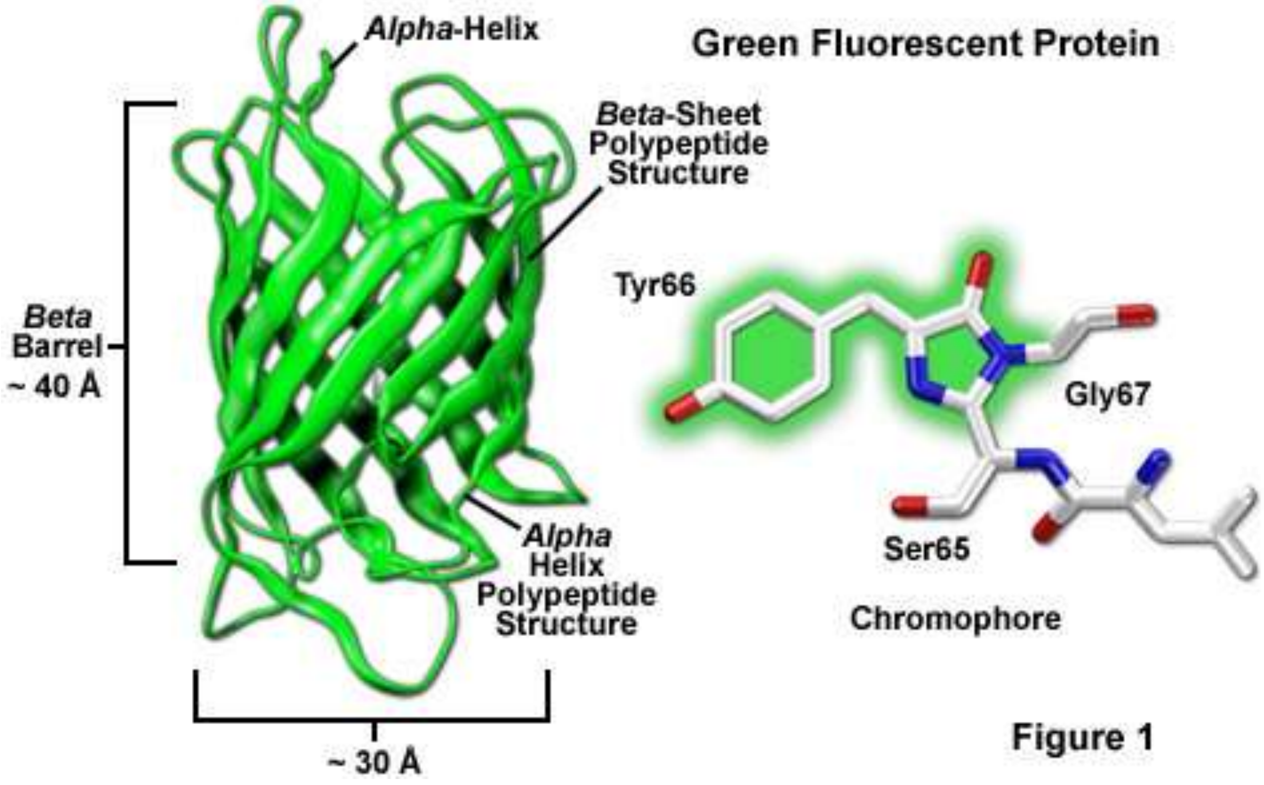
Light harvesting



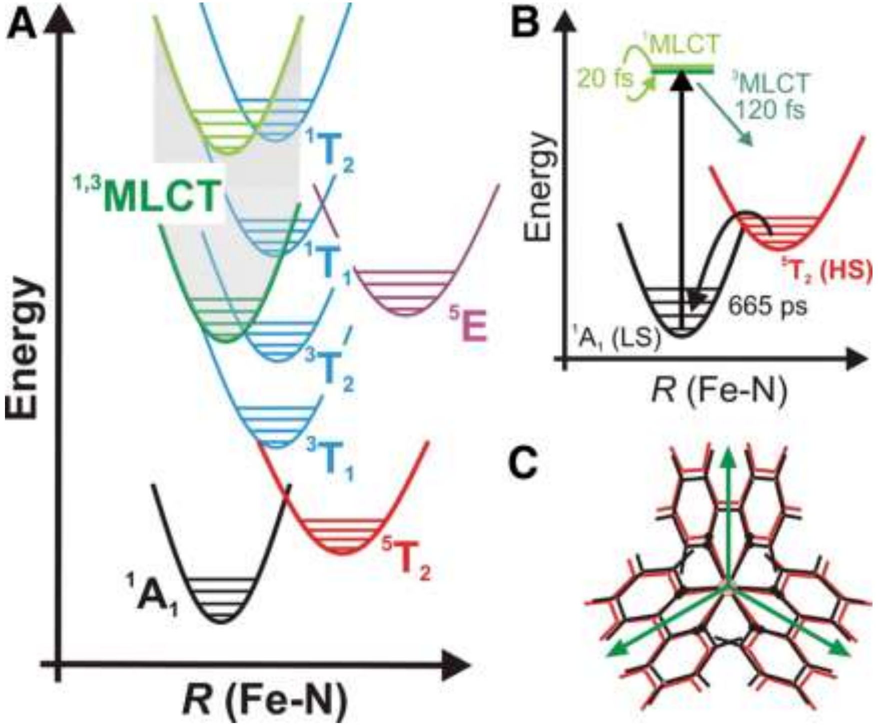


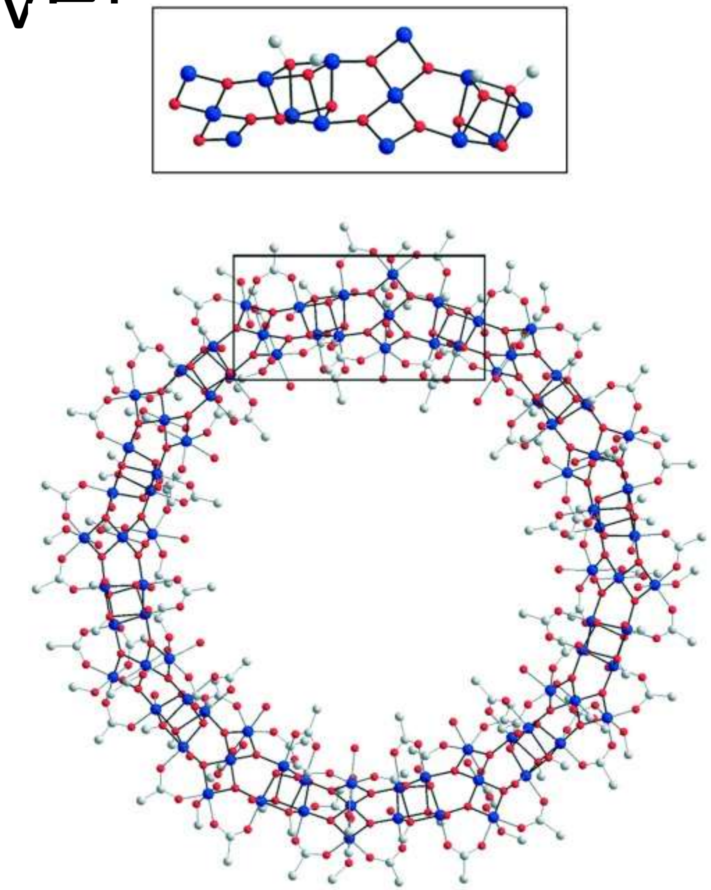


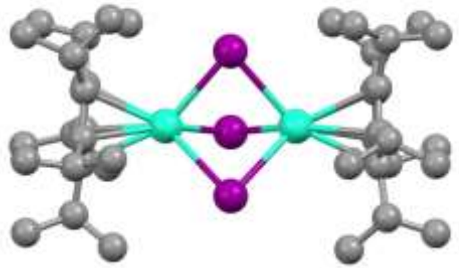
Green fluorescent protein



Light induced spin crossover





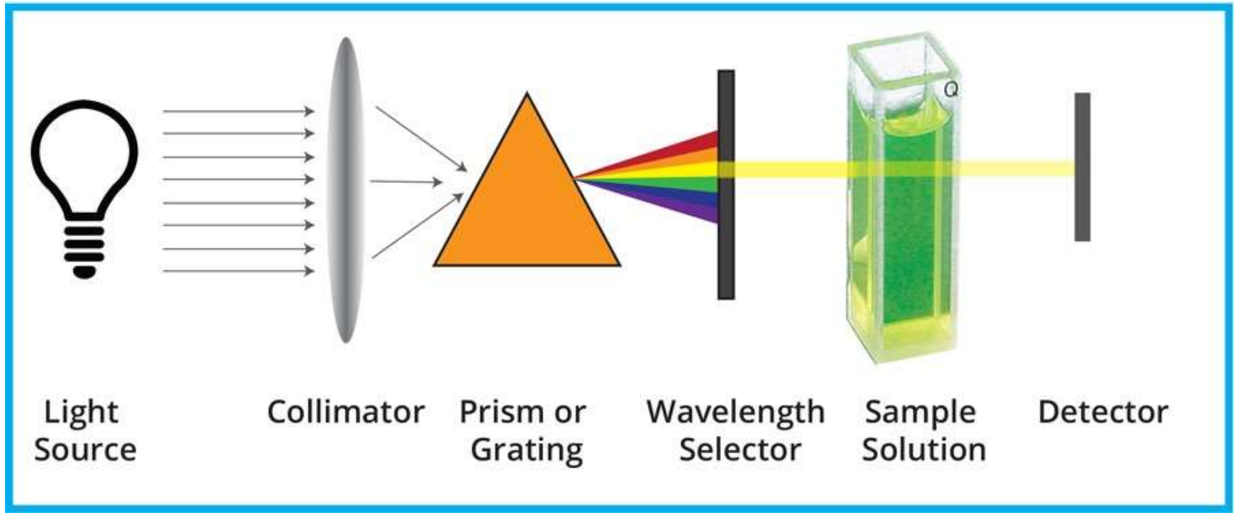


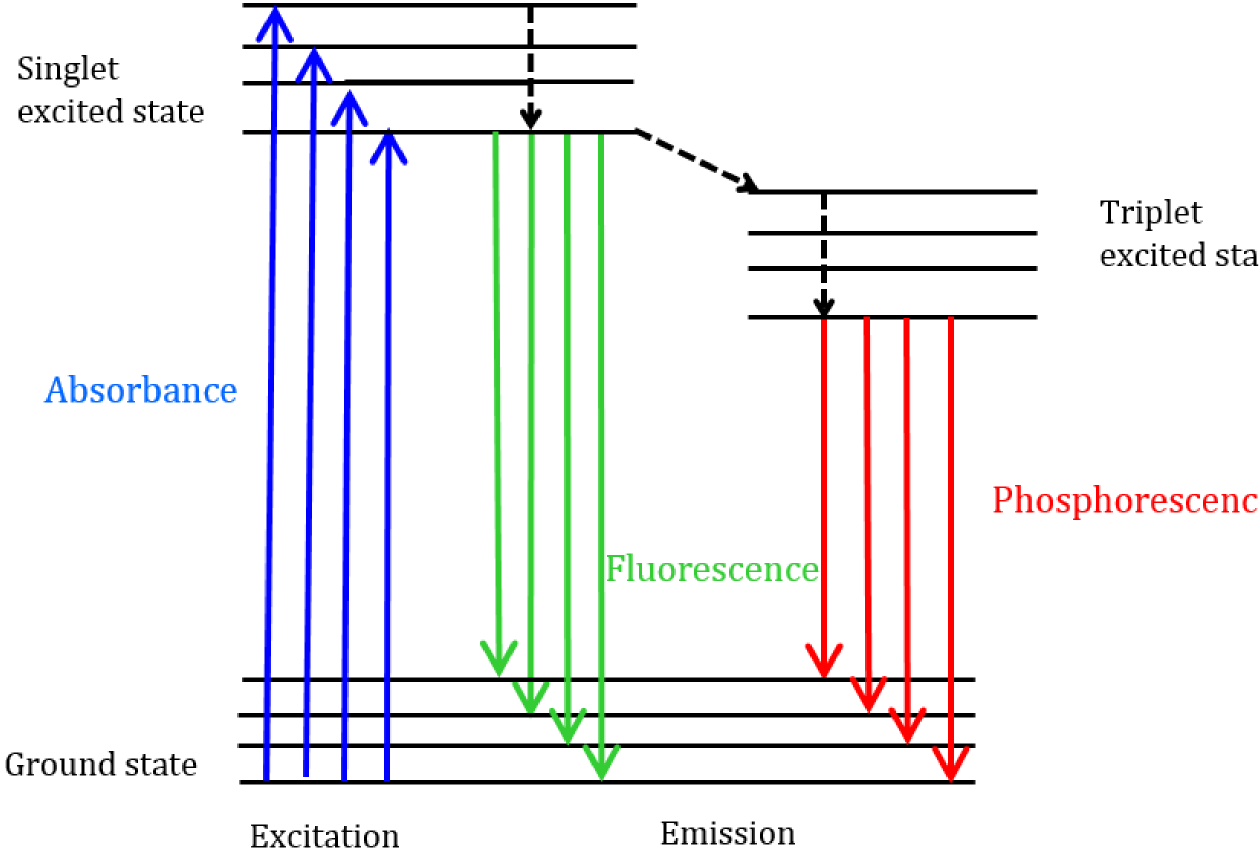
Change in electronic structure (spin) induced by external stimuli (light).

Molecular magnets and spin states in general

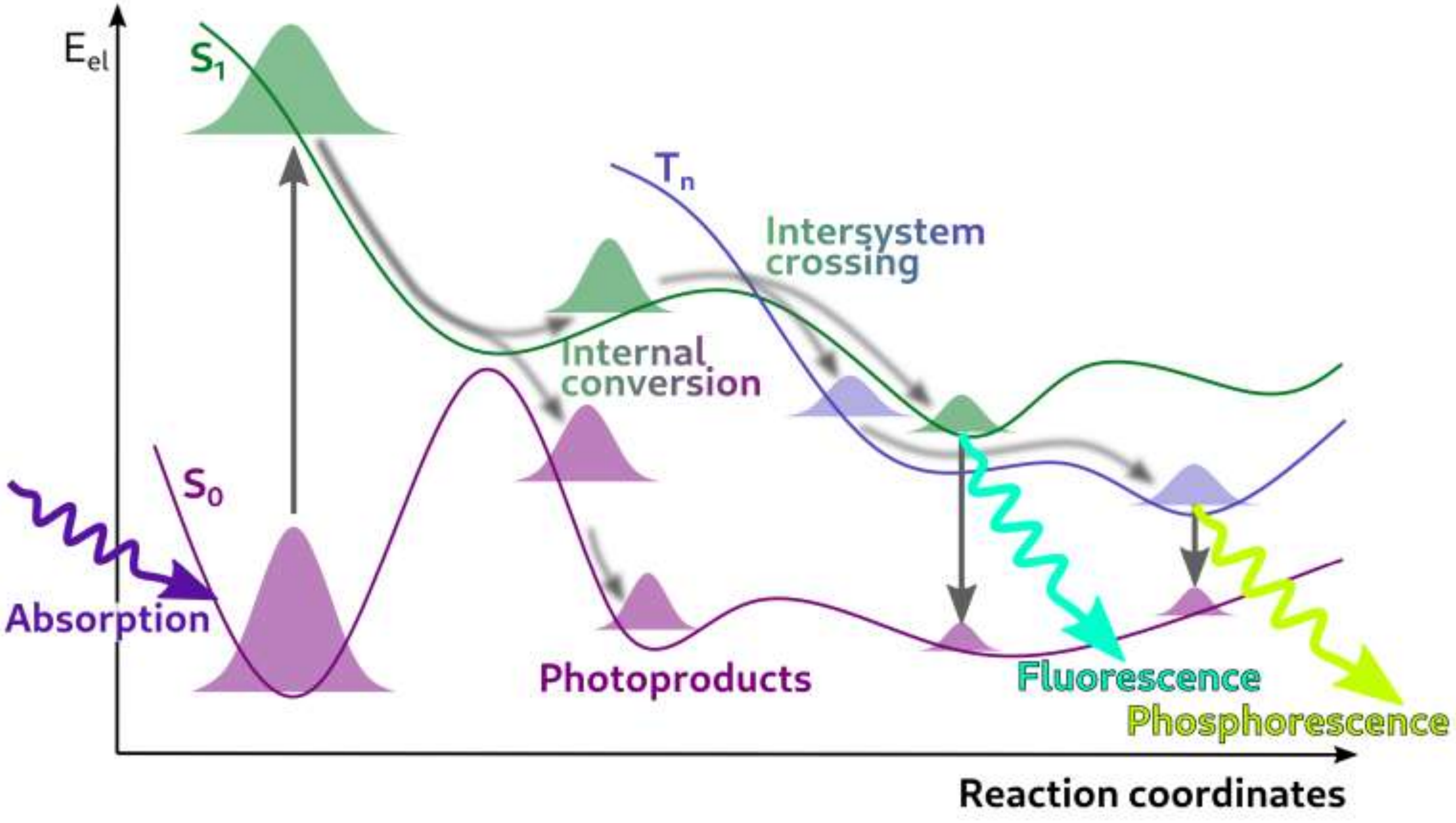
Schurkus, Chen, O’Rourke, Cheng, Chan, JPCL, (2020)

Spectroscopy to understand these processes



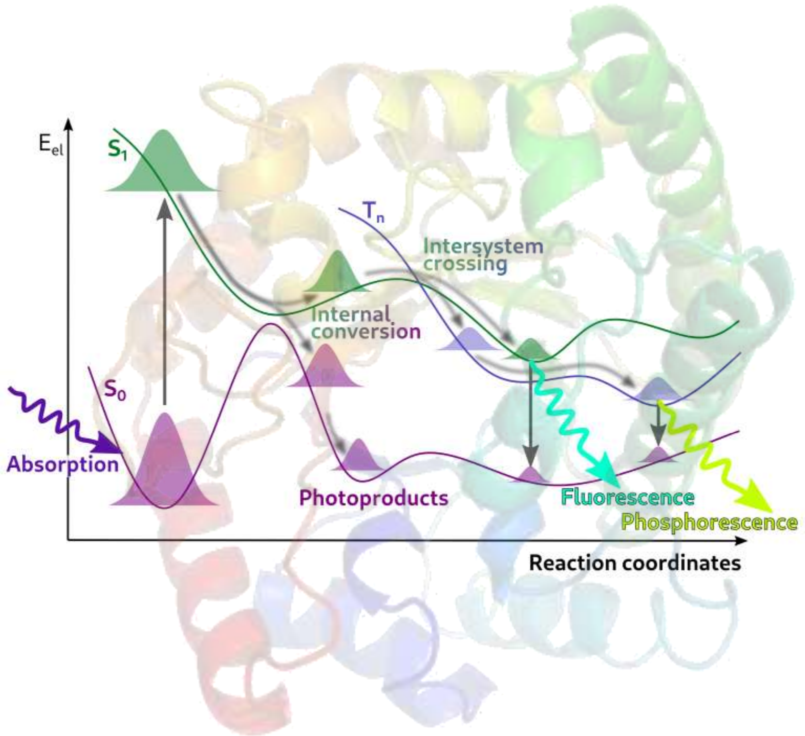


Excited state chemistry

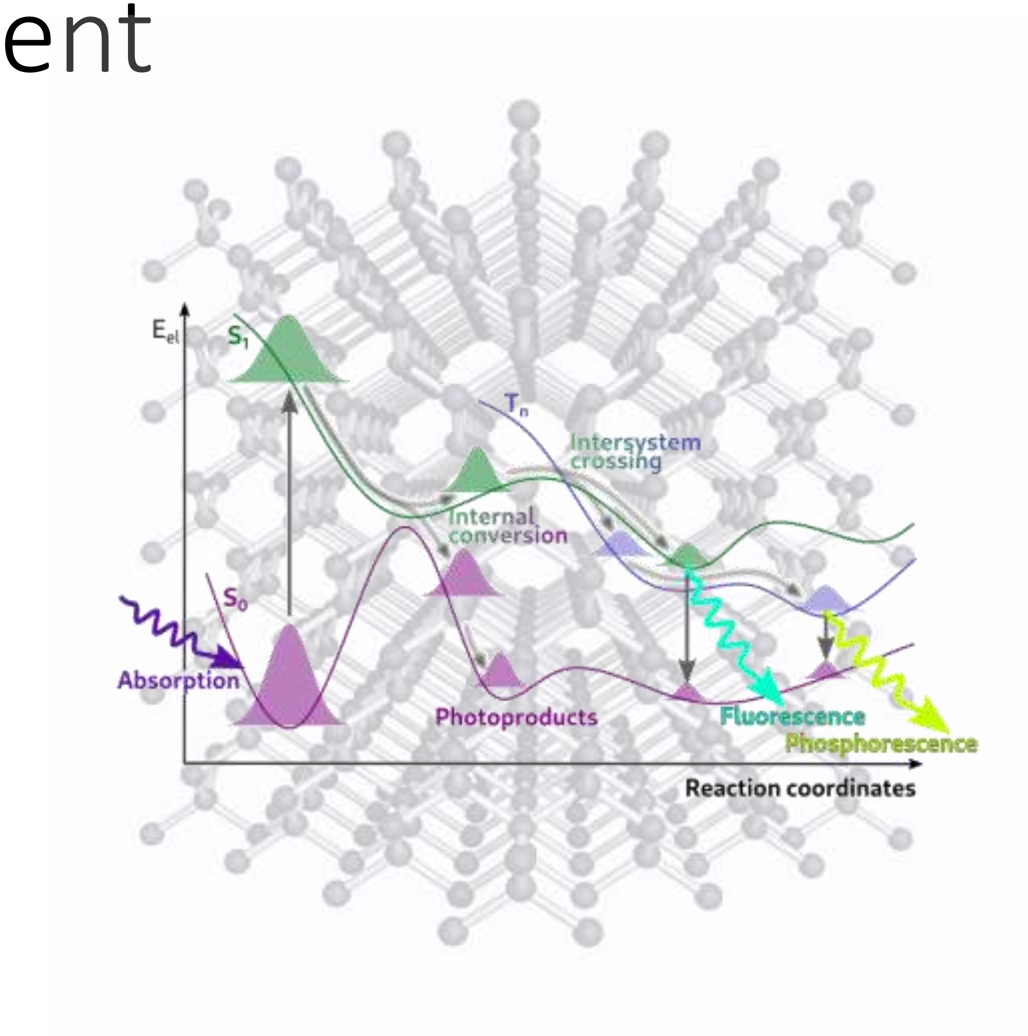


Choudhury, Santra, **DG**, *J Chem Theory Comput.*, 2024, **20**, 4951.

Excited state environment

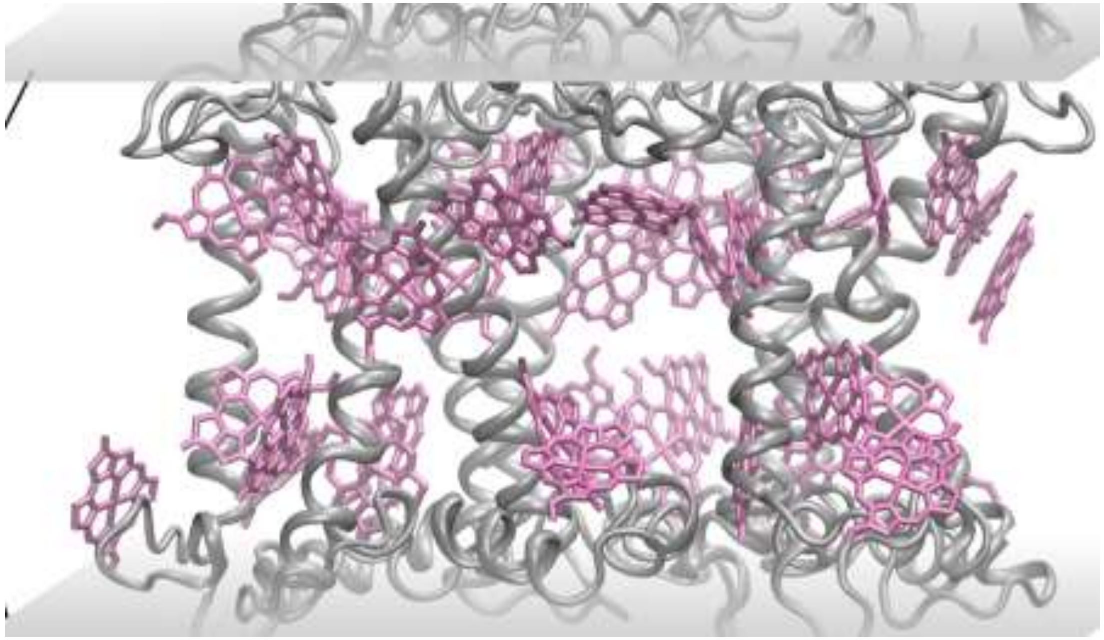


Biological environment



In crystal lattice

Multichromophore interactions



Multiple chromophores induce several interesting properties.

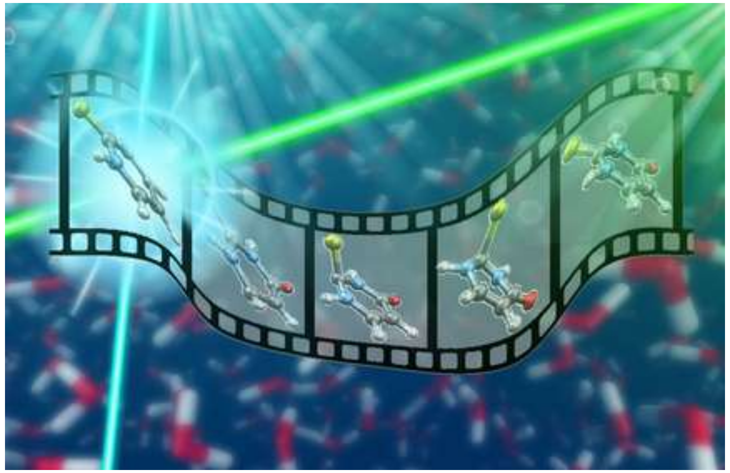
Energy transfer, e.g., photosynthetic systems.

Electron transfer.

Single reference QC methods

The electronic structure problem :

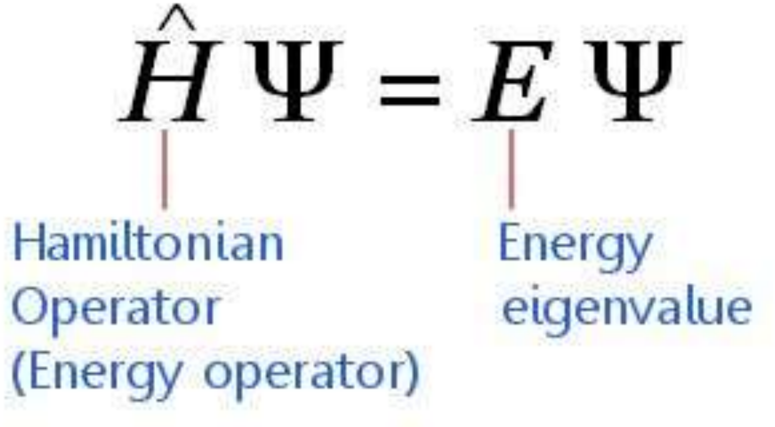
- Starts with Born Oppenheimer approximation
- Mean field approximation – orbitals solved with a Hartree-Fock self consistent field theory.
- Perturbative correction to obtain electronic correlation, e.g., MP2, CCSD etc.



Electronic structure of ground and excited states at each instant of the dynamics.

Mai, Gonzalez, Angew Chem, (2020)

Theoretical ground and excited states



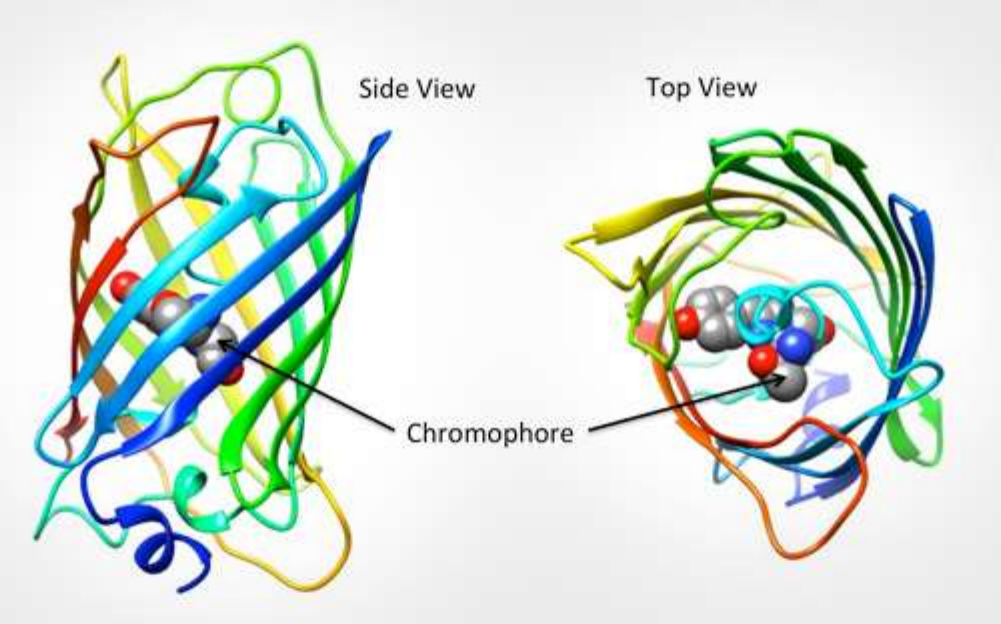
$$\hat{H}\,\Psi = E\,\Psi$$

Hamiltonian
Operator
(Energy operator)

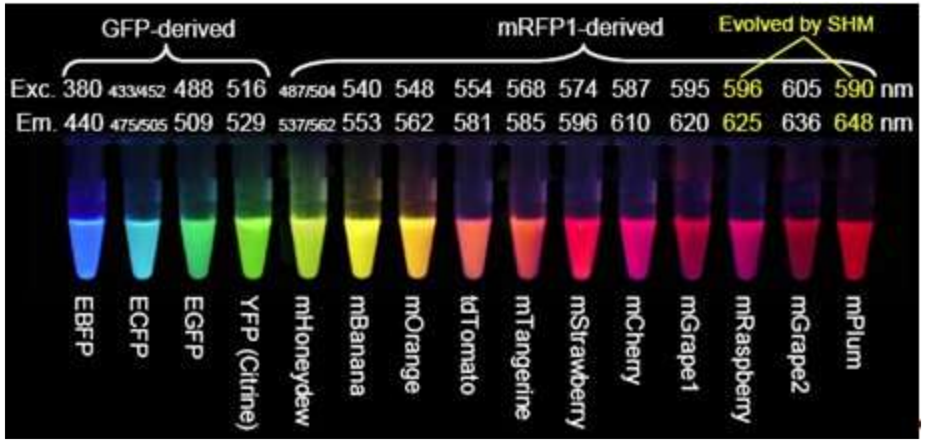
Energy
eigenvalue

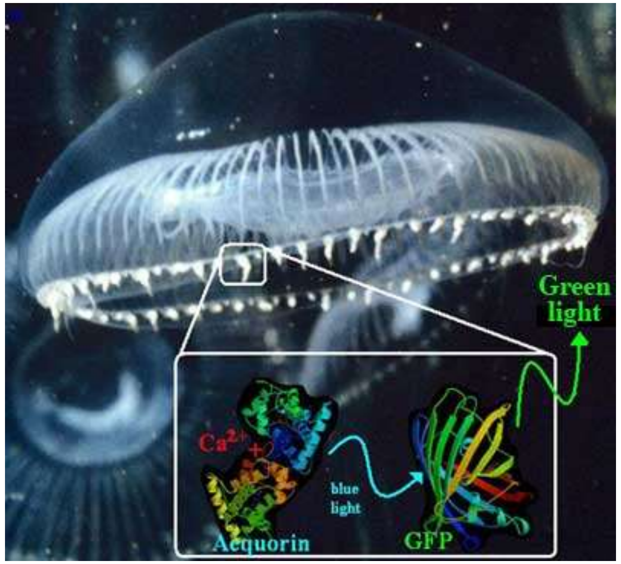
$$E = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}$$

Fluorescent protein



Mutation can tune the spectra considerably.

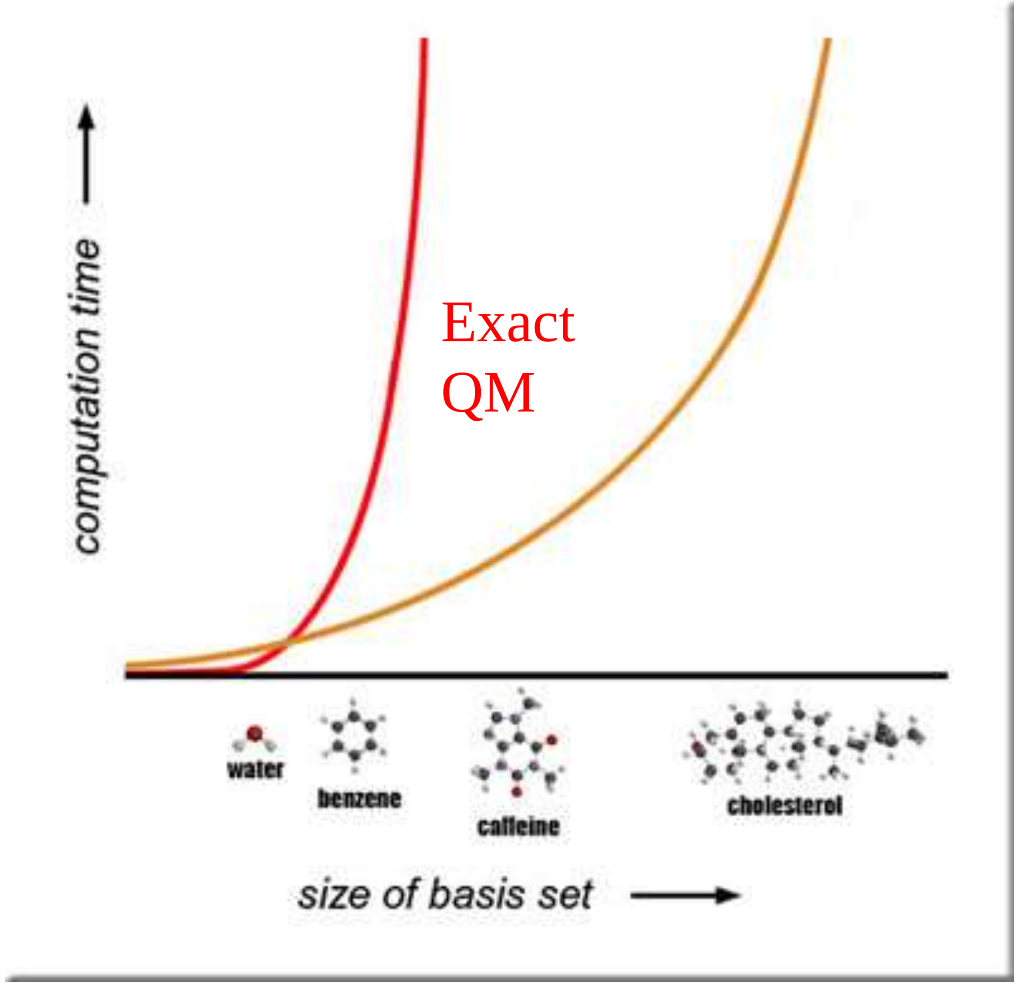




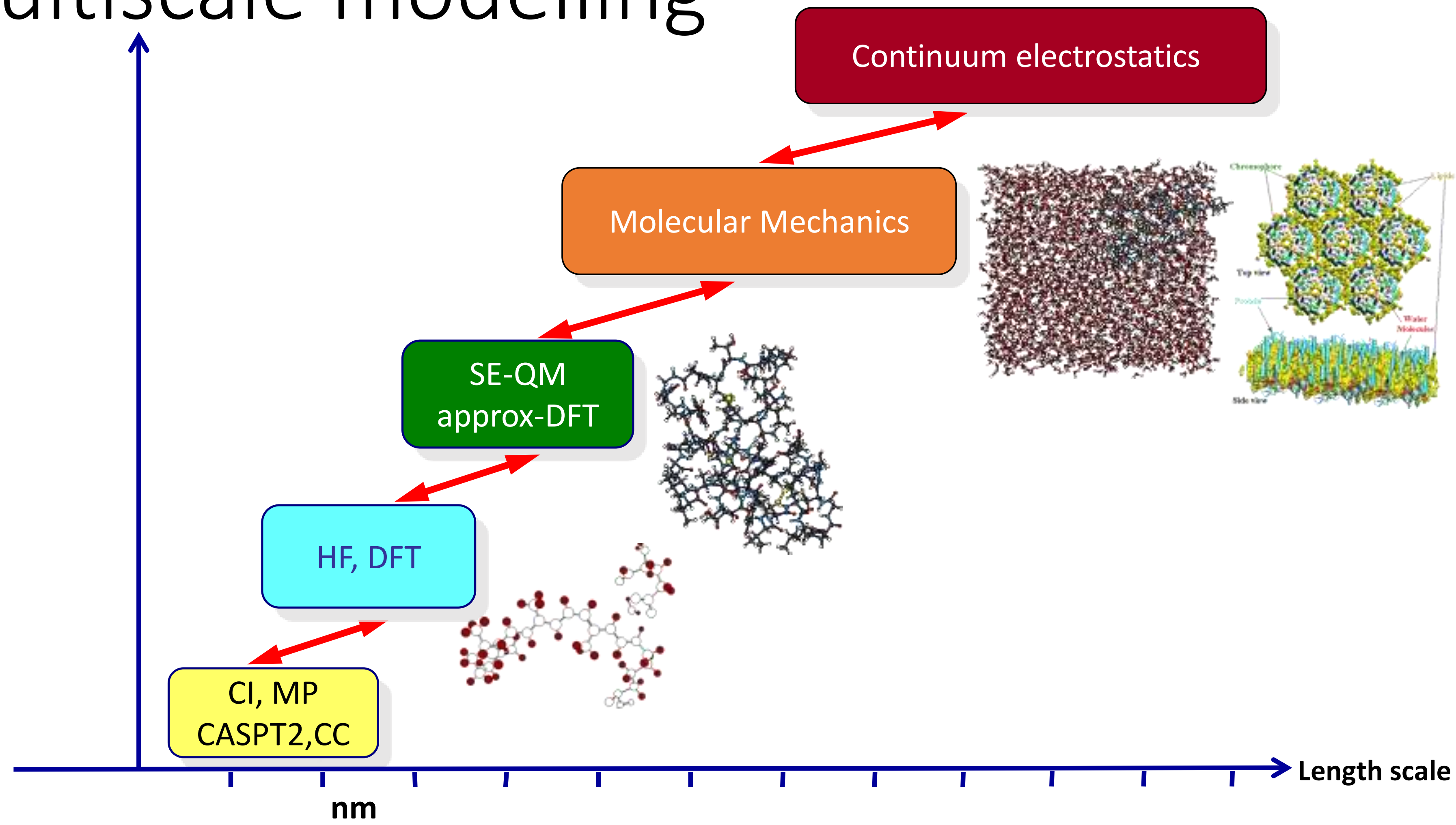
Computational approaches

Quantum mechanics (QM)

- Highly Accurate
- Electronic properties
- Computationally expensive

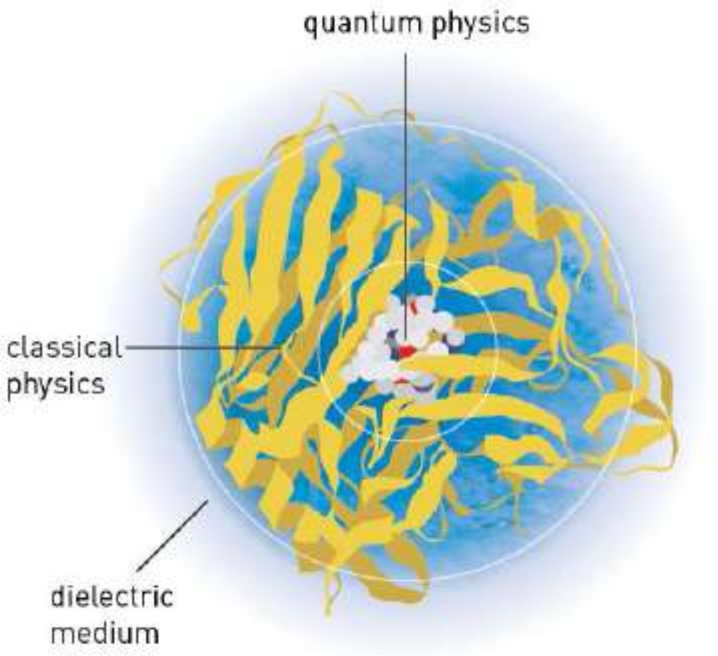


Multiscale modelling



Hybrid QM/MM

- Even with these approximations, there are too many degrees of freedom.
- Quantum chemical methods are too slow for 100-1000 atom problems.
- Best of both worlds – quantum and classical methods side by side.
- Speed of molecular mechanics.
- Accuracy of quantum mechanics.

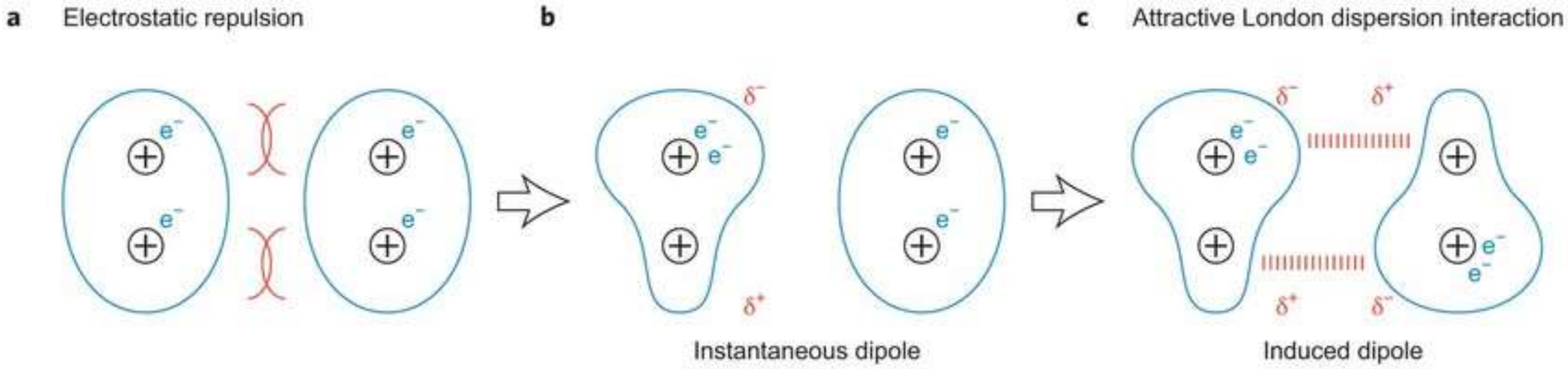


GLIMPSE AT MOLECULAR MECHANICS

What does it look like :

$$E_{MM} = \sum_{bonds} k_d \left(d - d_0\right)^2 + \sum_{angles} k_\theta \left(\theta - \theta_0\right)^2 + \sum_{dihedrals} k_\phi \left(1 + \cos\left(n\phi + \delta\right)\right)$$

$$+ \sum_{\substack{nonbonded \\ pairs}} \left\{ \varepsilon_{AB} \left[\left(\frac{\sigma_{AB}}{r_{AB}} \right)^{12} - \left(\frac{\sigma_{AB}}{r_{AB}} \right)^{6} \right] \right\} + \sum_{\substack{nonbonded \\ pairs}} \frac{1}{4\pi\varepsilon_0} \frac{q_A q_B}{r_{AB}}$$



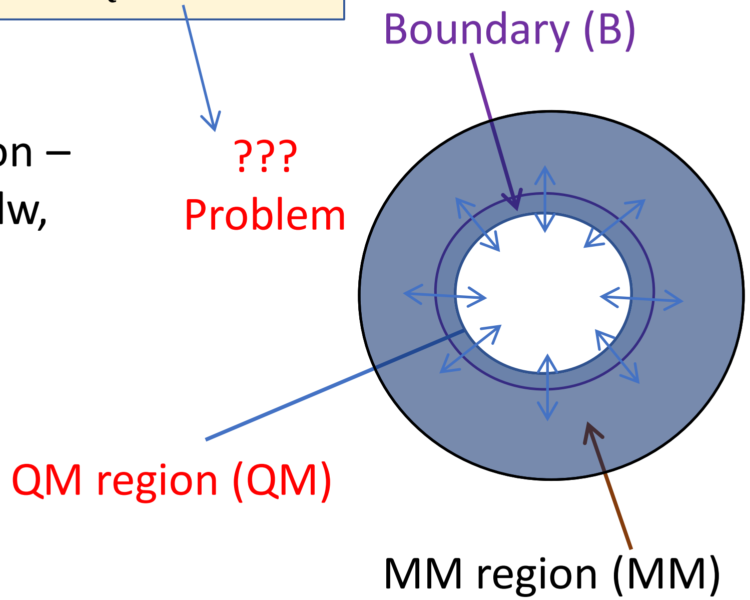
EMBEDDING - ADDITIVE

$$E_{system} = E_{QM}(\mathrm{QM}) + E_{MM}(\mathrm{MM}) + E_{QM-MM}(B)$$

$$\frac{\langle \psi H \psi \rangle}{\langle \psi \psi \rangle}$$

Energy of the MM region – bond, angle, torsion, vdw, electrostatics

???
Problem



- Polarization of the MM region on the QM region.
- QM-MM coupling is complicated
- Complexity

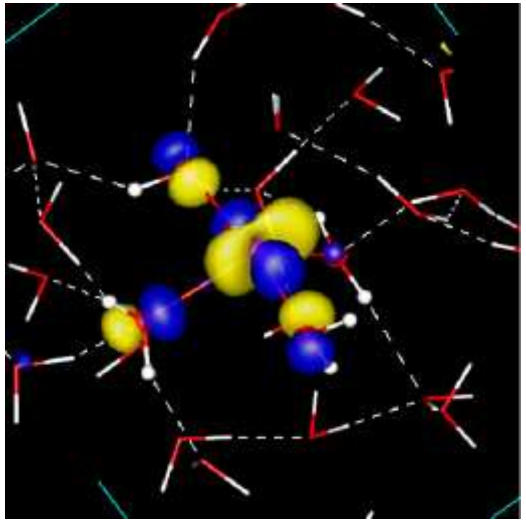
QM

MM

?

ADDITIVE – QM-MM INTERACTION ($E_{QM\text{-}MM}$)

- Electronic embedding
  - MM point charges affect the Hamiltonian (one electron terms) of the QM region.
  - Polarization is included.

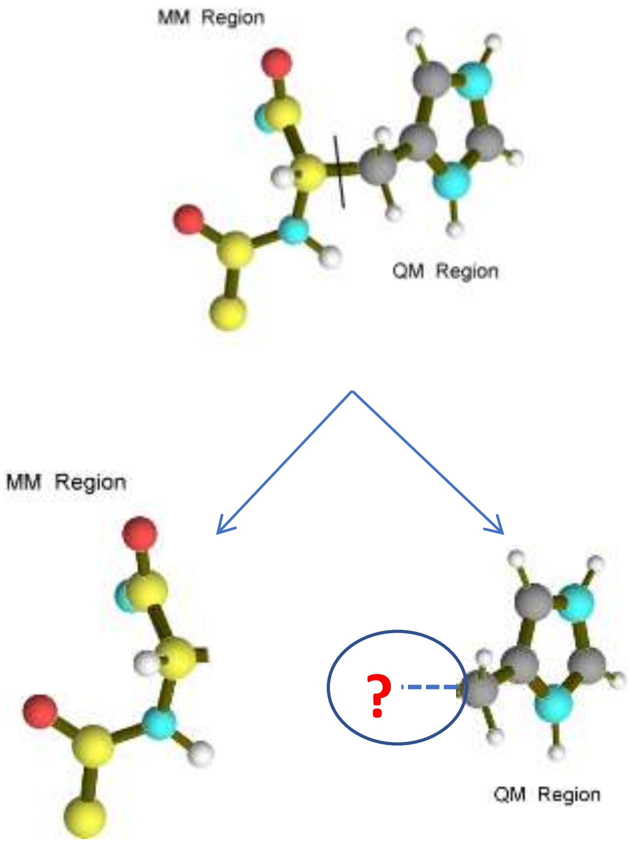


$$H = H_{QM} + H_{QM-MM}$$

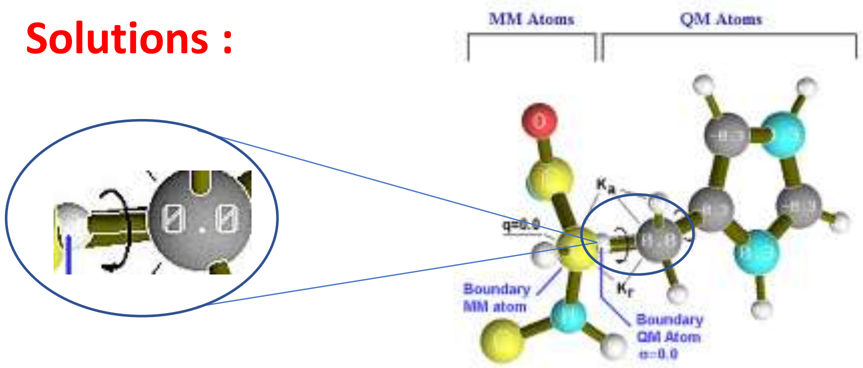
$$H_{QM-MM} = \sum_{i \in MM} q_i \int \frac{\rho_{QM}(r)}{|\mathrm{r} - \mathrm{r}_i|} dr$$

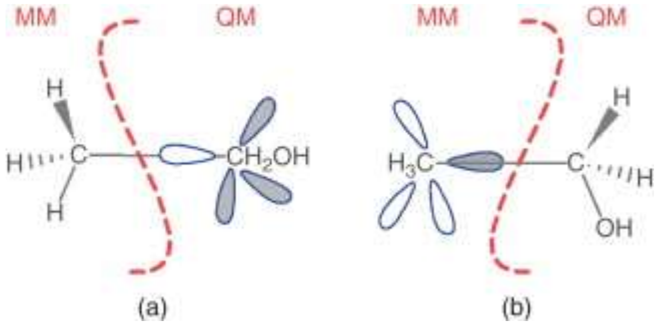
PROBLEM WITH THE QM-MM BOUNDARY

- Dangling bonds of the QM atom at the QM-MM



Solutions :



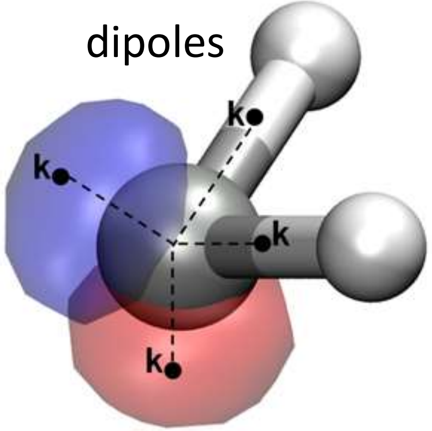


POLARIZABLE MOLECULAR MECHANICS

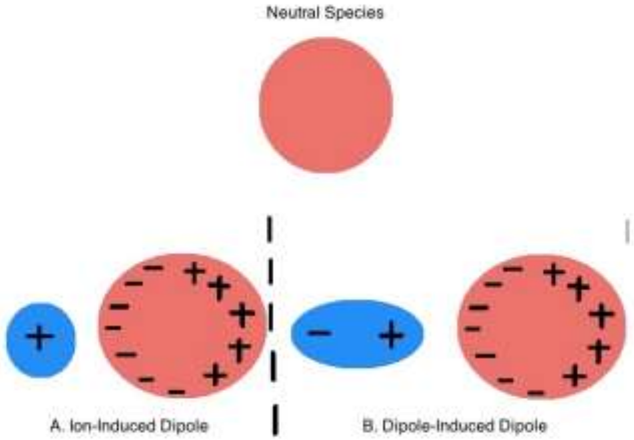
Induced Dipoles

Warshel, Levitt

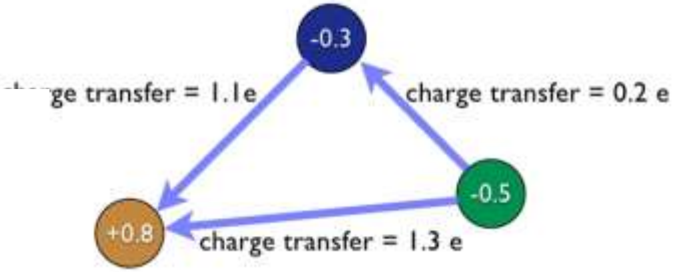
Distributed induced dipoles



Gordon, Kongsted, Ponder

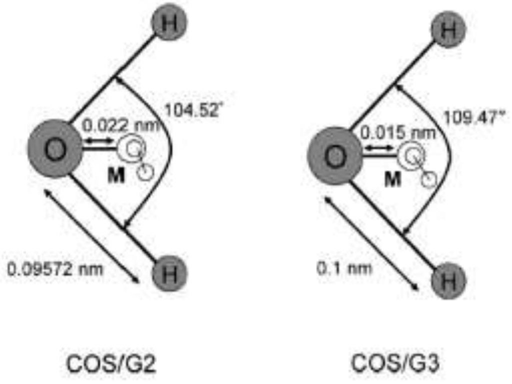


Fluctuating charges



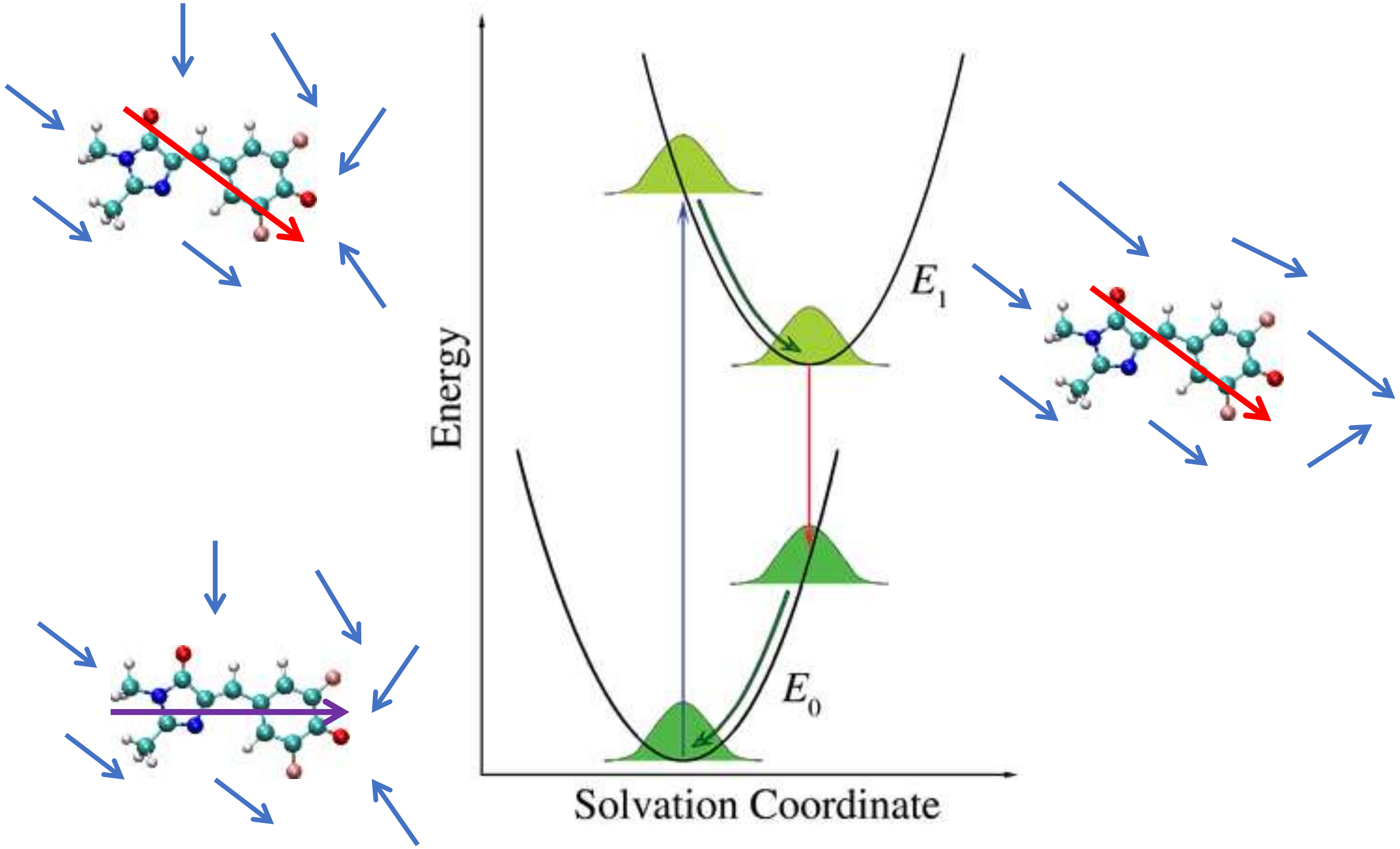
Berne, Friesner, Martinez

Drude oscillator

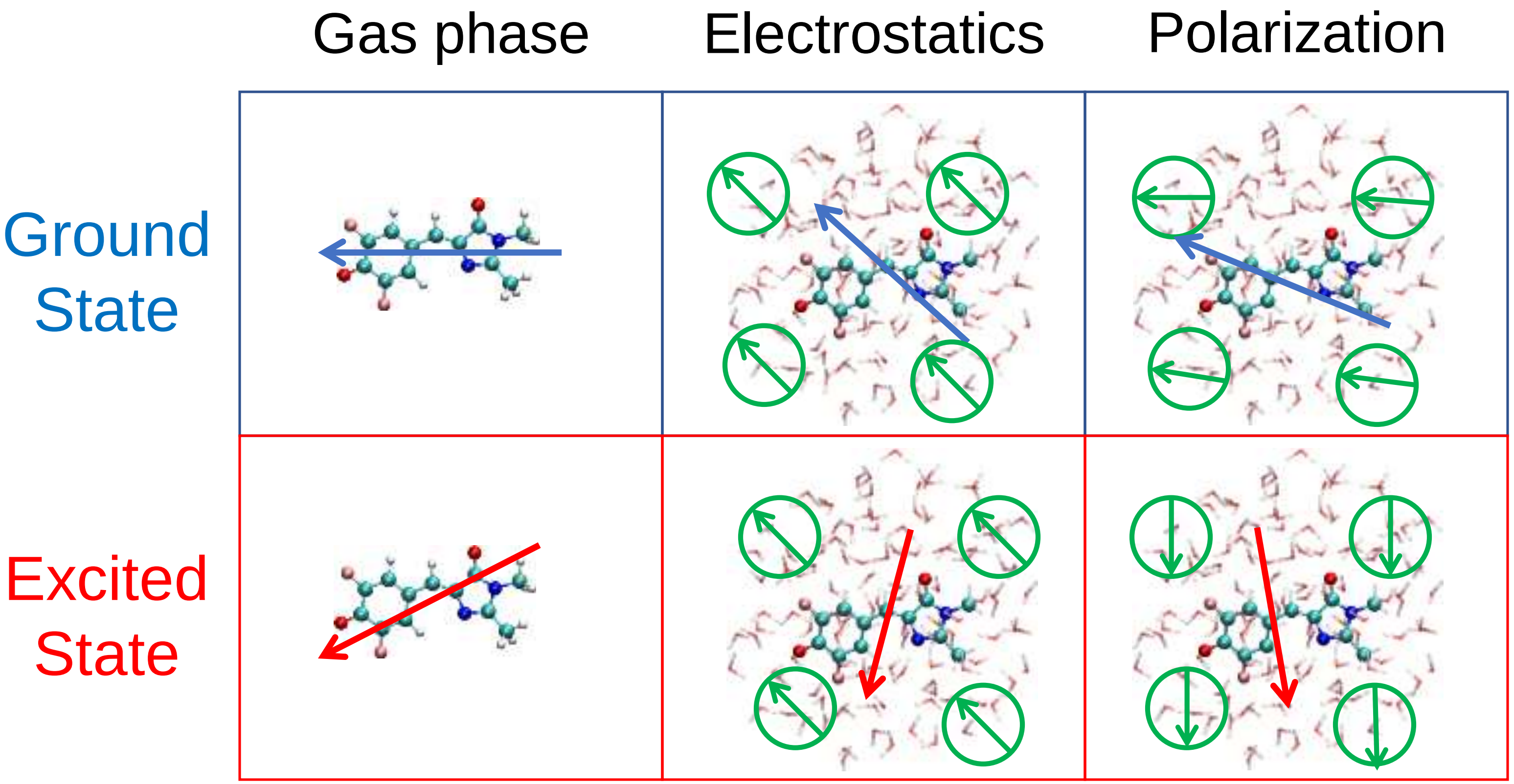


Roux, Jordan

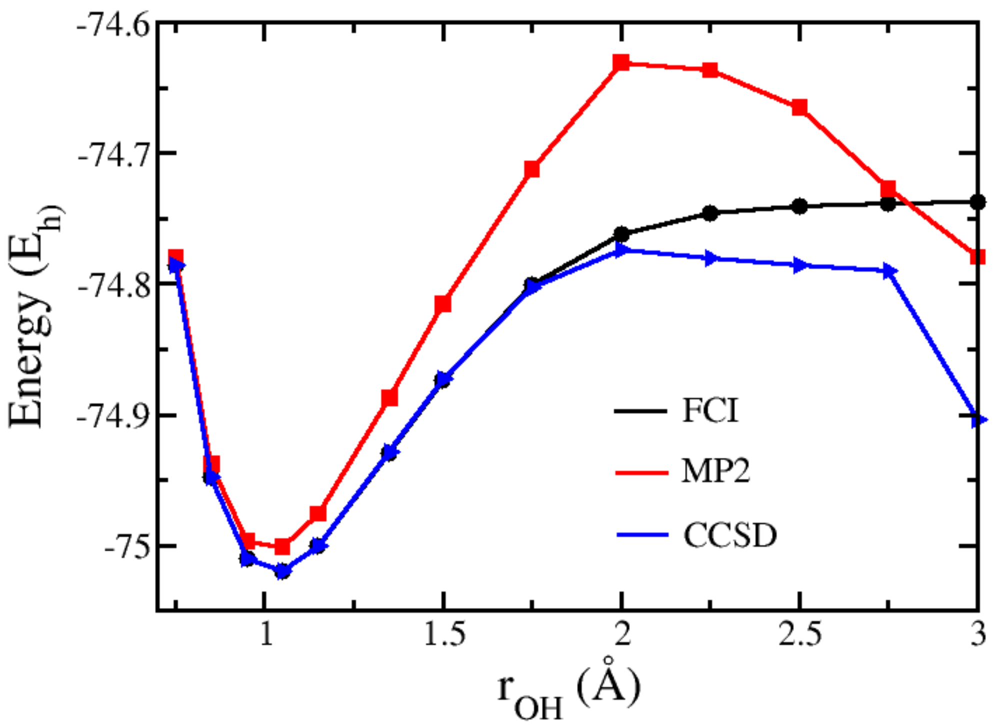
Environment effect on excited state

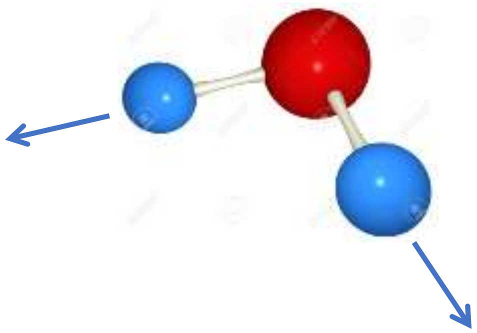


QM/EFP (excited state)



Difficulty with strong correlation



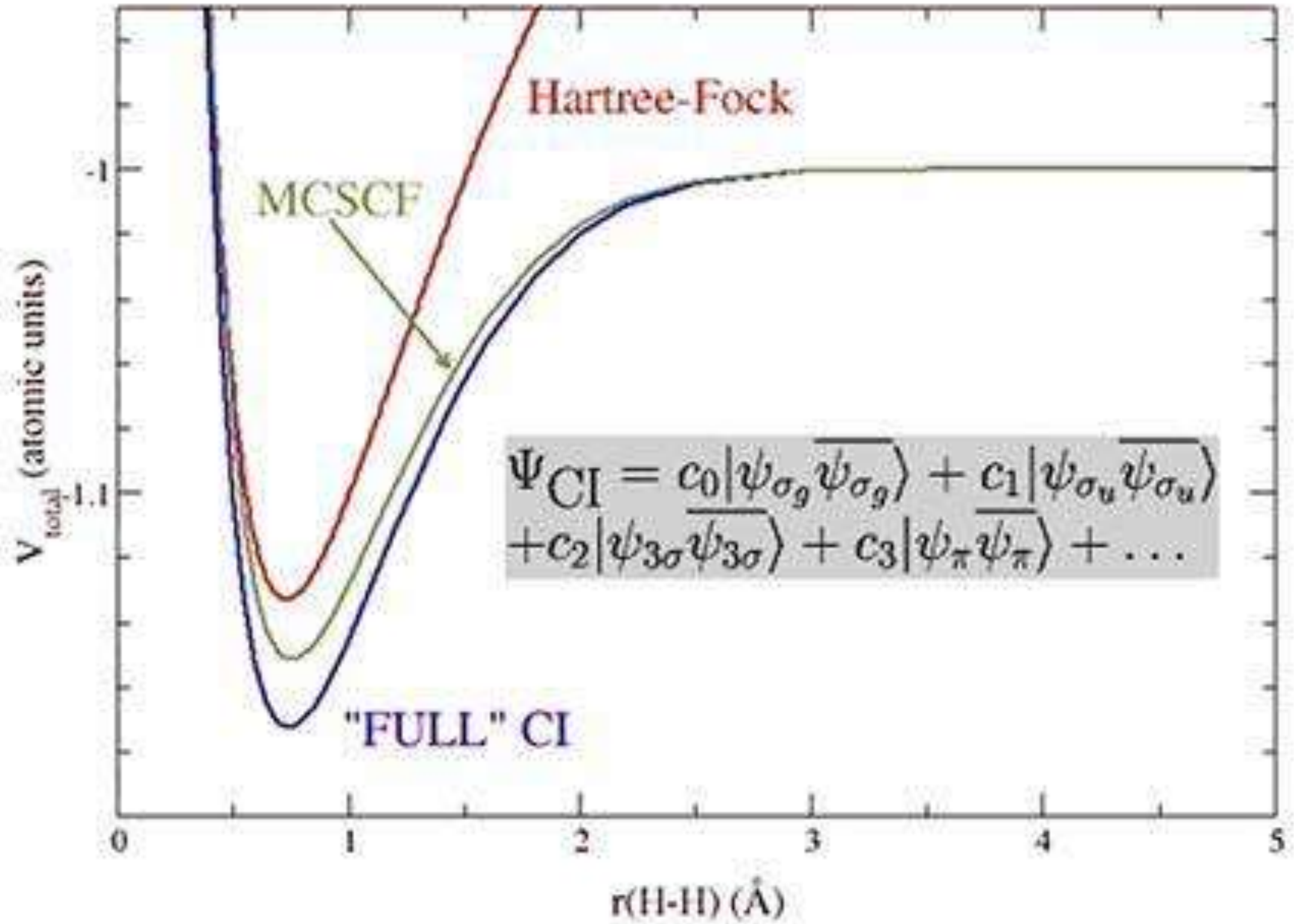


This effect shows up in :

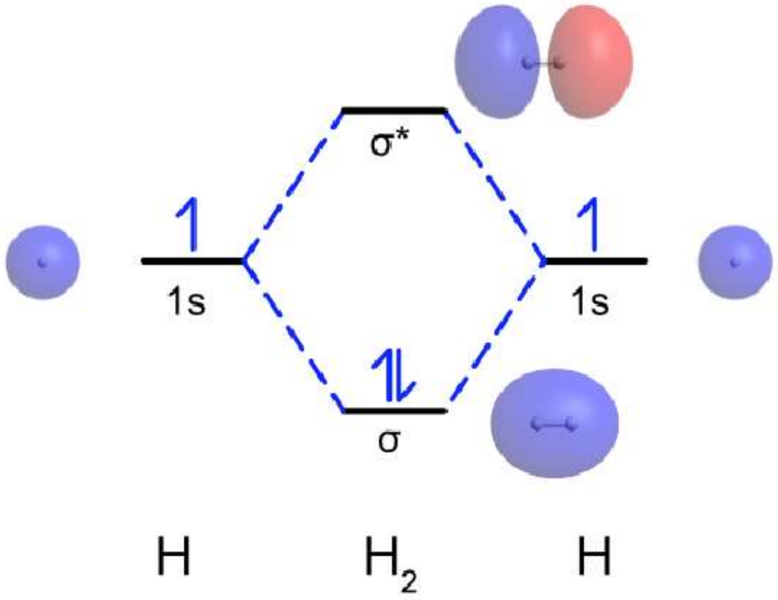
- Excited states
- Di-, tri-radicals
- Transition metal complexes
- Polyenes, graphene etc
- Metal clusters

Need for multireference or multiconfiguration methods in the valence space

Multireference

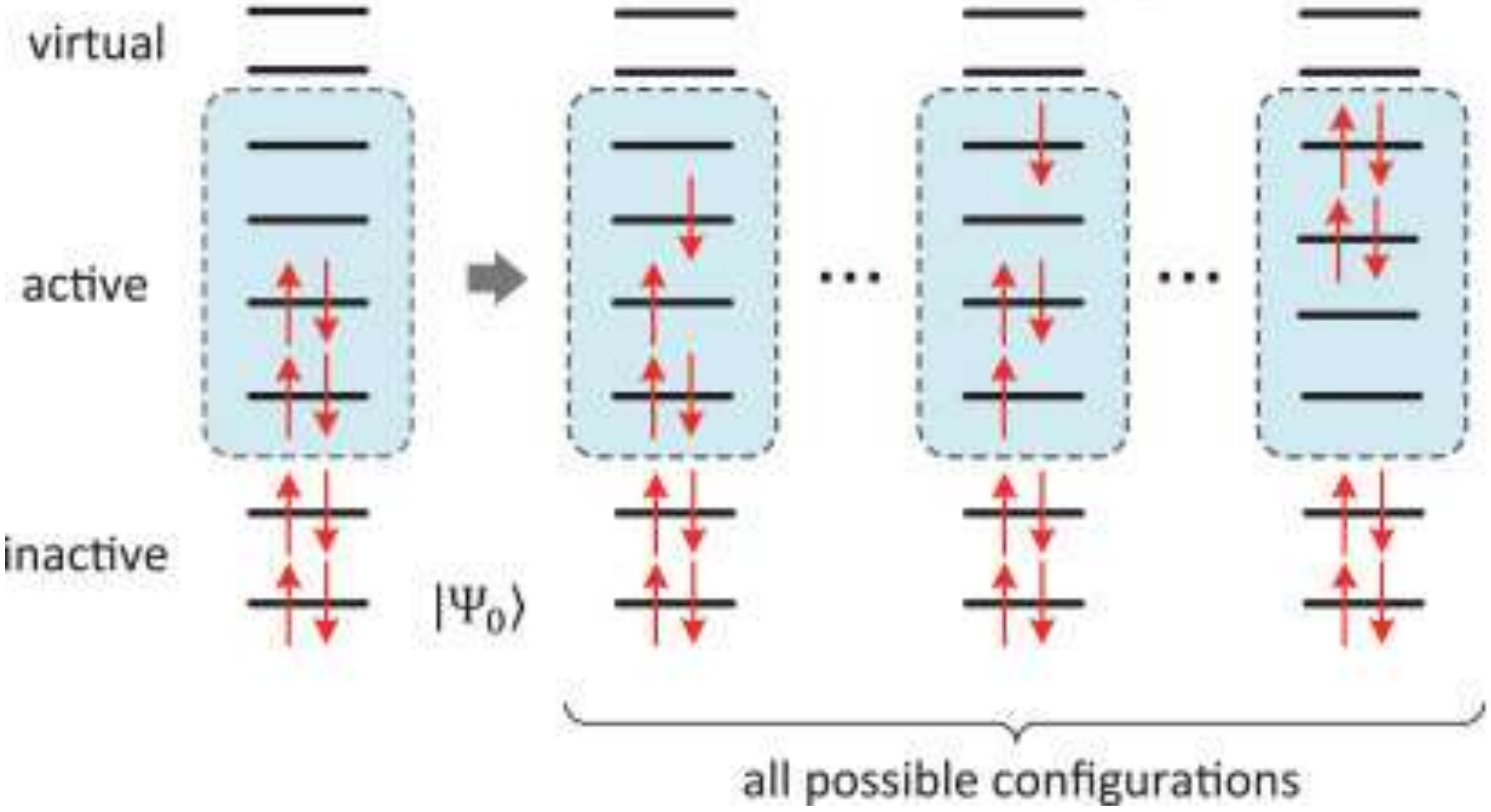


$$\Psi_{\mathrm{CI}} = c_0|\psi_{\sigma_g}\overline{\psi_{\sigma_g}}\rangle + c_1|\psi_{\sigma_u}\overline{\psi_{\sigma_u}}\rangle + c_2|\psi_{3\sigma}\overline{\psi_{3\sigma}}\rangle + c_3|\psi_{\pi}\overline{\psi_{\pi}}\rangle + \ldots$$



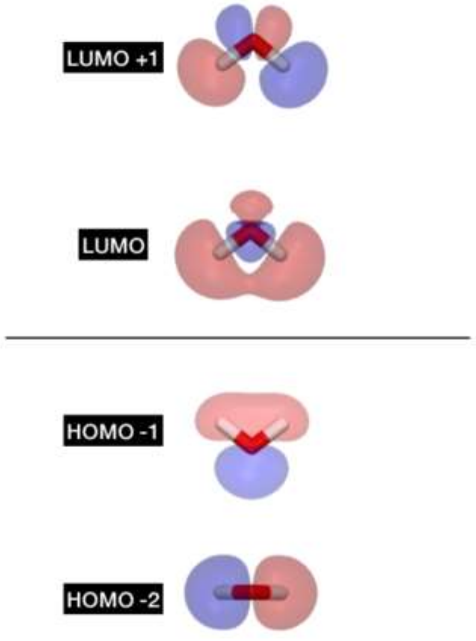
Multireference (CASSCF)

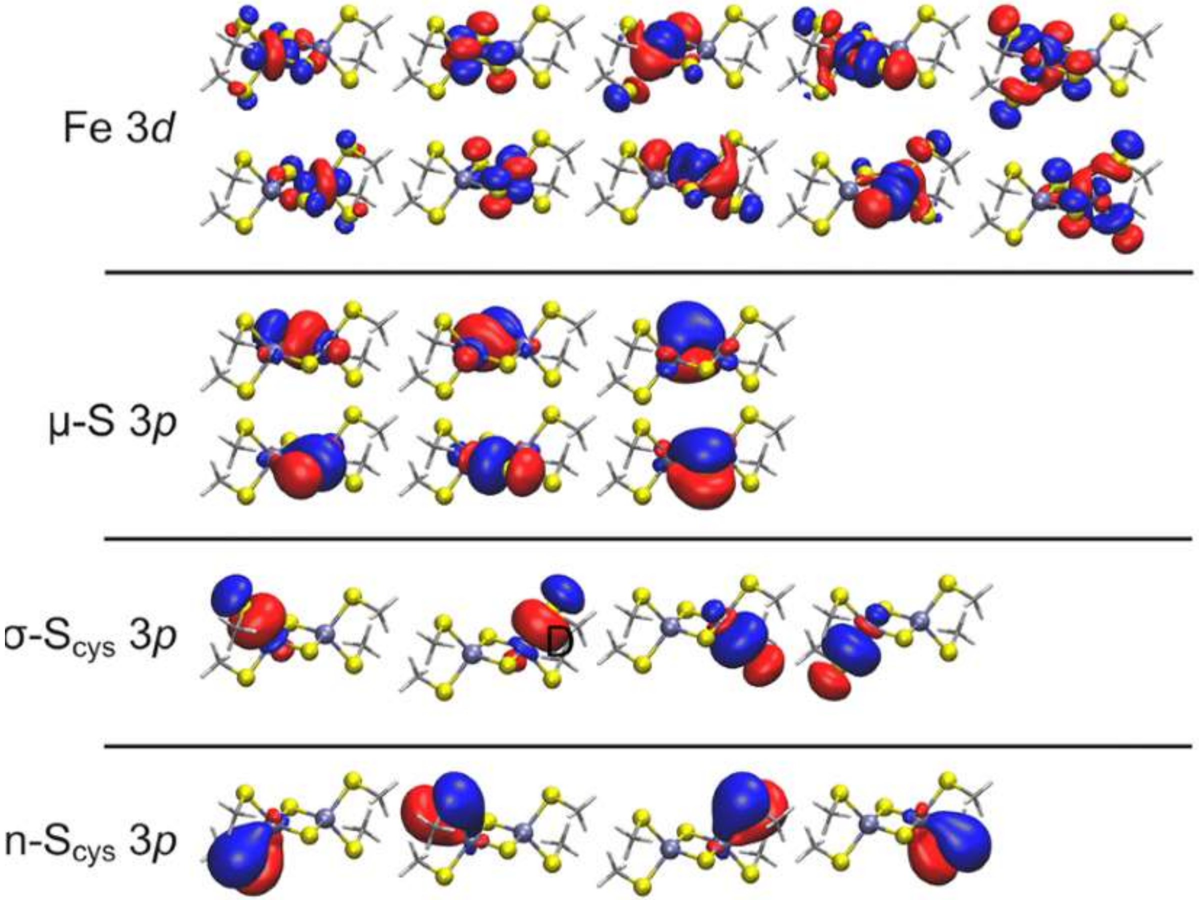
$$|\Phi\rangle_{CASSCF} = C_0|\Psi_0\rangle + \sum_{ra} C_a^r\,|\Psi_a^r\rangle + \sum_{\substack{a<b\\ r<s}} C_{ab}^{rs}\,|\Psi_{ab}^{rs}\rangle + \cdots$$



Active space

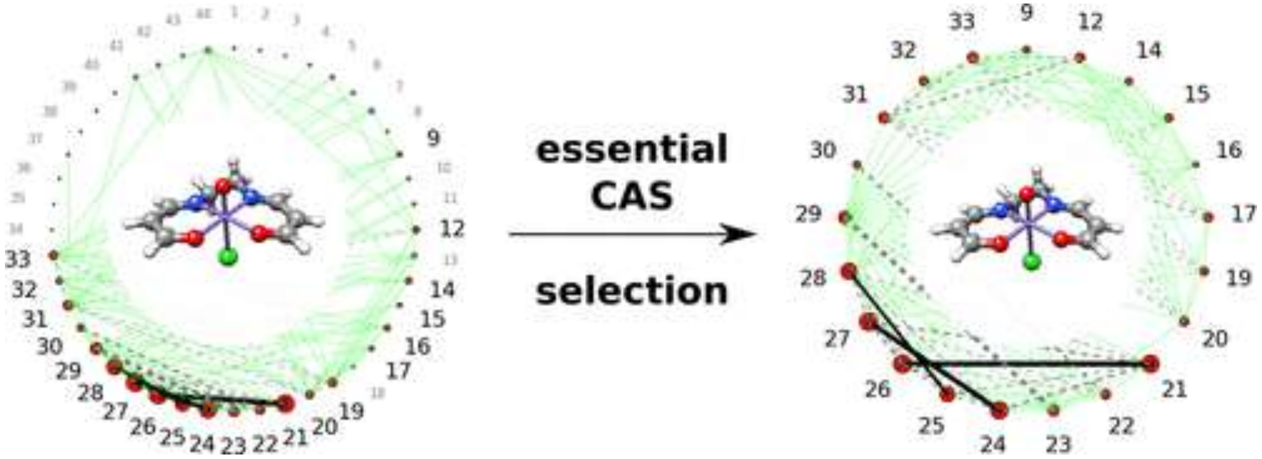
Most important orbitals where all the electron transfer or chemistry happens.





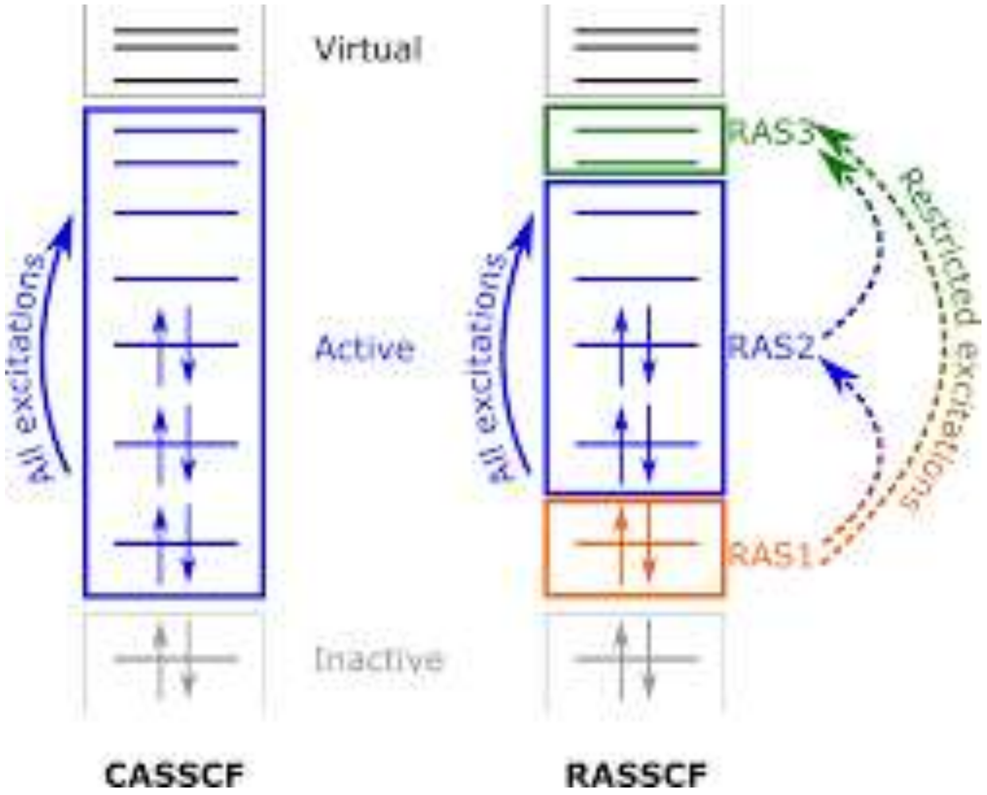
Selection of active space

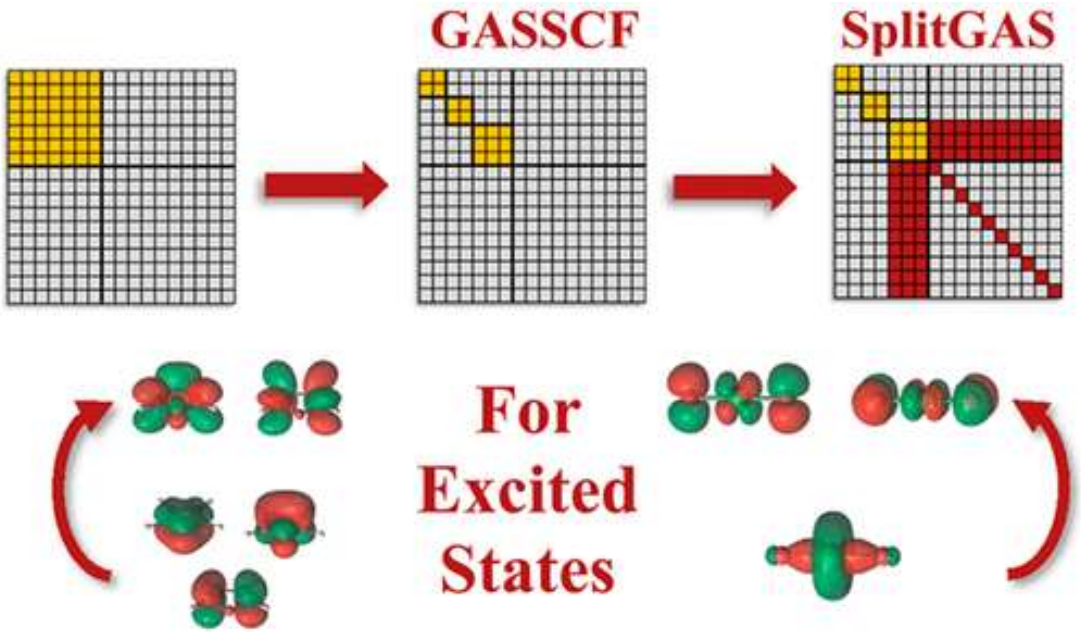
- Intuition based selection
- Selection based on chemical principles such as Lewis diagrams, VB theory etc
- Automated selection



Reiher et al, JCTC, 2016

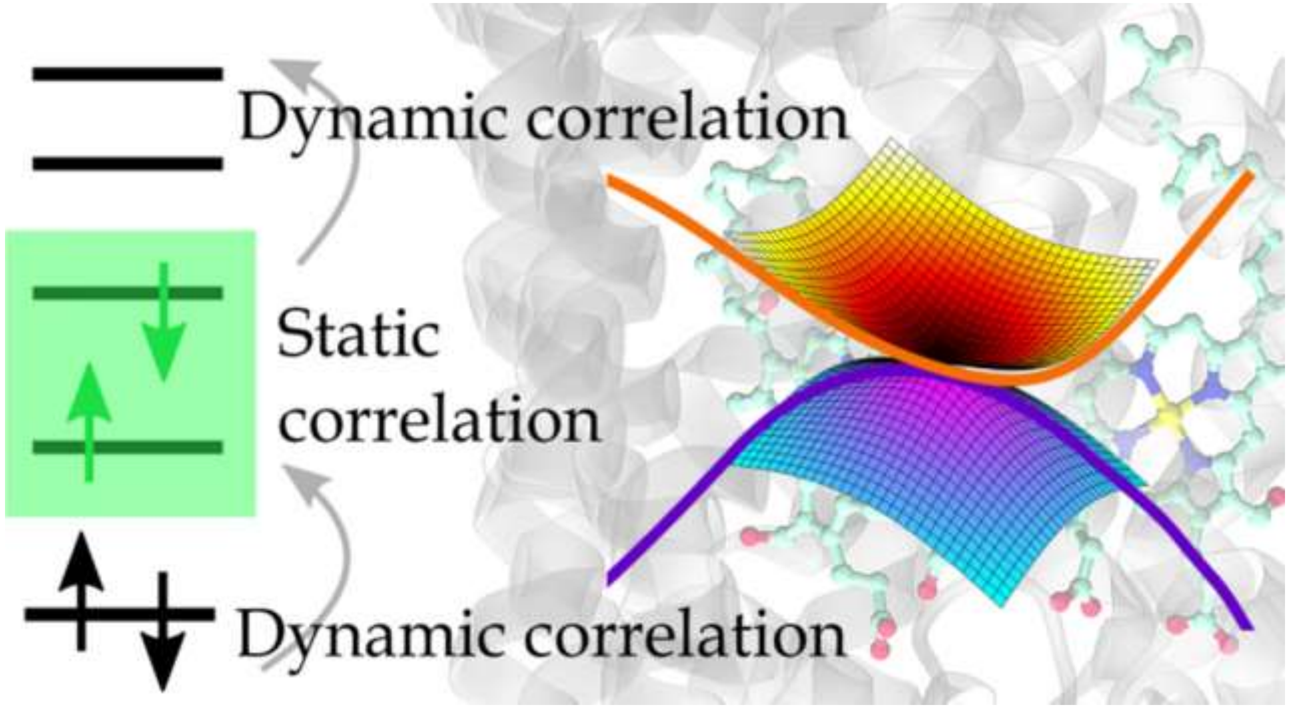
Variants of these calculations

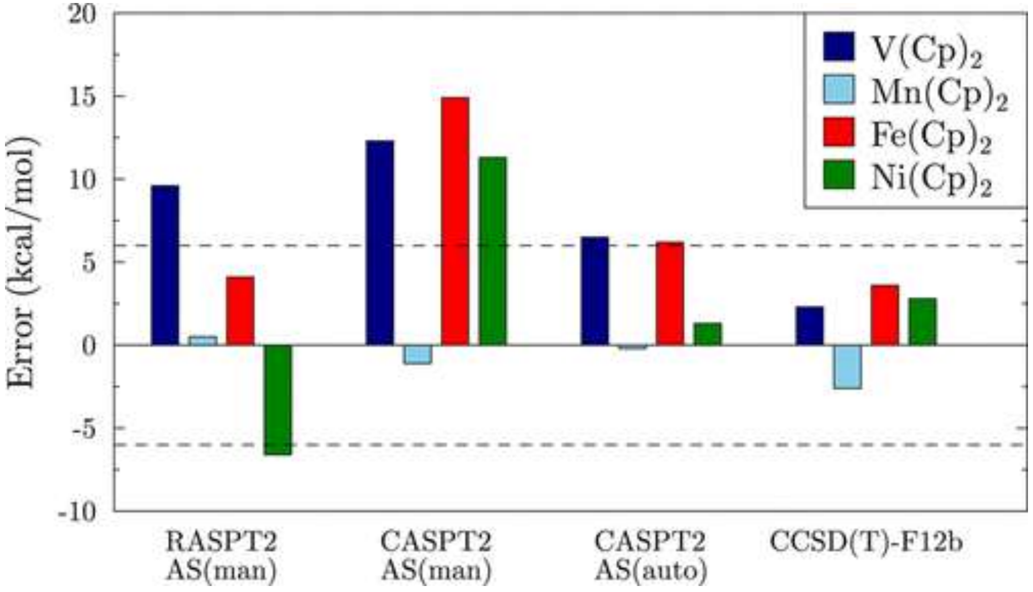




Casanova, WIREs Comput Mol Sci., 2021 (review)
Gagliardi, JCTC, 2015 (GASSCF)

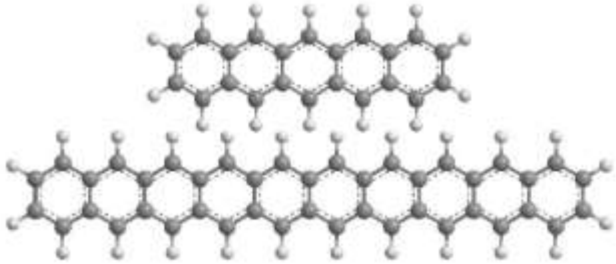
Static and dynamic correlation





Reiher, JCTC, 2016

Challenges in ST gap computation



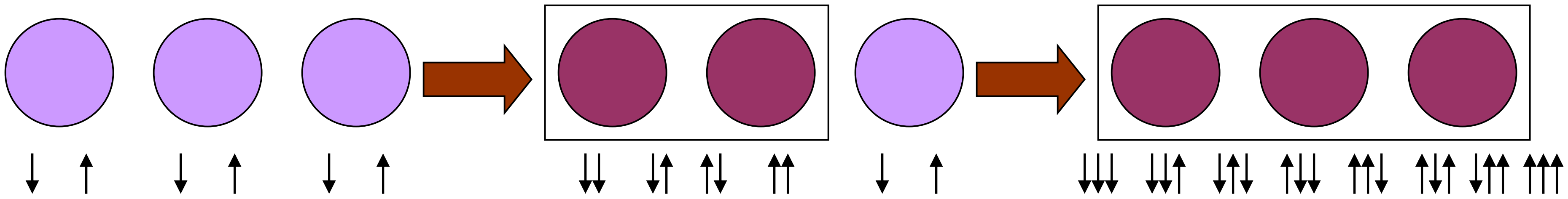
- CSFs in the active (valence) space is an exponentially scaling problem.

- CSF space is large ~10^{33} for 30 π orbitals with 30 electrons

- For a matrix diagonalization of this size, one requires to perform 10^{99} operations.

- Comparison – No of atoms in universe is 10^{82}

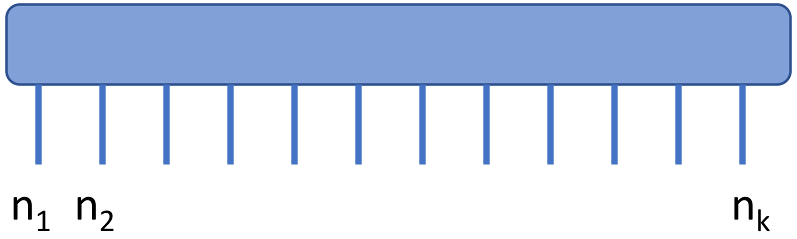
Exponential Hilbert space



2^N or d^N

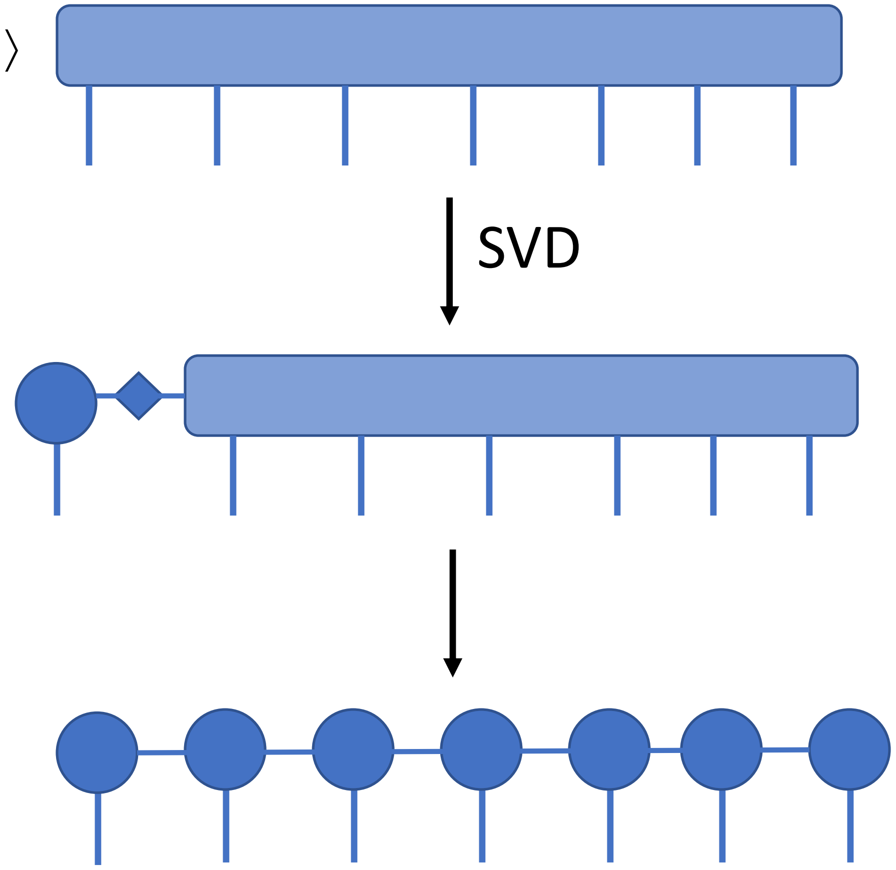
Thus, the exact wavefunction can be written as a many dimensional tensor

$$|\Psi_{FCI}\rangle = \sum_{n_1 n_2 n_3 \ldots} \Psi^{n_1 n_2 n_3 \ldots n_k} \, |n_1 n_2 n_3 \ldots . n_k\rangle$$



Matrix Product State ansatz

$$\sum_{n_1n_2n_3\ldots} \Psi^{n_1n_2n_3\ldots n_k}\,|n_1n_2n_3\ldots n_k\rangle$$



d^N

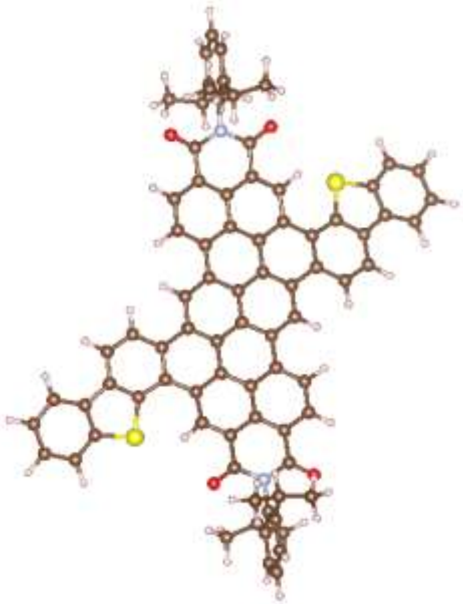
Exponential saving!

NdM^2

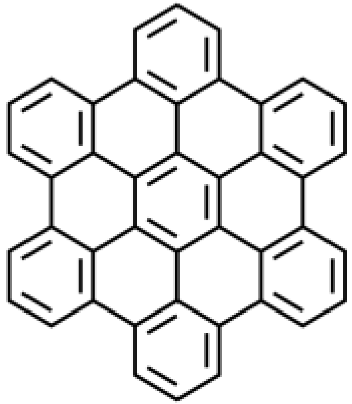
$$\Psi^{n_1n_2n_3\ldots n_k} \approx \sum_{i_1i_2i_3\ldots i_{k-1}} A^{n_1}_{i_1}\,{}_{i_1}A^{n_2}_{i_2}\,{}_{i_2}A^{n_3}_{i_3}\cdots{}_{i_{k-1}}A^{n_k}_{i_k}$$

Verstraete, Garcia-Ripoll, Cirac, PRL, (2004)
Kliesch, Gross, Eisert, PRL (2014)

Polyaromatic hydrocarbons



Delayed fluorescence

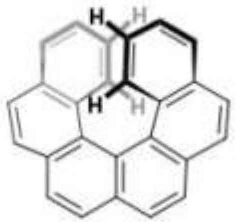


Electrochemical properties

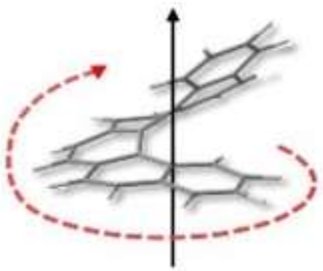
Jha, Dey, **DG**, Sankar, *Chemical Science*, 2024

Dey, **DG**, *J Phys Chem Lett*, 2022, 13, 11795

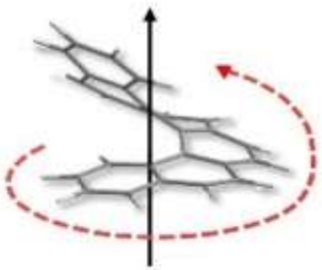
Molecular switches
Asymmetric catalysis



[6]Helicene



(*M*)-[6]Helicene



(*P*)-[6]Helicene

Acknowledgement

Funding :

SERB INDIA

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MISSION

विज्ञान एवं प्रौद्योगिकी विभाग
DEPARTMENT OF
SCIENCE & TECHNOLOGY

CSIR INDIA

Thank You!

QUANTIFYING AROMATICITY ACCORDING TO THE ENERGETIC CRITERION

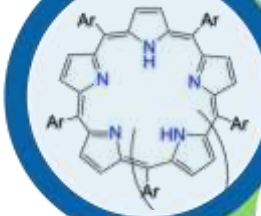
Mercedes Alonso

VUB ALGC GENERAL CHEMISTRY RESEARCH GROUP

ICESAA-4

4th International Conference on Excited State Aromaticity & Antiaromaticity

Talk Outline



The Concept of Aromaticity

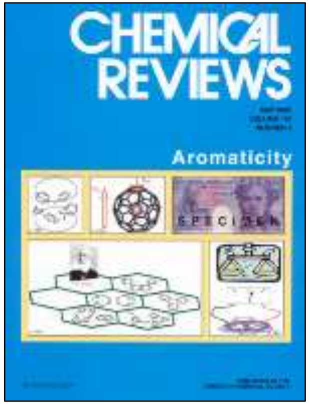
What is aromaticity and how should be quantified?

Quantifying Aromaticity through Energetic Descriptors

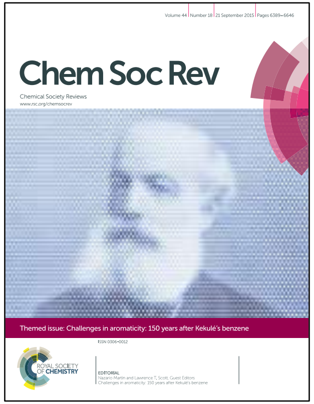
Applications to Larger Systems

The Concept of Aromaticity

Aromaticity is a theoretical concept of immense practical importance


Chem. Rev. **2001**, 101


Chem. Rev. **2005**, 105


Chem. Soc. Rev. **2015**, 44


J. Phys. Org. Chem. **2023**, 36


Chem. Sci. **2023**, 36

- A key concept for understanding molecular behaviour and designing novel materials
- Aromaticity is **not a quantum observable** and needs to be defined by convention

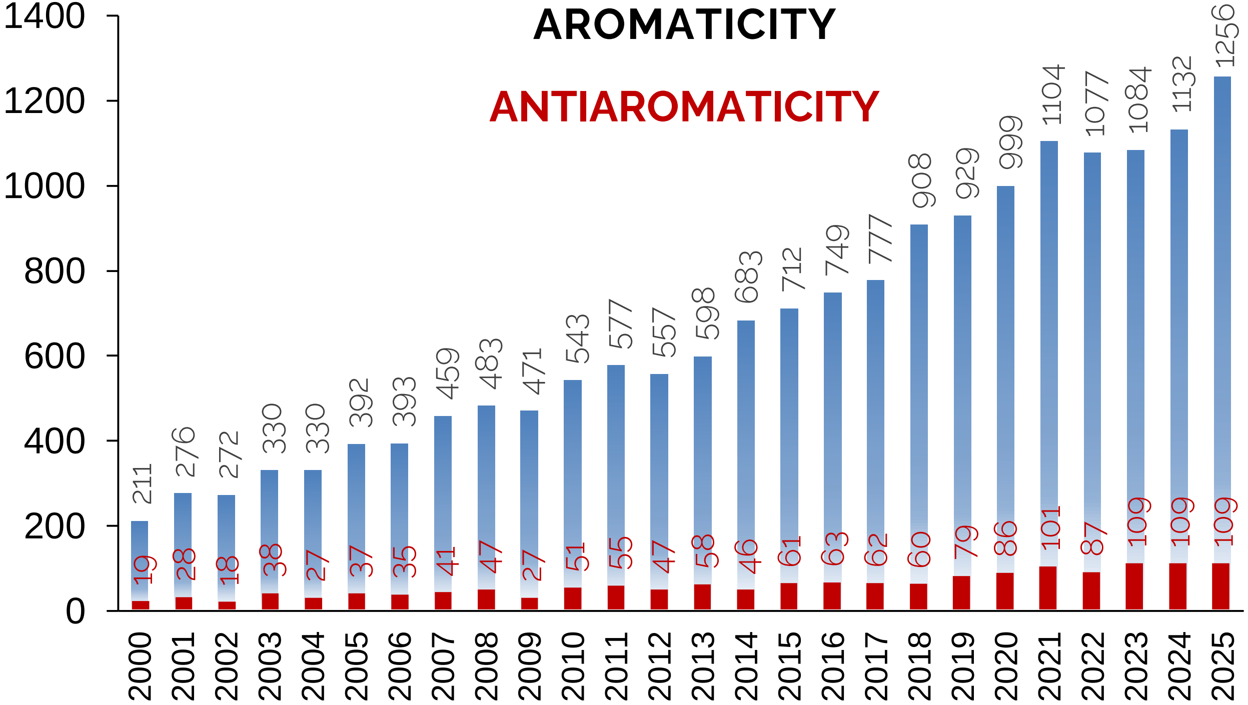
Krygowski, Cyrański, Czarnocki, Häfelinger, Katritzky, *Tetrahedron* **2000**, 56, 1783

Solà, *Front. Chem.* **2017**, 5, 22

Merino, et al., *Chem. Sci.* **2023**, 14, 5569

Impact of the Aromaticity Concept

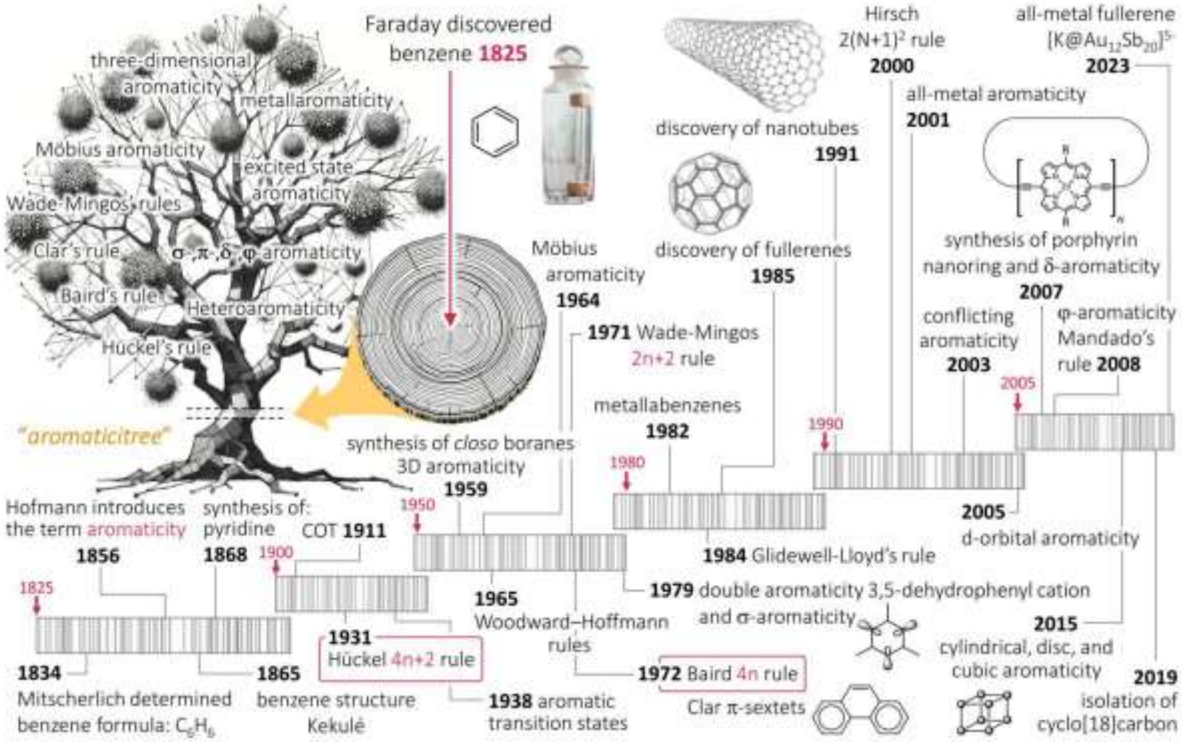
The continuous rise in the **bibliometric impact of aromaticity** highlights its enduring relevance as a central concept in Chemistry & related areas



WoS (Jan. 2026)

Dendrochronology of Aromaticity

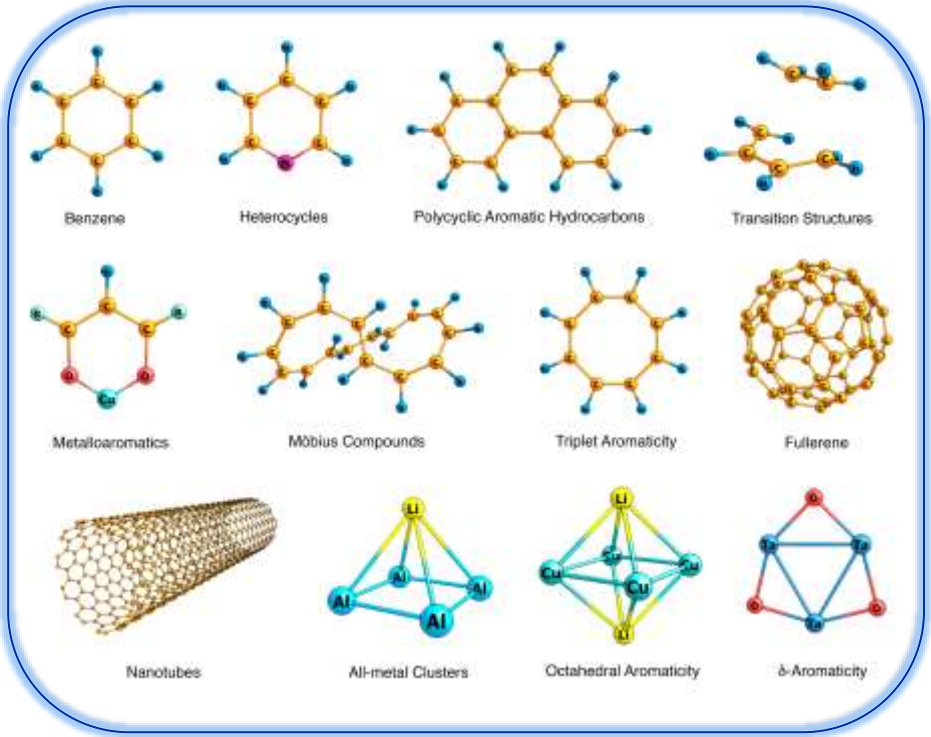
The concept of aromaticity has evolved dramatically in recent decades, giving rise to new types of aromatic compounds



PhD of Silvia Escayola (2024)

Hallmarks of Aromatic Compounds

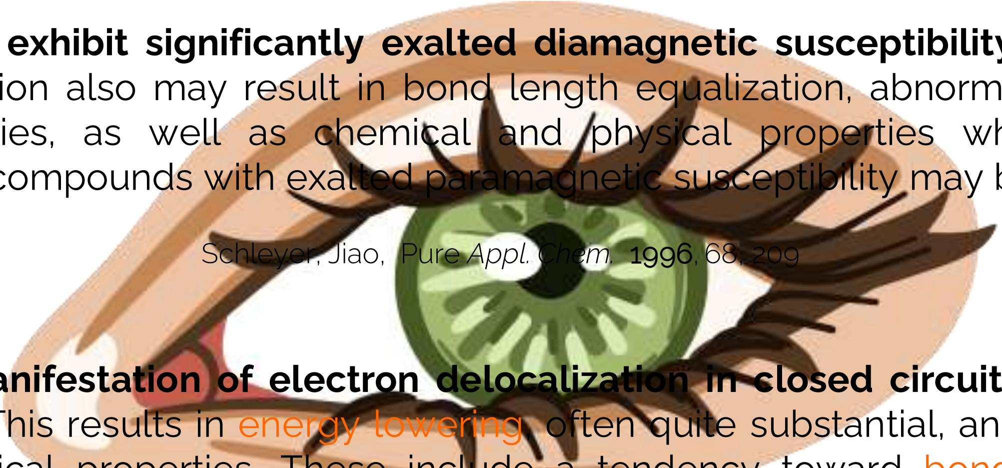
While aromaticity lacks a universal definition, most aromatic compounds share key features with the archetypal benzene



- Enhanced thermodynamic stability
- Conjugated systems
- Cyclic electron delocalization
- Tendency for substitution reactions
- Special magnetic properties

What is Aromaticity?

Aromaticity, like beauty, lies in the eye of the beholder. Both are easy to recognize, but difficult to define quantitatively



Definition 1:

Compounds which exhibit significantly exalted diamagnetic susceptibility are aromatic. Cyclic electron delocalization also may result in bond length equalization, abnormal chemical shifts and magnetic anisotropies, as well as chemical and physical properties which reflect energetic stabilization. Those compounds with exalted paramagnetic susceptibility may be antiaromatic.

Schleyer, Jiao, Pure *Appl. Chem.* **1996**, 68, 209

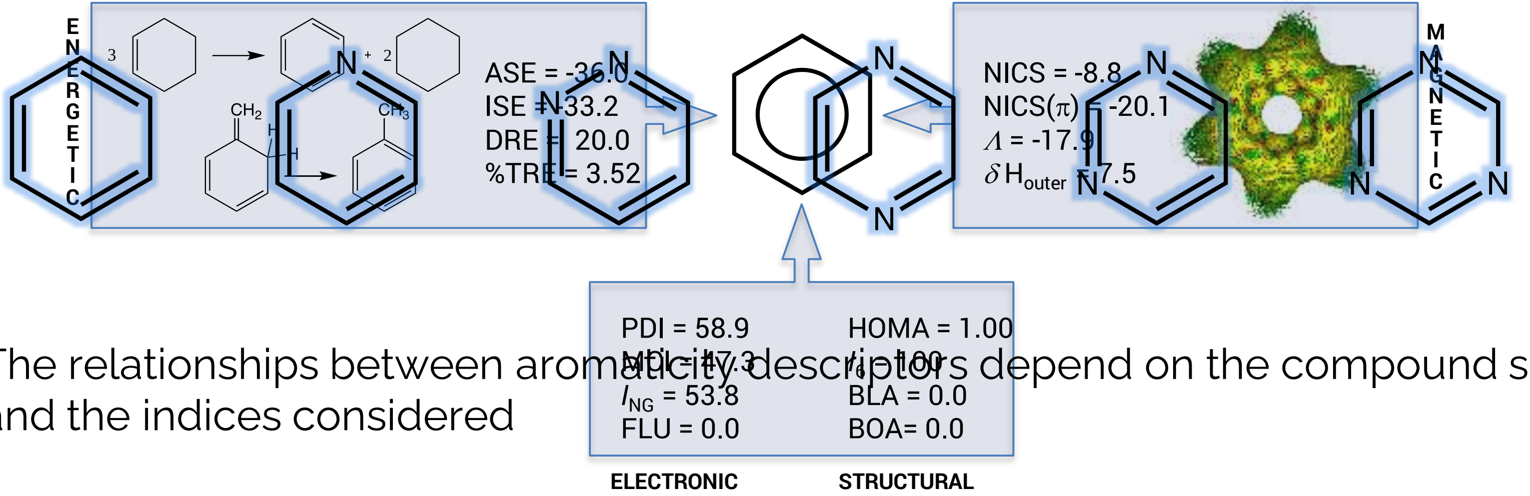
Definition 2:

Aromaticity is a manifestation of electron delocalization in closed circuits, either in two or in three dimensions. This results in energy lowering, often quite substantial, and a variety of unusual chemical and physical properties. These include a tendency toward bond length equalization, unusual reactivity, and characteristic spectroscopic features. Since aromaticity is related to induced ring currents, magnetic properties are particularly important for its detection and evaluation.

Schleyer et al., *Chem. Rev.* **2005**, 105, 3842

How Should Aromaticity Be Quantified?

Most authors advise to use **a set of aromaticity descriptors based on different criteria** to characterize (anti)aromaticity



ASE = -36.0
ISE = 33.2
DRE = 20.0
%TRE = 3.52

NICS = -8.8
NICS(π) = -20.1
Λ = -17.9
δH$_{outer}$ = 7.5

PDI = 58.9
MCI = 47.3
I_{NG} = 53.8
FLU = 0.0

HOMA = 1.00
I_6 = 100
BLA = 0.0
BOA= 0.0

ELECTRONIC **STRUCTURAL**

- The relationships between aromaticity descriptors depend on the compound set and the indices considered

the multidimensional character of aromaticity should not prevent a critical analysis of aromaticity descriptors

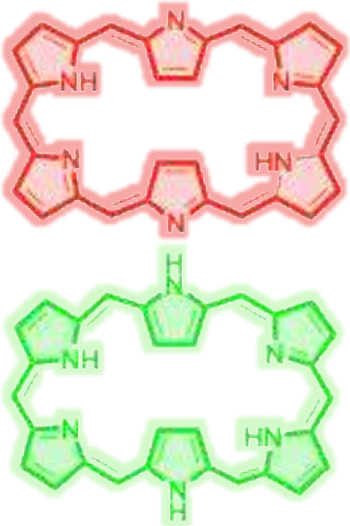
Energetic indices (ASE, ISE and DRE) in kcal mol^{-1}
Λ in ppm cgs, NICS indices and ^{1}H NMR in ppm, $\Delta\eta$ are given in kcal mol^{-1}
Electronic indices multiplied by 1000

Feixas, Matito, Poater, Solà, *J. Comput. Chem.* **2008**, 29, 1543; *J. Chem. Theory Comput.* **2010**, 6, 1118

Aromaticity Criteria

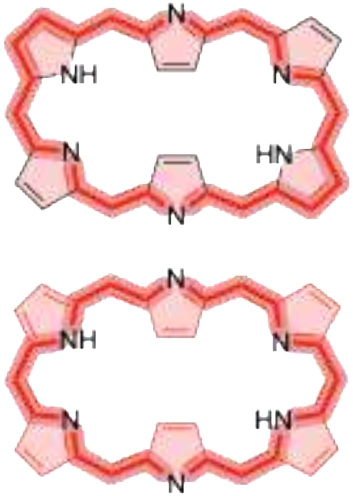
Different criteria have been proposed to quantify aromaticity, including energetic, structural, electronic, reactivity, and magnetic measures

Global



entire macrocycle

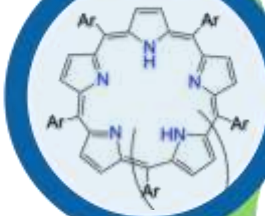
Local



specific pathways/subunits

De Vleeschouwer, Desmet, Alonso, *Chem. Methods* **2025**, 5, e202500064

Talk Outline



The Concept of Aromaticity

Quantifying Aromaticity through Energetic Descriptors

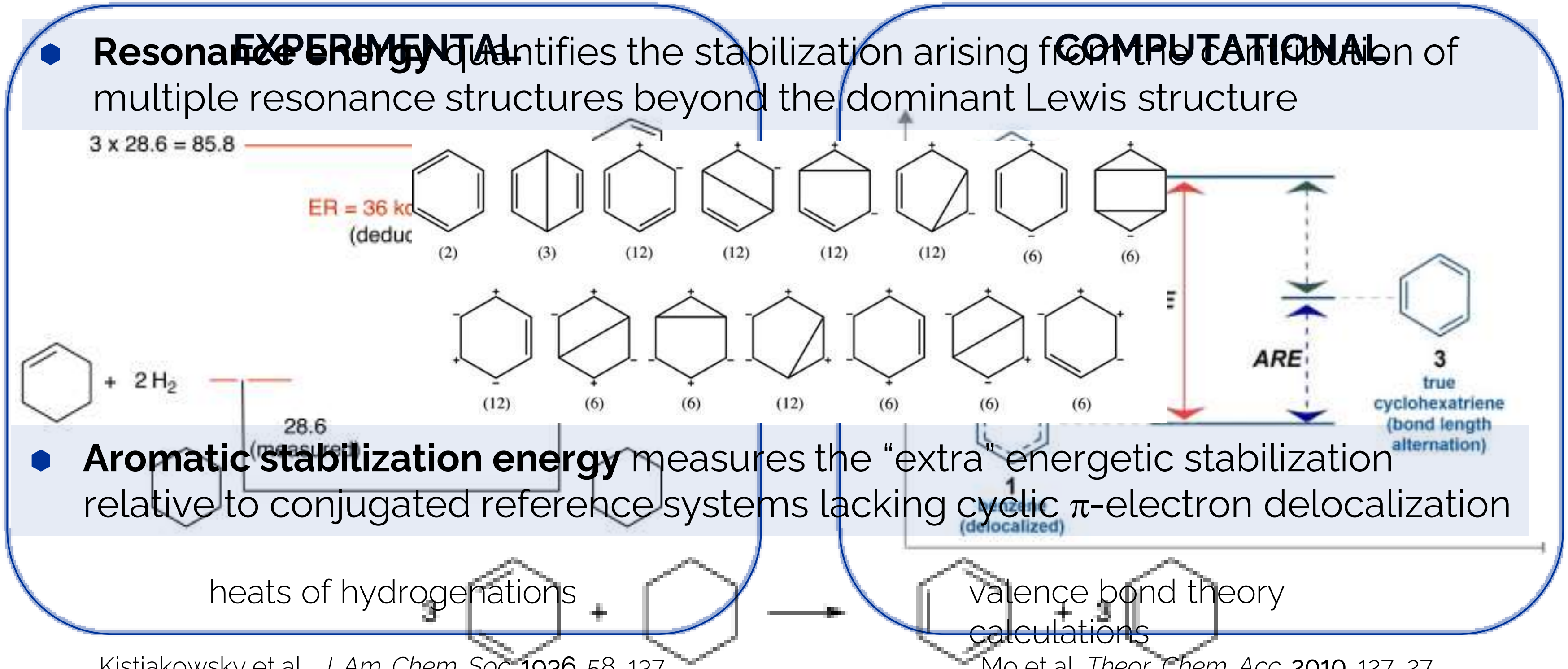
What are the strengths and limitations of energetic descriptors in assessing aromaticity?

Applications to Larger Systems

Energetic Descriptors

Energetic indices quantify the enhanced stability of aromatic compounds relative to nonaromatic reference systems: **RE** and **ASE**

- **Resonance energy** quantifies the stabilization arising from the contribution of multiple resonance structures beyond the dominant Lewis structure
- **Aromatic stabilization energy** measures the "extra" energetic stabilization relative to conjugated reference systems lacking cyclic π-electron delocalization



EXPERIMENTAL

heats of hydrogenations

Kistiakowsky et al, *J. Am. Chem. Soc.* **1936**, 58, 137

COMPUTATIONAL

valence bond theory calculations

Mo et al, *Theor. Chem. Acc.* **2010**, 127, 27

Energetic Descriptors

Energetic indices quantify the enhanced stability of aromatic compounds relative to nonaromatic reference systems: **RE** and **ASE**

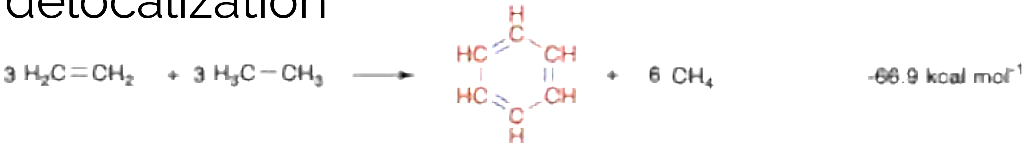
PROBLEMS

- ⊗ strong dependence on the choice of the reference nonaromatic structure
- ⊗ uncertainty in the experimental data
- ⊗ dependence on the level of theory
- ⊗ contamination of energetic values by other effects: hyperconjugation, strain, hybridization

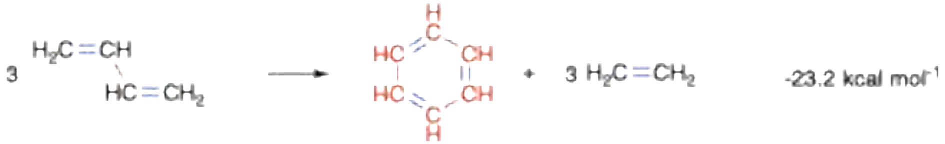
Alonso, Fernández, Aromaticity (Elsevier), **2021**, 195-235

Aromatic Stabilization Energies

ASE quantifies the "extra" energetic stability of benzene relative to appropriate conjugated references lacking cyclic π-electron delocalization

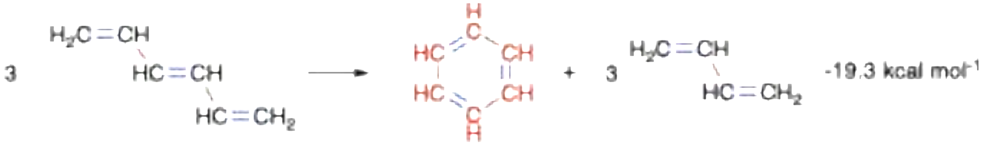


Isodesmic: equal number of formal single and double bonds in both sides



Homodesmotic: same number of bonds between atoms in each hybridization state

$C^{(sp3)}$-$C^{(sp3)}$, $C^{(sp2)}$-$C^{(sp2)}$, $C^{(sp3)}$-$C^{(sp2)}$

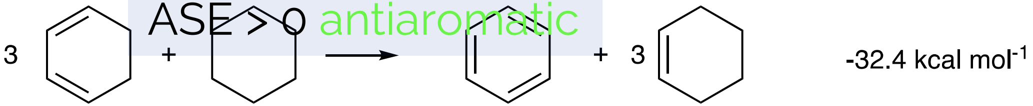


Superhomodesmotic: valence environments around every pair of bonded atoms is also conserved

Homodesmotic reactions based on **cyclic reference systems** are recommended

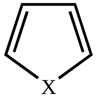
ASE <0 aromatic

ASE > 0 antiaromatic

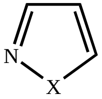


Aromatic Stabilization Energies

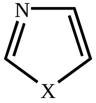
Benchmarking six equations for evaluating the ASEs of 105 five-membered rings, including aromatic, nonaromatic and antiaromatic systems



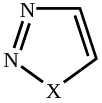
1: X = O
2: X = S
3: X = NH
4: X = PH



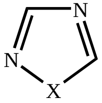
5: X = O
6: X = S
7: X = NH
8: X = PH



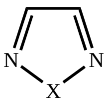
9: X = O
10: X = S
11: X = NH
12: X = PH



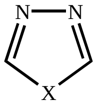
13: X = O
14: X = S
15: X = NH
16: X = PH



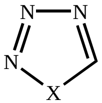
17: X = O
18: X = S
19: X = NH
20: X = PH



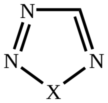
21: X = O
22: X = S
23: X = NH
24: X = PH



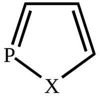
25: X = O
26: X = S
27: X = NH
28: X = PH



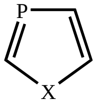
29: X = O
30: X = S
31: X = NH
32: X = PH



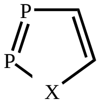
33: X = O
34: X = S
35: X = NH
36: X = PH



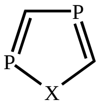
40: X = O
41: X = S
42: X = NH
43: X = PH



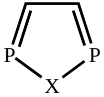
44: X = O
45: X = S
46: X = NH
47: X = PH



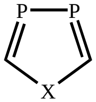
48: X = O
49: X = S
50: X = NH
51: X = PH



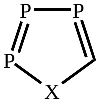
52: X = O
53: X = S
54: X = NH
55: X = PH



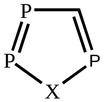
56: X = O
57: X = S
58: X = NH
59: X = PH



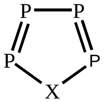
60: X = O
61: X = S
62: X = NH
63: X = PH



64: X = O
65: X = S
66: X = NH
67: X = PH

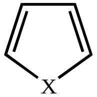


68: X = O
69: X = S
70: X = NH
71: X = PH



72: X = O
73: X = S
74: X = NH
75: X = PH

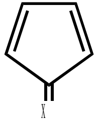
Heterocyclic five-membered compounds



76: X = BeH^-
77: X = B^-
78: X = BH
79: X = BH_2^-
82: X = CF_2
83: X = N^-
84: X = NH_2^+
85: X = Al^-

86: X = AlH
87: X = AlH_2^-
88: X = SiH^-
89: X = SiH^+
90: X = SiH_2
91: X = P^-
92: X = PH_2^+
93: X = GaH

94: X = GaH_2^-
95: X = GeH^-
96: X = GeH^+
97: X = GeH_2
99: X = AsH
98: X = As^-
100: X = AsH_2^+
101: X = Se

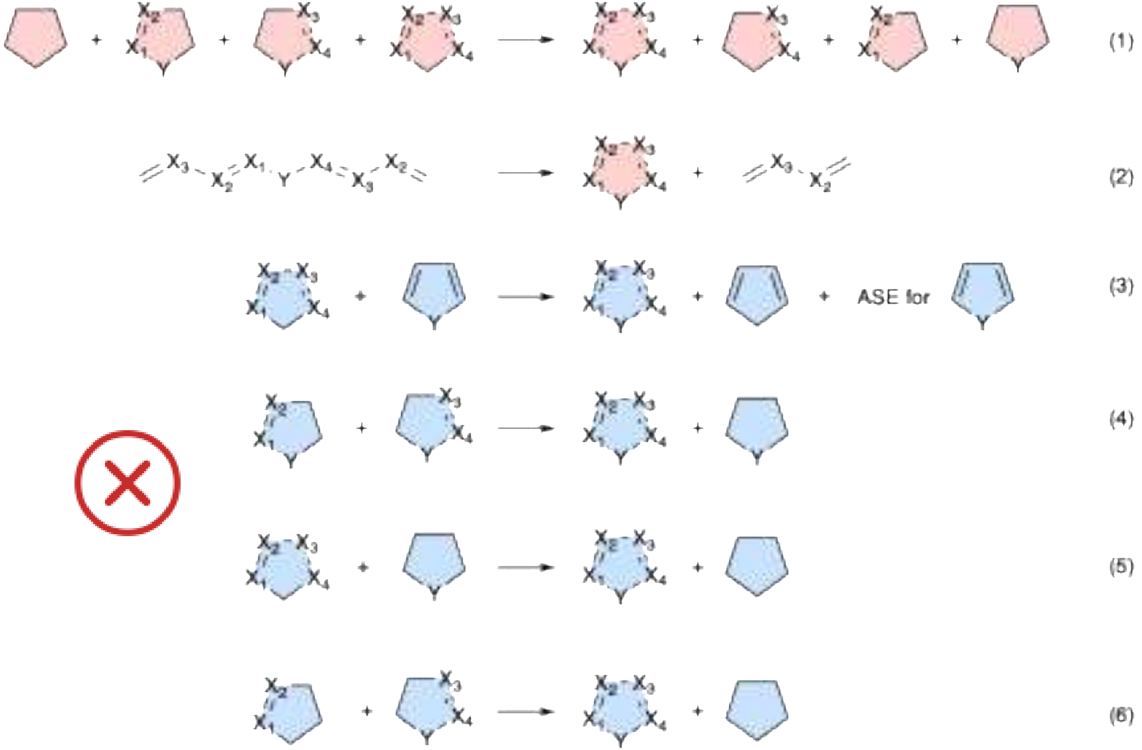


102: X = CH_2
103: X = O
104: X = S
105: X = Se

C4H4X monocycles

Aromatic Stabilization Energies

Benchmarking six equations for evaluating the ASEs of 105 five-membered rings, including aromatic, nonaromatic and antiaromatic systems



Homodesmotic

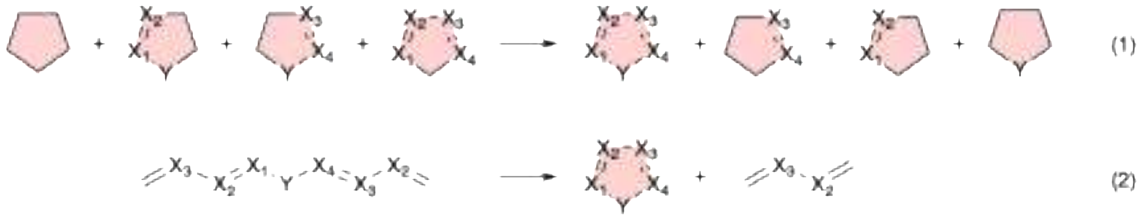
Isodesmic

- ⊗ spurious contributions
- ⊗ hybridization, homoconjugation, hyperconjugation or strain not counterbalanced

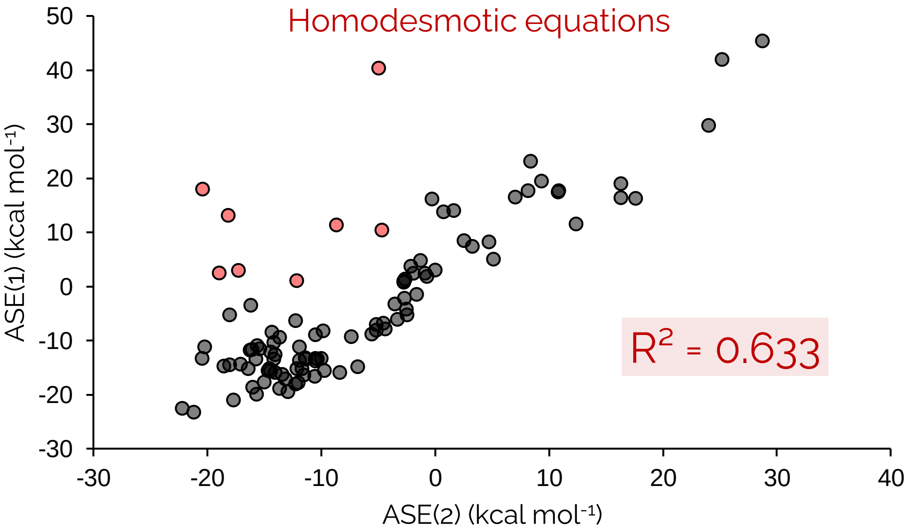
Cyrański et al, *Tetrahedron* **2003**, 59, 1657

Aromatic Stabilization Energies

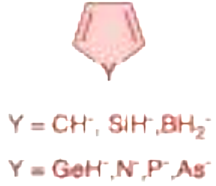
Benchmarking six equations for evaluating the ASEs of 105 five-membered rings, including aromatic, nonaromatic and antiaromatic systems



- ✓ Additional effects are minimized using cyclic references
- ⊗ Linear polyene references fail to account for strain effects



$R^2 = 0.633$

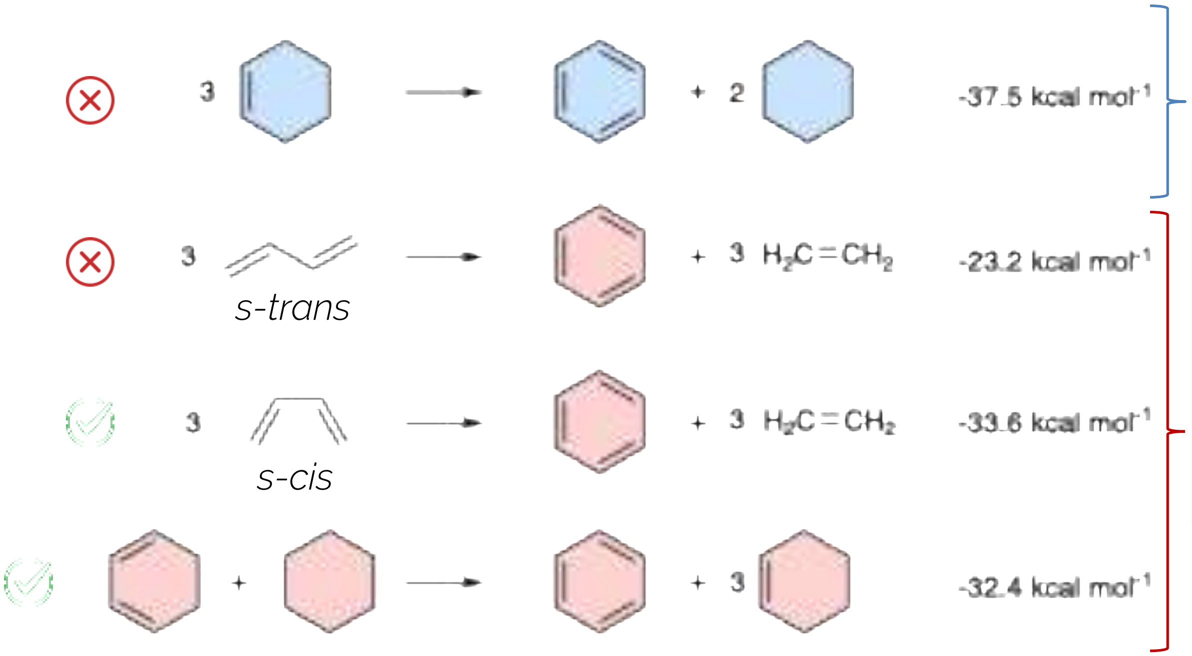


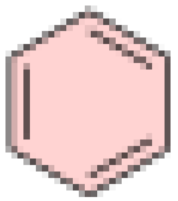
⊗ ASE(2) perturbed by topological charge stabilization effects in anionic polyene references

Cyrański et al, *Tetrahedron* **2003**, 59, 1657

Aromatic Stabilization Energies

Cyclic reference systems are crucial for reliable ASE evaluations from homodesmotic reactions, as illustrated for the archetypal benzene





-32.7 kcal mol^{-1}

Mathematical derivation eliminating energy differences due to strain, resonance, hyperconjugation & bonding effects

Schleyer, Manoharan, Jiao, Stahl, *Org. Lett.* **2001**, 3, 3643

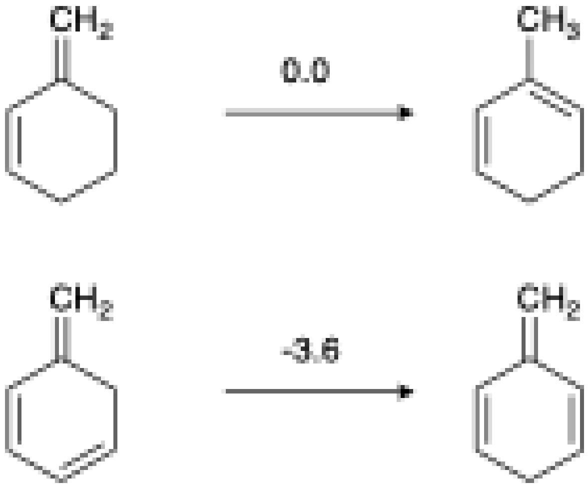
Fishtik, Datta, *J. Phys. Chem. A* **2003**, 107, 10471

Isomerization Stabilization Energies (ISE)

Derived from the energy difference between a methyl derivative of a given system and its nonaromatic exocyclic methylene isomer

Two alternative methylene isomers

syn-anti corrections



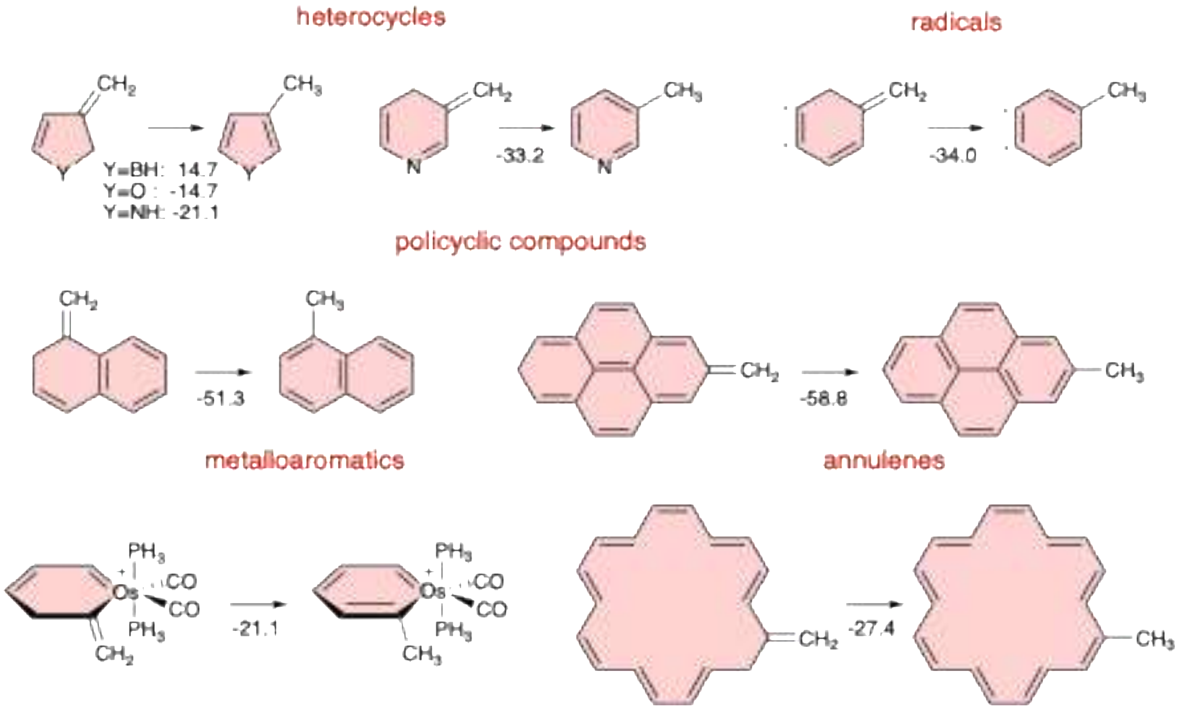
To eliminate *anti-syn* mistmatches at both sides

After applying *syn-anti* corrections, the ISE$_{corr}$ values derived from both equations coincide

Schleyer, Pühlhofer, *Org. Lett.* **2002**, 4, 2873

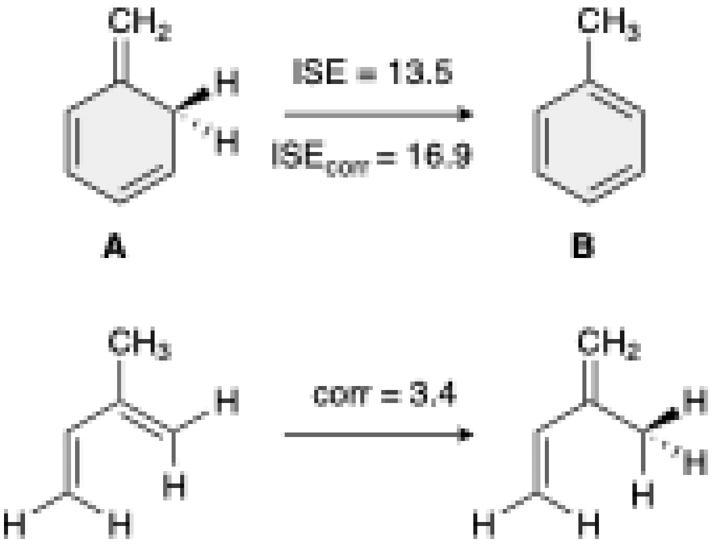
Isomerization Stabilization Energies (ISE)

This approach works remarkably well for evaluating ASEs across diverse systems due to effective error cancellation of noncyclic delocalization effects, such as ring strain

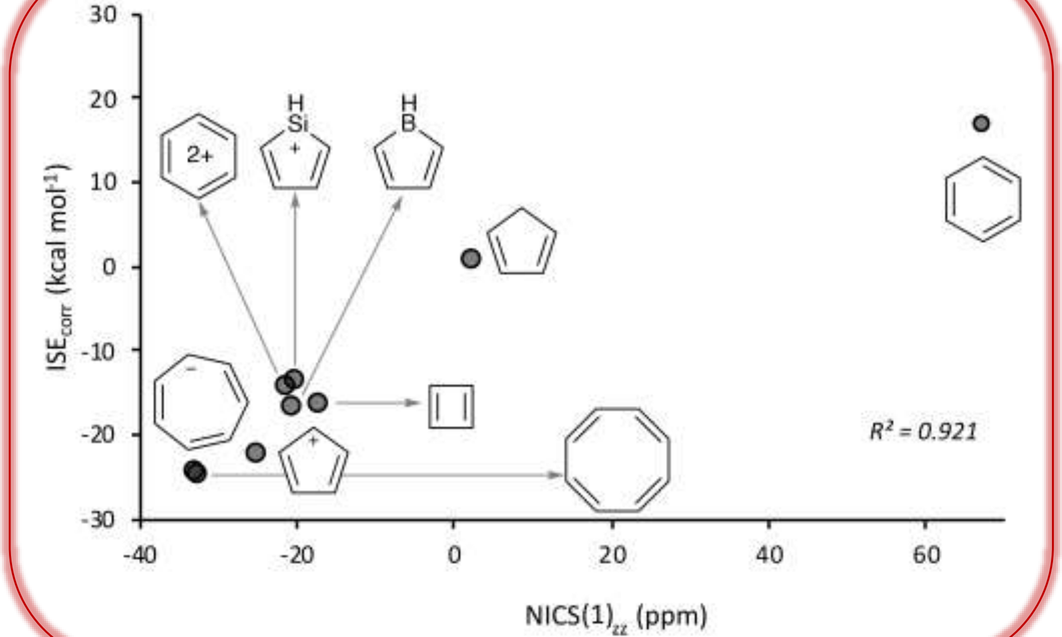


Excited-State Aromaticity

The ISE method can be extended to evaluate the stabilization energies of benzene in the T1 states



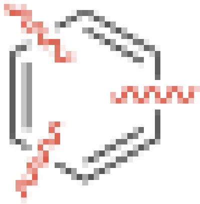
fragment geometries were fixed to **A** and **B**



Zhu, An, Schleyer, *Org. Lett.* **2013**, 15, 2442

ASE from Energy Decomposition Analysis

A different methodology based on EDA to quantify the relative strength of aromaticity in aromatic and antiaromatic organic compounds



D_{6h}

fragments: 3 C_2H_2

$$\Delta E_{\mathrm{int}} = \Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{Pauli}} + \Delta E_{\mathrm{orb}}$$

$$\Delta E_{\mathrm{orb}} = \sum_{\Gamma} \Delta E_{\Gamma}$$

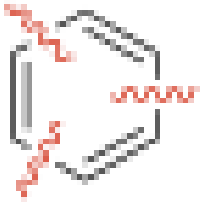
ΔE_{orb} decomposed into contributions from orbitals belonging to different irreducible representations

- Enables quantitative estimation of intrinsic orbital interaction strengths from orbitals having σ, π, and δ symmetries
- For planar systems, the ΔE_{orb} term contains contributions arising from σ and π orbitals, giving ΔE_{σ} and ΔE_{π}

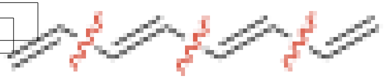
Fernández, Frenking, *Faraday Discuss.* **2007**, 135, 403

ASE from Energy Decomposition Analysis

The ΔE_π term directly measures the strength of conjugation in a **planar molecule** without recourse to external reference systems



$ASE_{EDA} = \Delta E_\pi(\text{cyclic molecule}) - \Delta E_\pi(\text{acyclic reference})$



D_{6h}

cyclic

$\Delta E_\pi = -107.7$

ASE = 4

cal mol^{-1}

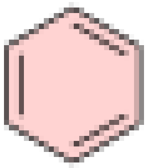
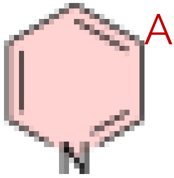
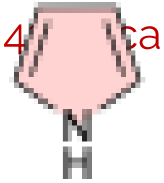
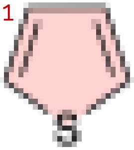
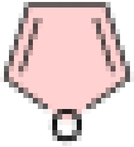
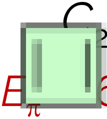
C

2h

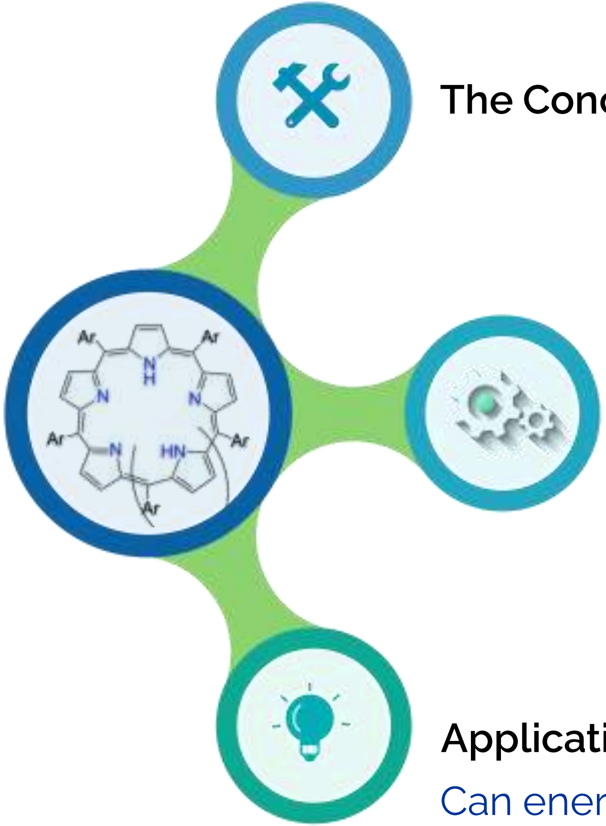
ΔE

π

65.5

						
ΔE_π	-107.7	-113.5	-98.0	-77.6	-77.7	-9.6
acyclic						
	X = CH	X = CH	X = NH	X = S	X = O	
ΔE_π	-65.5	-67.8	-76.9	-55.7	-61.5	-41.5
ASE	42.5	45.7	21.1	21.9	16.2	-31.9

Talk Outline



The Concept of Aromaticity

Quantifying Aromaticity through Energetic Descriptors

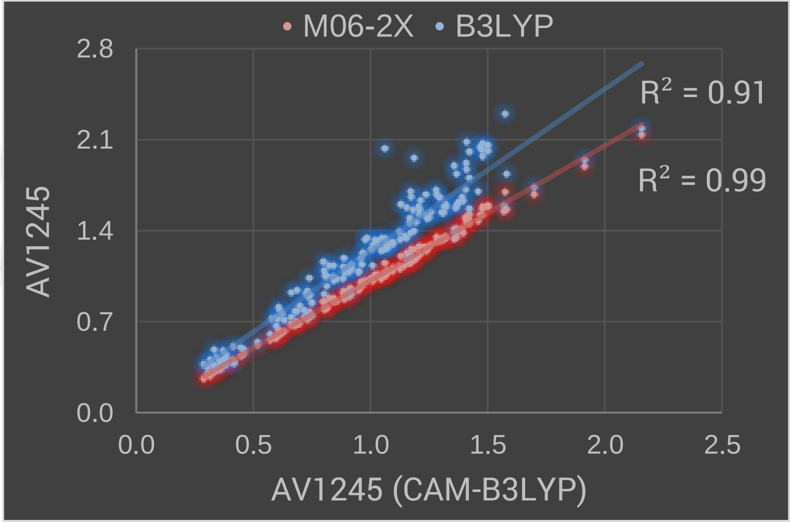
Applications to Larger Systems

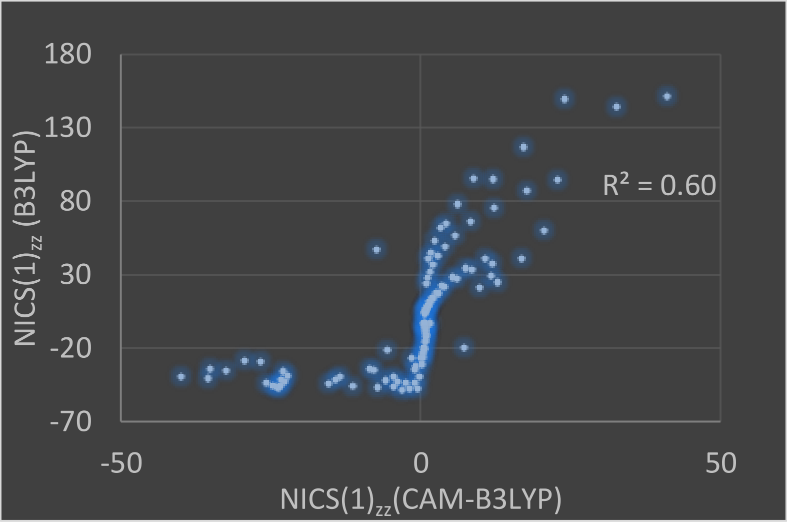
Can energetic descriptors reliably quantify aromaticity in large and complex systems?

Challenges in Quantifying ASE in Larger Systems

Multiple conjugation pathways and nonplanar topologies complicate global and local aromaticity assessment

- Intricate *local* vs *macrocyclic* ring current interplay
- Delocalization error changes the magnitude of descriptors





antiaromatic [4n] [4n+2] [4n]

Casademont-Reig, Woller, Contreras-García, Alonso, Torrent-Sucarrat, Matito, *PCCP* **2018**, 20, 2787

Leyva-Parra, Pino-Rios, Inostroza, Solà, Alonso, Tiznado, *Chem. Eur. J.* **2024**, 30, e202302415

Van Nyvel, Alonso, Solà, *Chem. Sci.* **2025**, 16, 5613

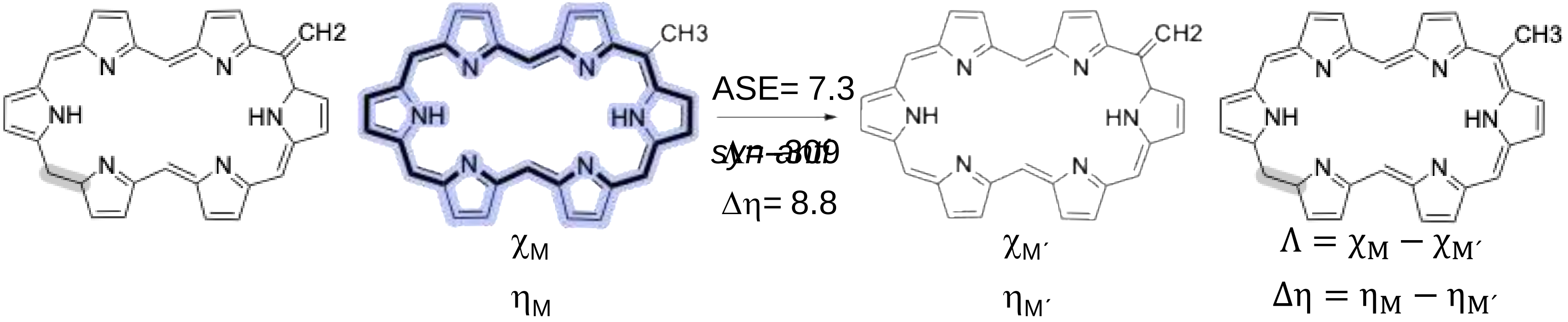
Expanded Porphyrins

Devising suitable reaction schemes for flexible macrocycles is difficult

Isomerization approach to assess global aromaticity **ASE**

- ASE >0 aromatic
- ASE < 0 antiaromatic

Magnetic susceptibility exaltation (Λ) and relative hardness ($\Delta\eta$)



ASE= 7.3

syn-anti

$\Lambda = -209$

$\Delta\eta = 8.8$

χ_M

η_M

$\chi_{M'}$

$\eta_{M'}$

$$\Lambda = \chi_M - \chi_{M'}$$

$$\Delta\eta = \eta_M - \eta_{M'}$$

- ⊗ *syn-anti* corrections required
- ⊗ dependence on the level of theory
- ⊗ contamination of energetic values
- ✓ two additional global descriptors: Λ and $\Delta\eta$

Alonso, Fernández, in *Aromaticity*, Elsevier, 2021, 195

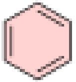
ASE and $\Delta\eta$ are given in kcal mol^{-1} and Λ in ppm cgs

Global Aromaticity of Macrocycles

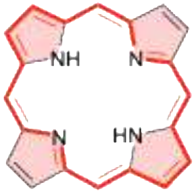
To what extent does aromaticity or antiaromaticity contribute to the stabilization or destabilization of expanded porphyrins?

Isomerization approach

ASE, $\Delta\eta > 0$ aromatic $\Lambda < 0$
ASE, $\Delta\eta < 0$ antiaromatic $\Lambda > 0$

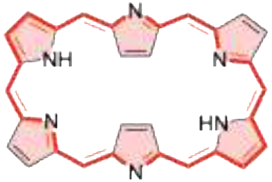


ASE = 34.3
Δη = 55.3
Λ = -18

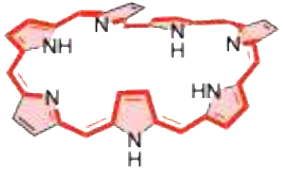


18P
ASE = 11.1
Δη = 9.2
Λ = -176

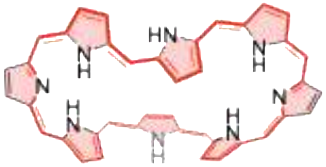
22P
ASE = 13.6
Δη = 11.8
Λ = -301



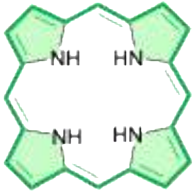
26P
ASE = 7.4
Δη = 7.1
Λ = -400



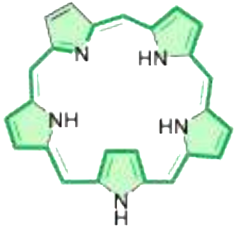
32M
ASE = 5.8
Δη = 4.9
Λ = -219



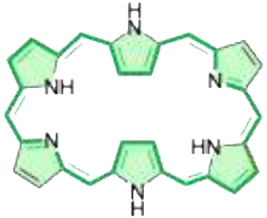
36M
ASE = 2.7
Δη = 3.8
Λ = -344



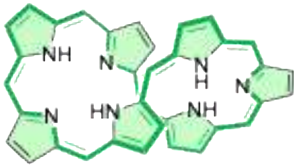
20P
ASE = -5.2
Δη = -17.8
Λ = -156



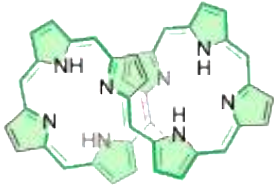
24P
ASE = -2.4
Δη = -13.5
Λ = 307



28P
ASE = -4.8
Δη = -11.9
Λ = 1019



32F
ASE = -2.4
Δη = -10.1
Λ = 149

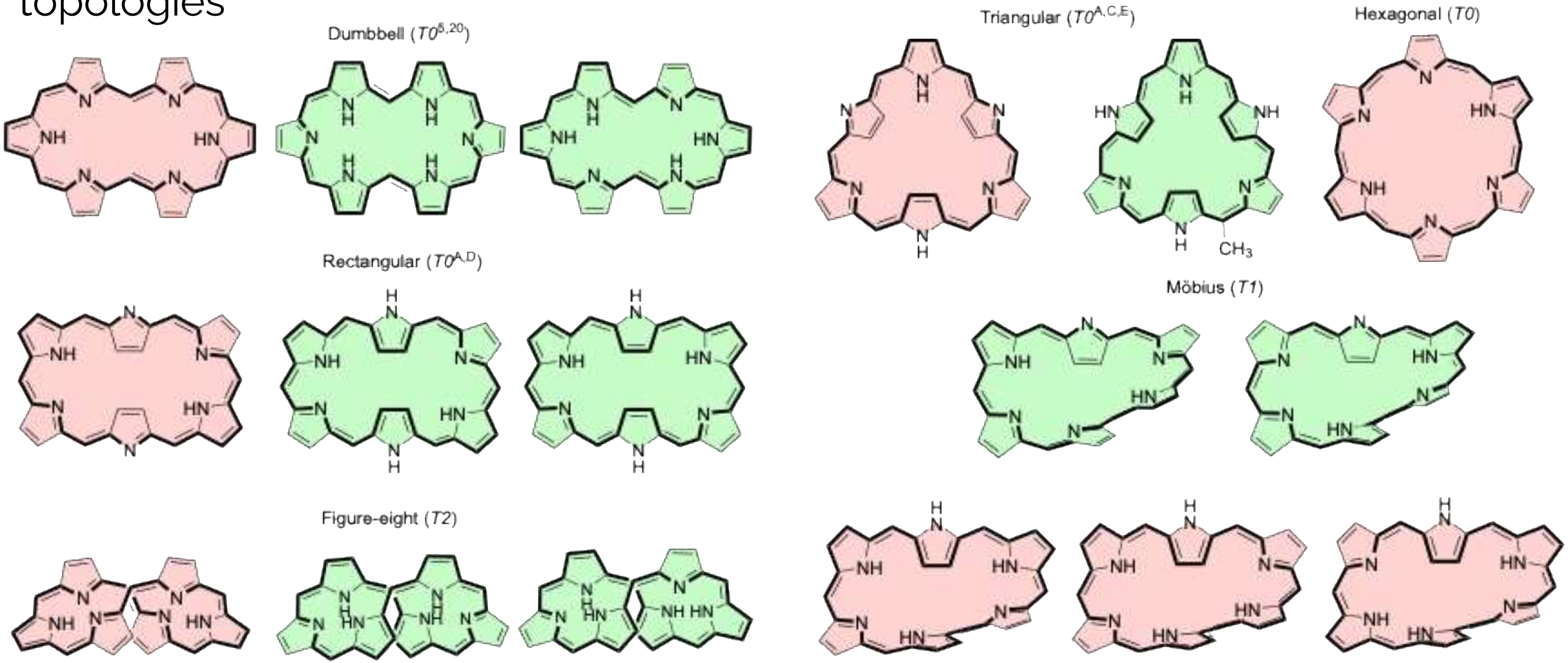


36F
ASE = -2.1
Δη = -3.8
Λ = 22

✓ Clear-cut distinction between globally aromatic and antiaromatic macrocycles

Global Aromaticity of Macrocycles

Conformational stability is mainly governed by ring strain and intramolecular hydrogen bonding, but aromatic stabilization is key for viable Möbius topologies

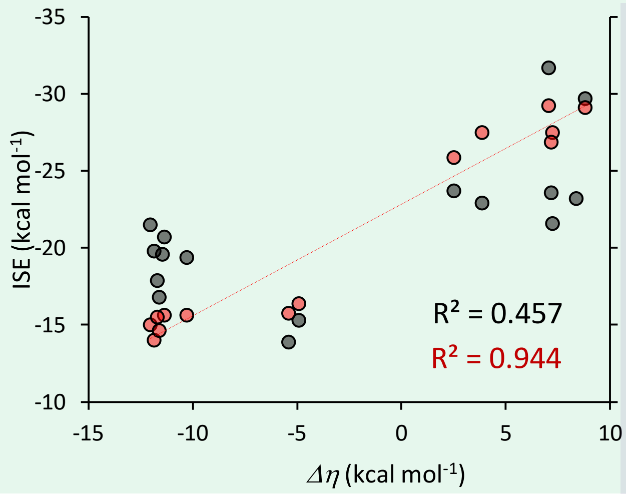


Alonso, Geerlings, De Proft, *Chem. Eur. J.* **2012**, 18, 10916

Do Energetic Descriptors Agree with other Criteria?

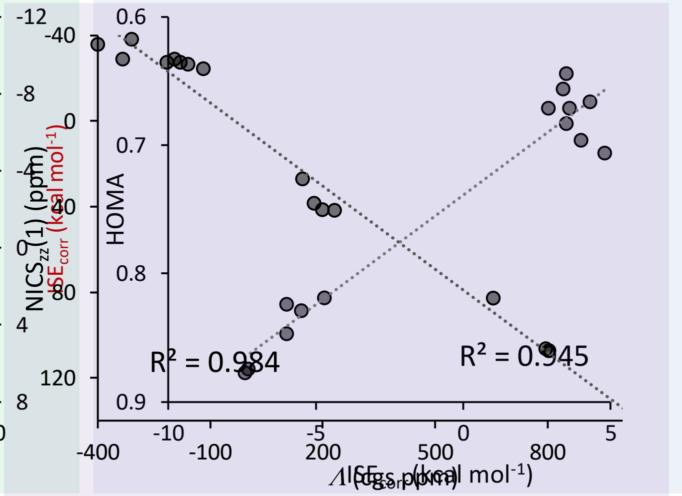
Corrected ISE values align with other aromaticity descriptors

reactivity

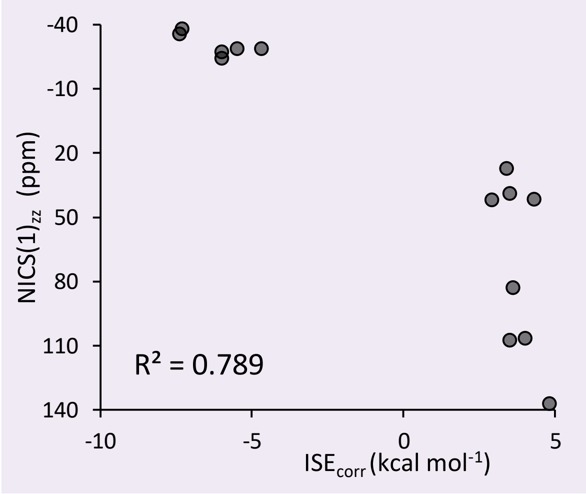


magnetic

structural



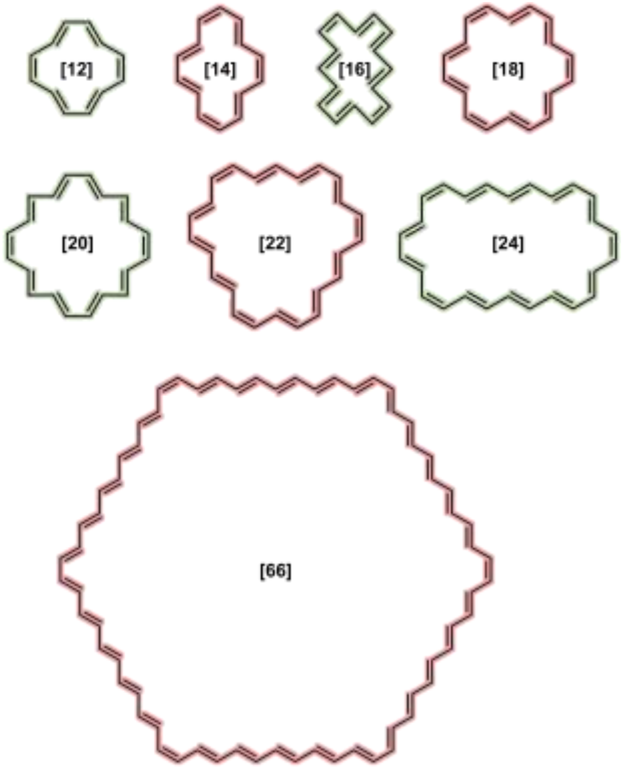
magnetic



- Aromatic macrocycles are energetically stabilized with positive relative hardness values and exhibit diamagnetic susceptibility exaltations along with negative NICS indices
- Exaltation from ISE method perfectly correlates with magnetic descriptors

Limits of Hückel and Baird Rules

How do aromaticity and antiaromaticity influence the stability of singlet and triplet annulenes?



L. Van Nyvel

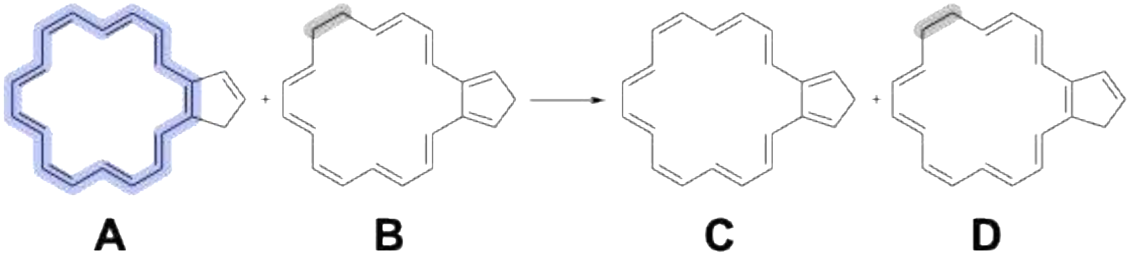
M. Solà

Van Nyvel, Alonso, Solà, *Chem. Sci.* **2025**, 16, 5613

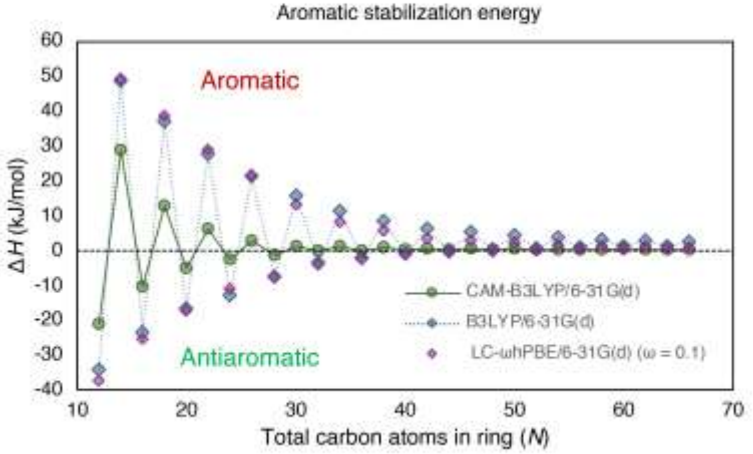
Limits of Hückel and Baird Rules

How do aromaticity and antiaromaticity influence the stability of singlet and triplet annulenes?

indene-isoindene approach



ASE = (C+D)- (A+B)



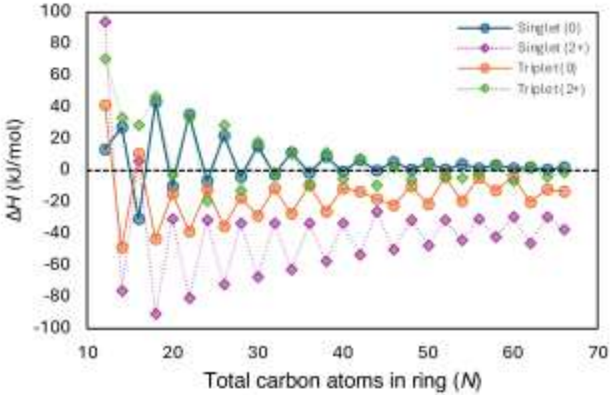
- Neutral singlet annulenes with [4n+2]/[4n] π-electrons show positive/negative ASE values
- ASE is inversely to ring size, approaching zero for very large annulenes

Van Nyvel, Alonso, Solà, *Chem. Sci.* **2025**, 16, 5613

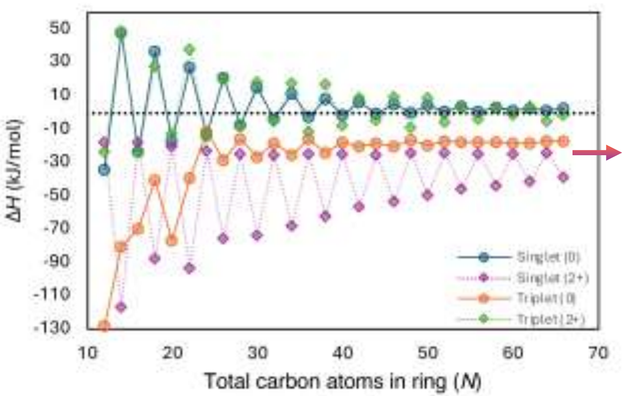
Triplet and Charged Annulenes

The location of the neutral triplet and singlet dication annulene curves is unexpected, suggesting that all structures with $N > 16$ would be antiaromatic

Ⓐ Minimum energy geometries



Ⓑ **A-D** constrained to be planar



Spin-density localization destabilizes derivative **B**, shifting the ASE curves

Singlet (0): $\mathbf{A}_S^0 + \mathbf{B}_S^0 \rightarrow \mathbf{C}_S^0 + \mathbf{D}_S^0$

Singlet (2+): $\mathbf{A}_S^{2+} + \mathbf{B}_S^{2+} \rightarrow \mathbf{C}_S^{2+} + \mathbf{D}_S^{2+}$

Triplet (0): $\mathbf{A}_T^0 + \mathbf{B}_T^0 \rightarrow \mathbf{C}_T^0 + \mathbf{D}_T^0$

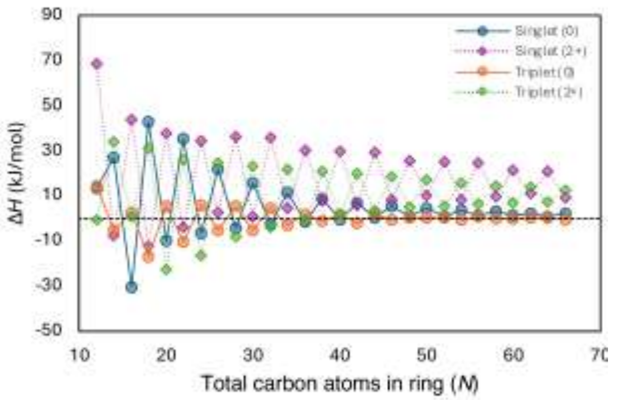
Triplet (2+): $\mathbf{A}_T^{2+} + \mathbf{B}_T^{2+} \rightarrow \mathbf{C}_T^{2+} + \mathbf{D}_T^{2+}$

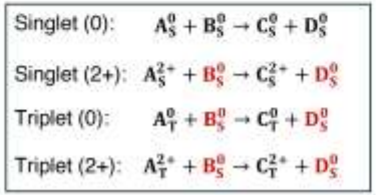
Triplet and Charged Annulenes

The location of the neutral triplet and dication singlet annulene curves is unexpected, suggesting that all structures with $N > 16$ would be antiaromatic

- Expected behavior: **mirror-image trends** for neutral and triplet annulenes as well as neutral and charged structures bearing the same multiplicity
- For large *N*, ASE values converge for predicted aromatic and antiaromatic systems according to aromaticity rules
- Hückel and Baird rules lose significance for larger annulenes

Ⓒ Planarity enforced only to **B** & **D**





Singlet (0):	$A_S^0 + B_S^0 \rightarrow C_S^0 + D_S^0$
Singlet (2+):	$A_S^{2+} + B_S^0 \rightarrow C_S^{2+} + D_S^0$
Triplet (0):	$A_T^0 + B_S^0 \rightarrow C_T^0 + D_S^0$
Triplet (2+):	$A_T^{2+} + B_S^0 \rightarrow C_T^{2+} + D_S^0$

Van Nyvel, Alonso, Solà, *Chem. Sci.* **2025**, 16, 5613

Take-Home Messages

- Enhanced energetic stability is regarded as the **prime origin of aromaticity**
- REs and ASEs are **reference-dependent** and susceptible to **spurious contributions**
- A **theoretical link** between energetic and magnetic aromaticity criteria is still missing
- Aromaticity quantification requires a **multidimensional lens**—relying on single descriptors or photophysical properties alone can lead to misleading interpretations

Alonso, Fernández, *Aromaticity* (Elsevier) **2021**, 195-235

De Vleeschouwer, Desmet, Alonso, *Chem. Methods* **2025**, 5, e202500064

Fundamentals of Photochemistry

ICESAA-4,
8-11 January, 2026
THIRUVANANTHAPURAM KERALA, INDIA

Victor Gray
victor.gray@kemi.uu.se
www.excitingmolecules.com
Uppsala University
Sweden

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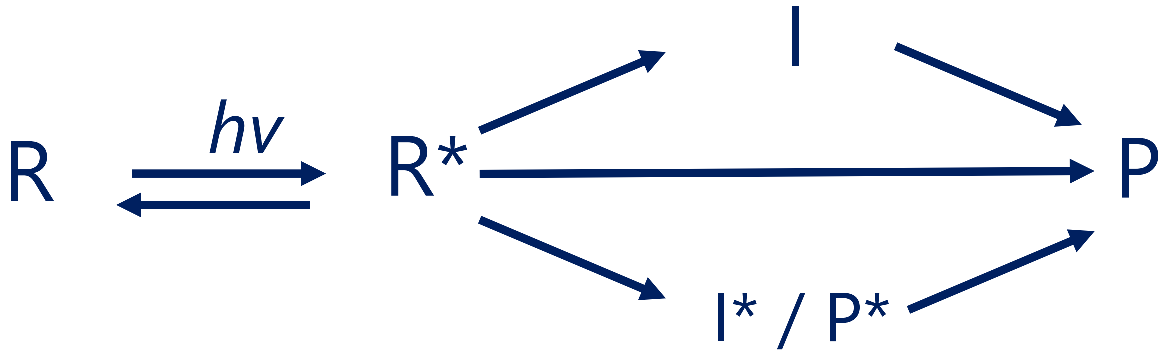
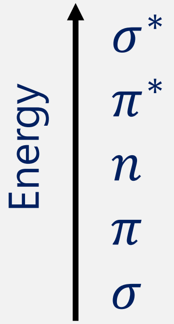
Chemistry and Photochemistry

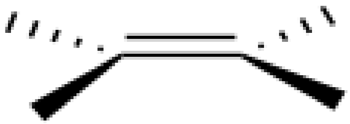


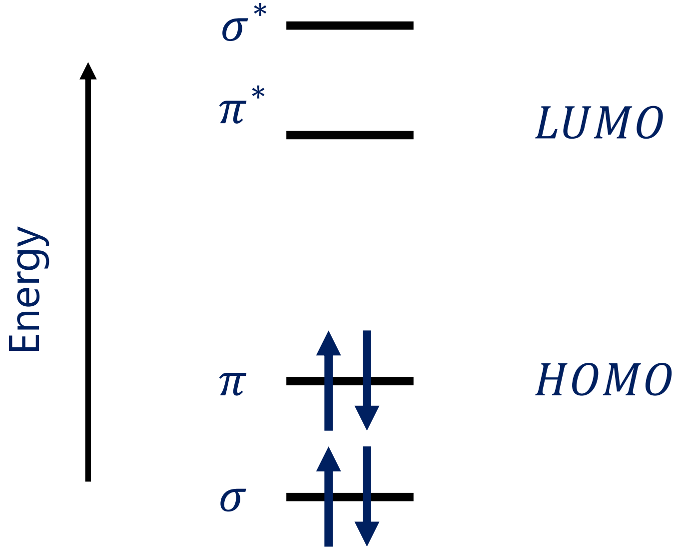
$$\begin{tikzcd}
 & & I \arrow[dr] & \\
R \arrow[r, shift left, "h\nu"] & R^* \arrow[l, shift left] \arrow[ur] \arrow[rr] \arrow[dr] & & P \\
 & & I^* / P^* \arrow[ur] &
\end{tikzcd}$$

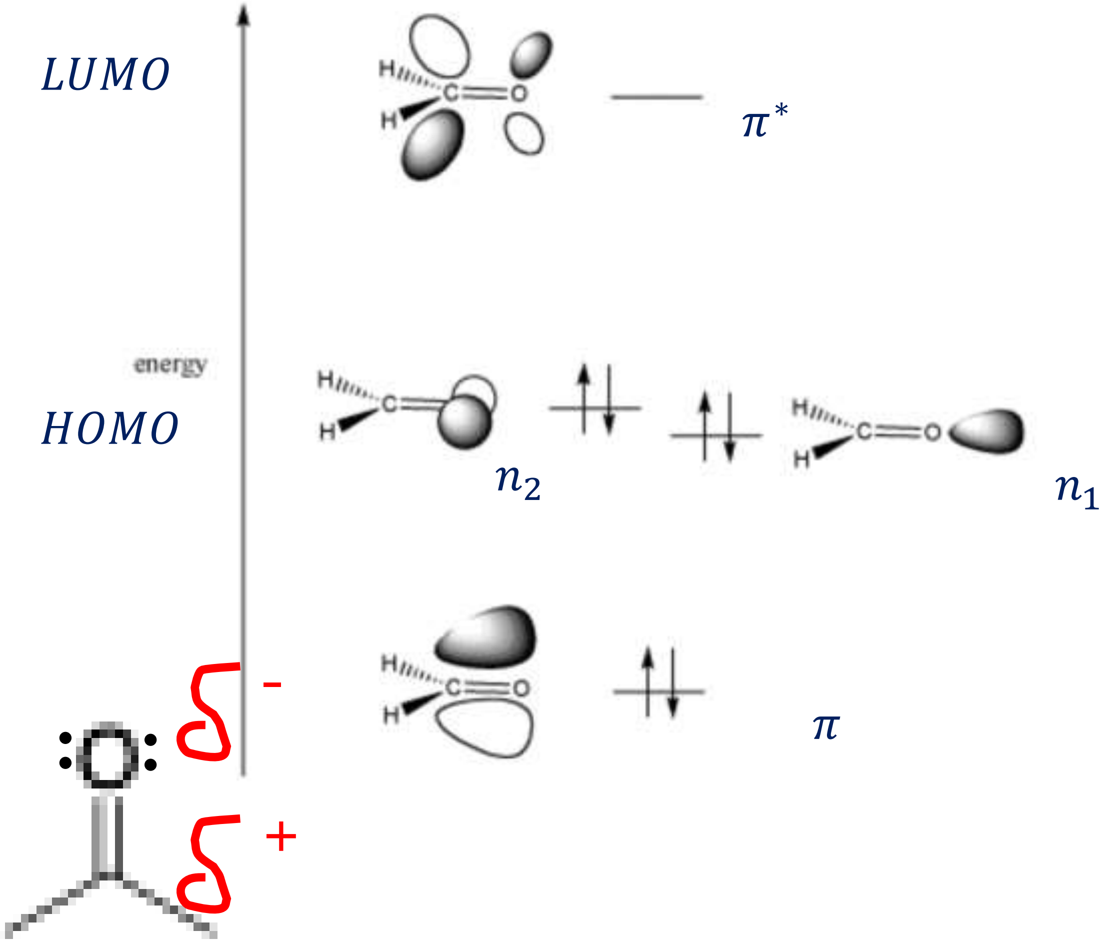
Molecular Orbital

Typical order of bonds:









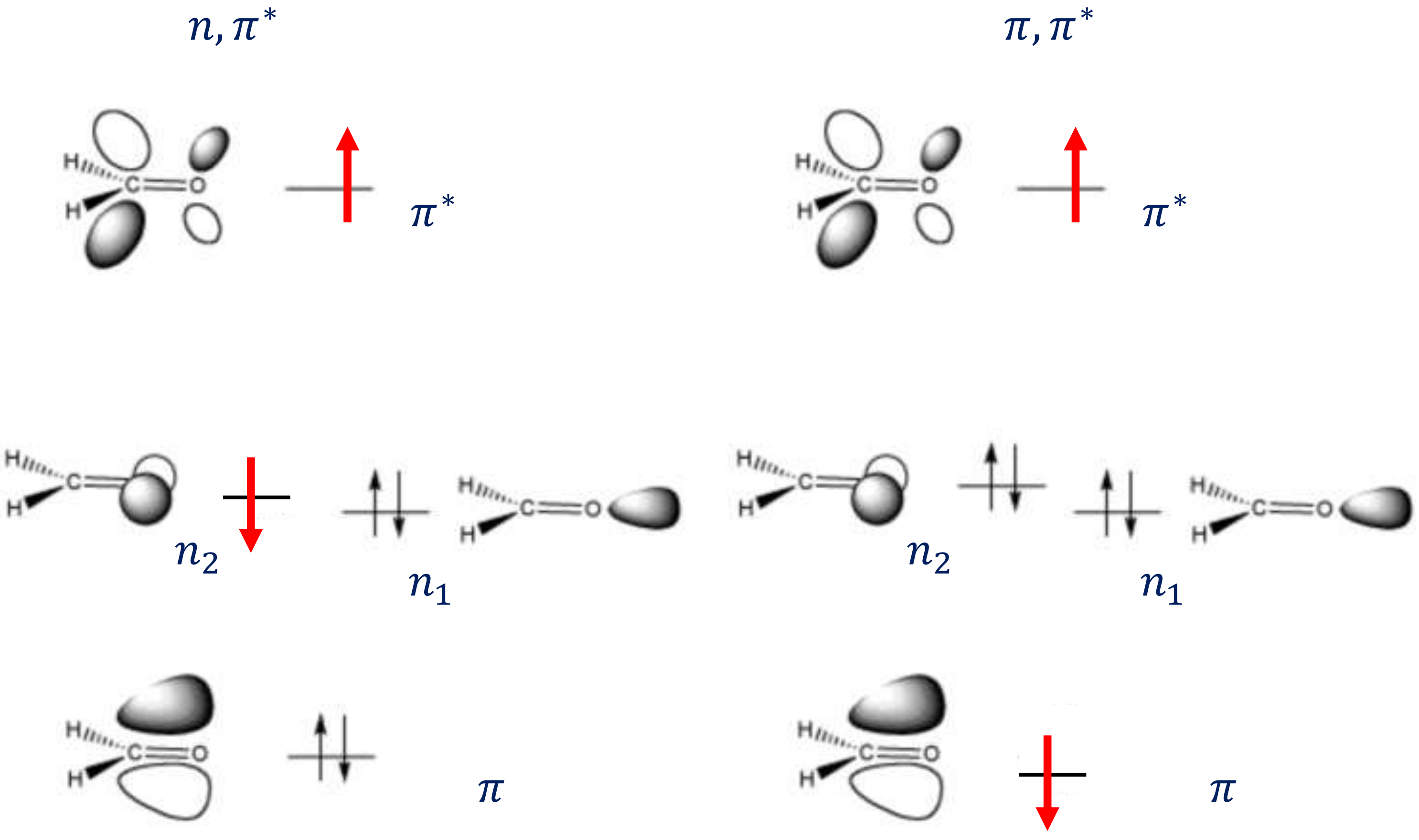
From Ground State to Excited State

Which orbitals are involved can matter:
$\pi \rightarrow \pi^*$: no net π –bond

$n_2 \rightarrow \pi^*$: oxygen becomes electrophilic, obtains radical character

Excited states are better reductants and oxidants

Denote the excited states by the singly occupied orbitals:
$\pi \rightarrow \pi^*$ results in a π, π^*
$n \rightarrow \pi^*$ results in a n, π^*



Outline

1. 1st Law of Photochemistry: No Absorption, No Photochemistry
2. Inter System Crossing
3. The Fate of Excited States and Jablonski Diagram
4. Electron and Energy Transfer

1

1st Law of Photochemistry: No Absorption, No Photochemistry

I. Absorption of light and transition dipole moments
II. Selection rules
III. Frank-Conon Principle

Absorption Spectra and Beer-Lamberts law

Absorbance (A) :

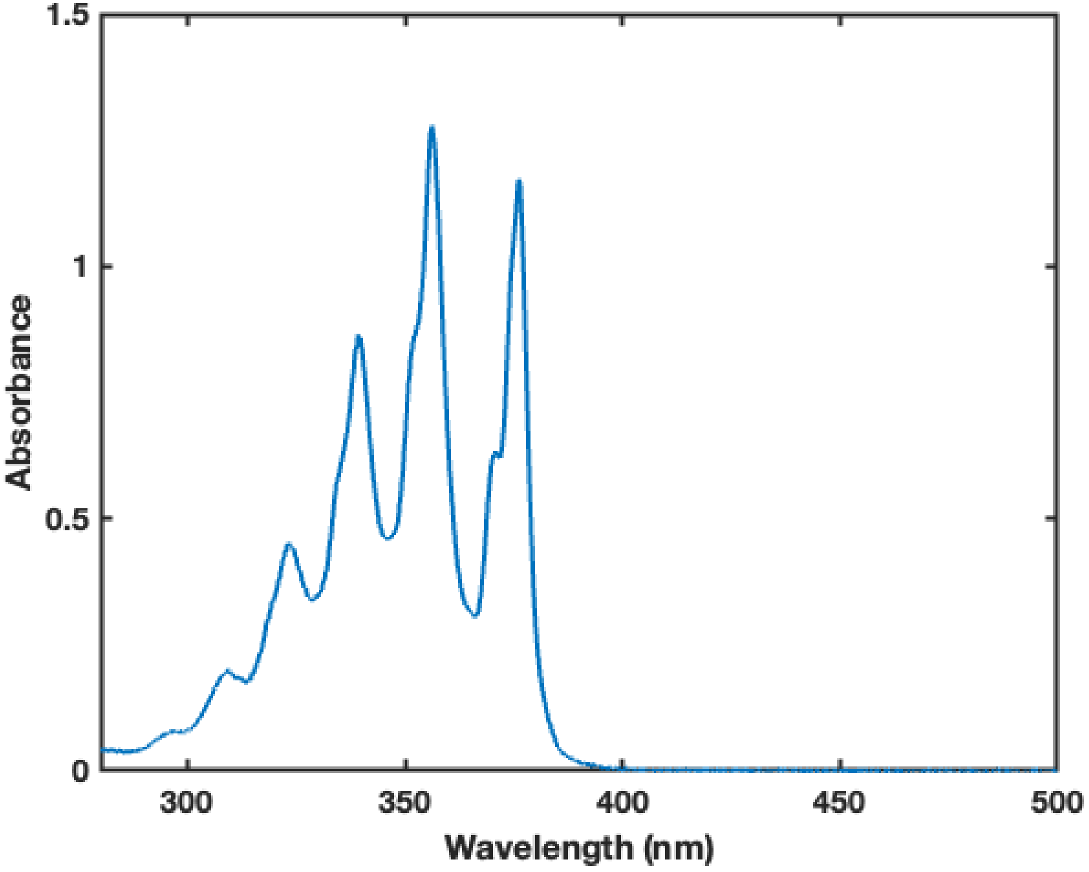
$$A = -\log(\mathrm{T}) = \log\left(\frac{I_0}{I}\right) = \varepsilon l c$$

ε = Molar absorptivity (extinction coefficient)
$\varepsilon(\lambda)$ varies with wavelength Unit: $M^{-1}\,cm^{-1}$

l = pathlength Unit: cm

c = molar concentration Unit: M (mol/L)

Anthracene



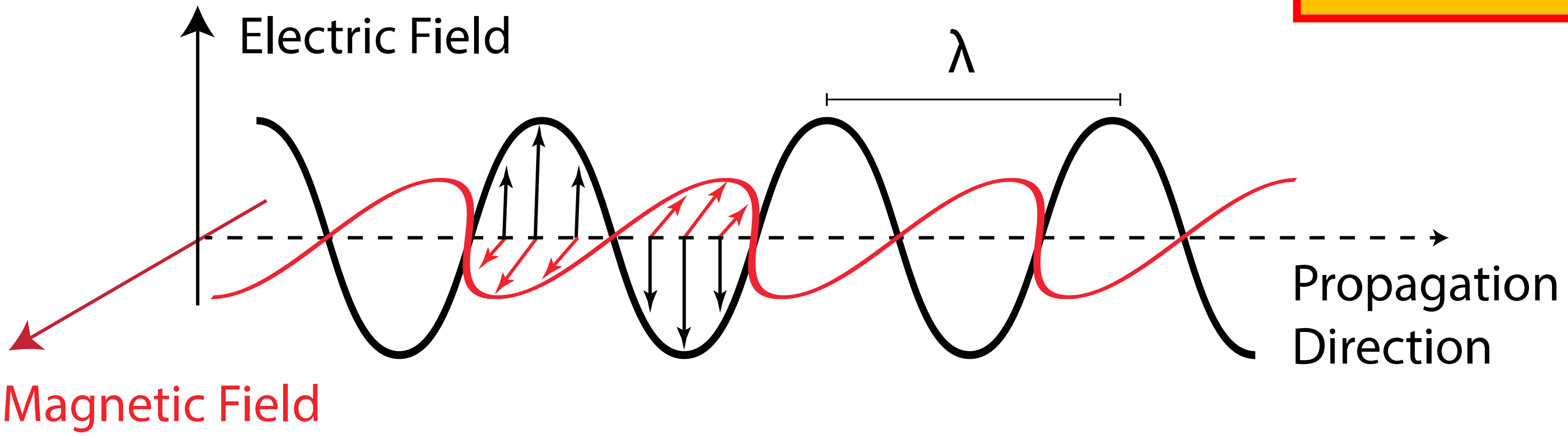
Light

Light – An electromagnetic wave and particle (photon)

$$E = h\nu$$

$$c = \lambda\nu$$

$$E = hc/\lambda$$



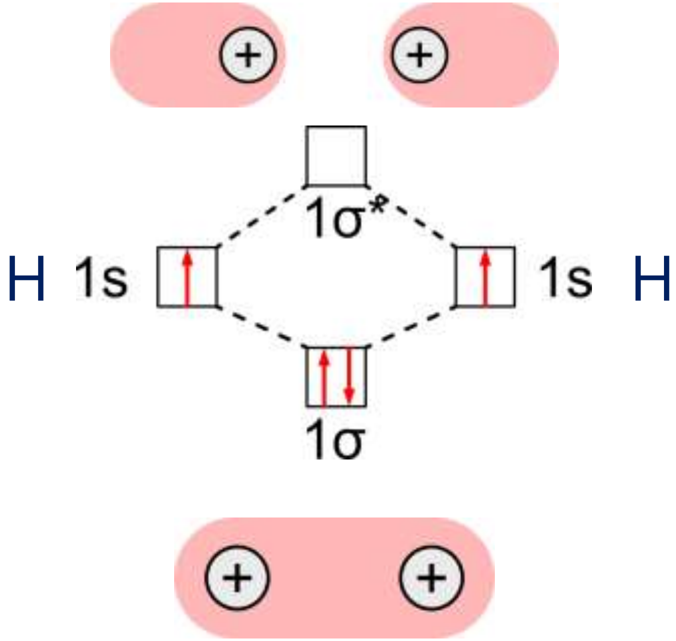
Electric field component is what we will focus on

Absorption of Light

Requirement for light absorption:

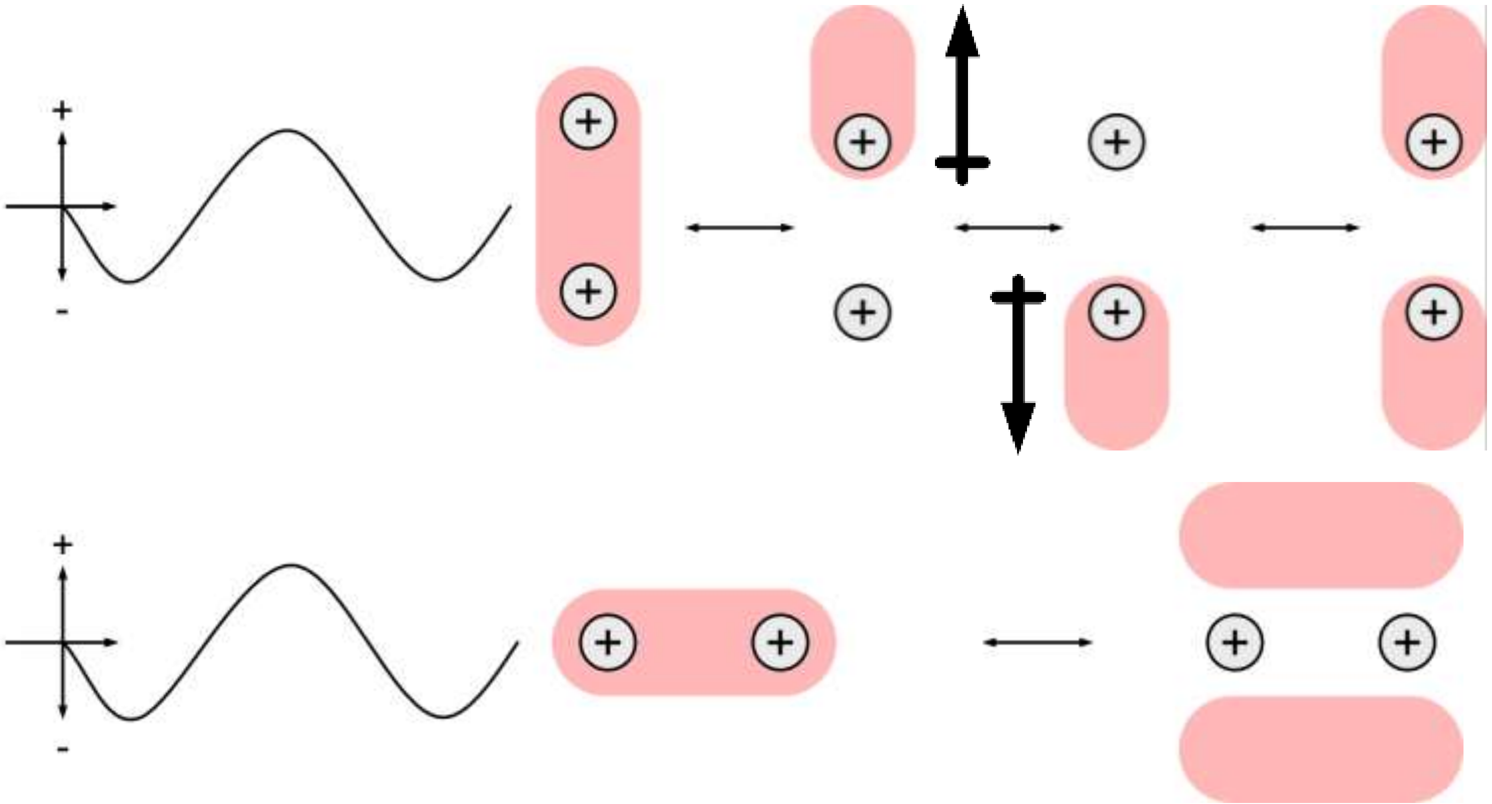
$$\Delta E = E_2 - E_1 = h\nu$$

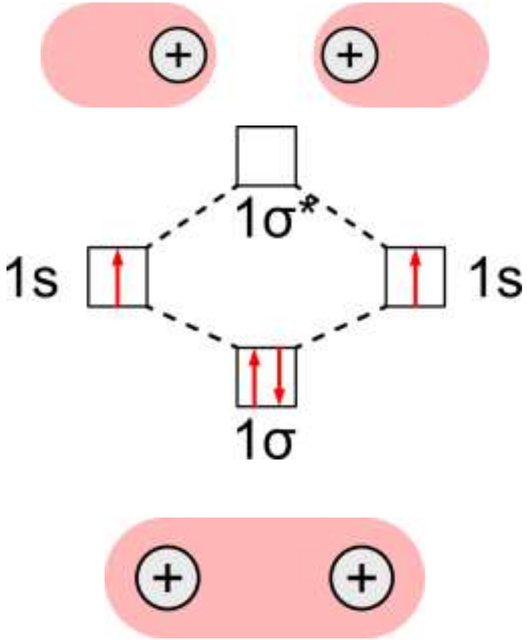
Initial state of Energy E_1: σ^2
Final State of Energy E_2: σ, σ^*



Absorption of Light

Light interacting with Hydrogen Molecule



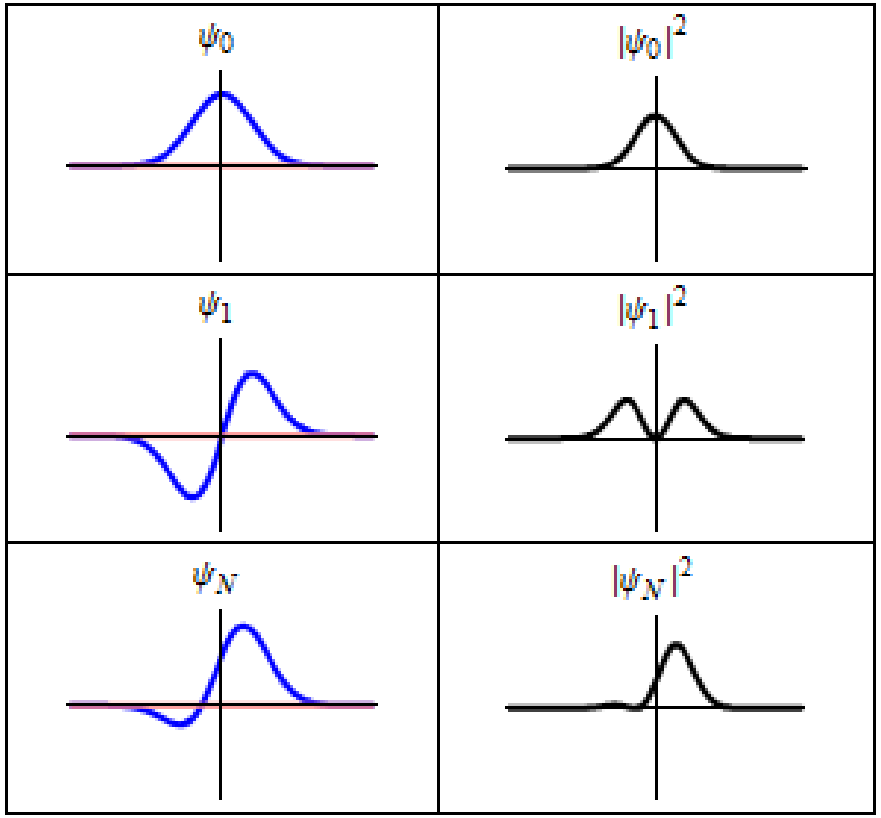


Transition Dipole Moment

Dipole operator (for one electron): $\hat{\mu} = e\,\boldsymbol{r}$

$$\mu_{if} = \int \Psi_f^* \hat{\mu} \Psi_i \, d\tau$$

$\hat{\mu}$ is an odd function, → initial and final states must have different symmetries → Laporte rule



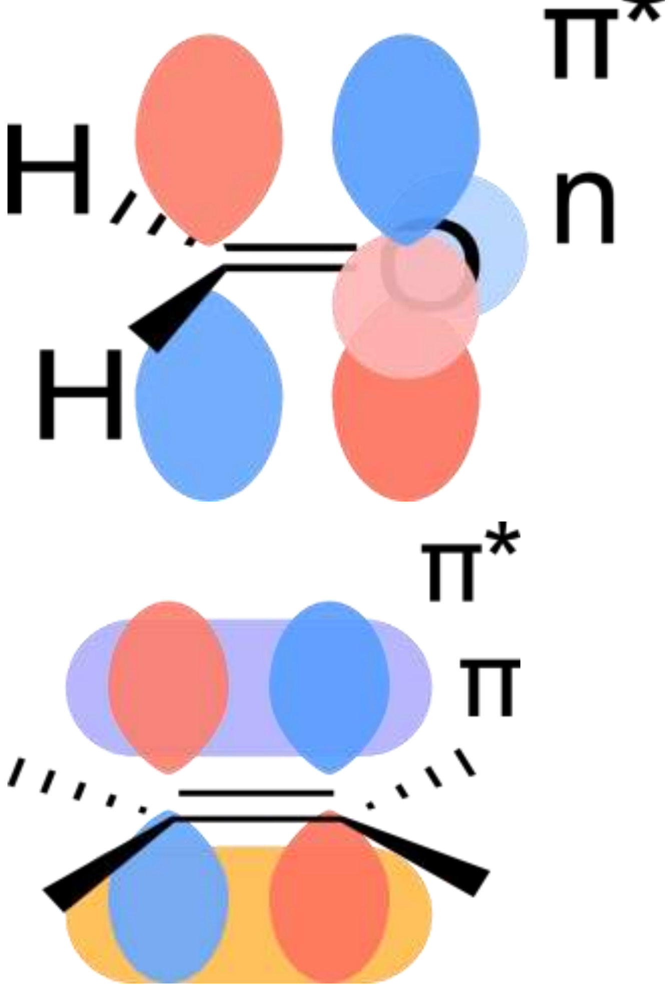
Wikipedia/transition dipole moment

Transition Dipole Moment

Dipole operator (for one electron): $\hat{\mu} = e\,\boldsymbol{r}$

$$\mu_{if} = \int \Psi_f^* \hat{\mu} \Psi_i d\tau$$

$|\mu_{if}|^2 = 0$ → forbidden transition (e.g. $n \rightarrow \pi^*$)
$|\mu_{if}|^2 > 0$ → allowed transition (e.g. $\pi \rightarrow \pi^*$)



Transition Dipole Moment

Probability of transition ∝ $|\mu_{if}|^2$

$$|\mu_{if}|^2 = 9.18 \times 10^{-3} \int \left(\frac{\epsilon}{\nu}\right) d\nu$$

$$f_{if} = 4.325 \times 10^{-9} \int (\epsilon) d\nu$$

Where f_{if} is the oscillator strength and ϵ the molar absorption coefficient

Transition Probability

Probability of transition $\propto \left|\mu_{if}\right|^2 = |\int \Psi_f^* \hat{\mu} \Psi_i d\tau|^2$

Born-Oppenheimer approximation – nuclear motion (**R**) much slower than electron motion (**r**). We also treat the spin (s) separately.

$$\Psi(\mathbf{r}, \mathbf{R}, s) = \psi(\boldsymbol{r})\phi(s)\chi(\boldsymbol{R})$$

Probability of transition

$$\propto \left|\int \psi(\boldsymbol{r})_f^* \hat{\mu}(\boldsymbol{r})\psi(\boldsymbol{r})_i d\boldsymbol{r}\right|^2 \left|\int \phi(s)_f^* \phi(s)_i ds\right|^2 \left|\int \chi(\boldsymbol{R})_f^* \chi(\boldsymbol{R})_i d\boldsymbol{R}\right|^2$$

Transition dipole moment

Spin Overlap ($\Delta S = 0$)

Franck-Condon Factor

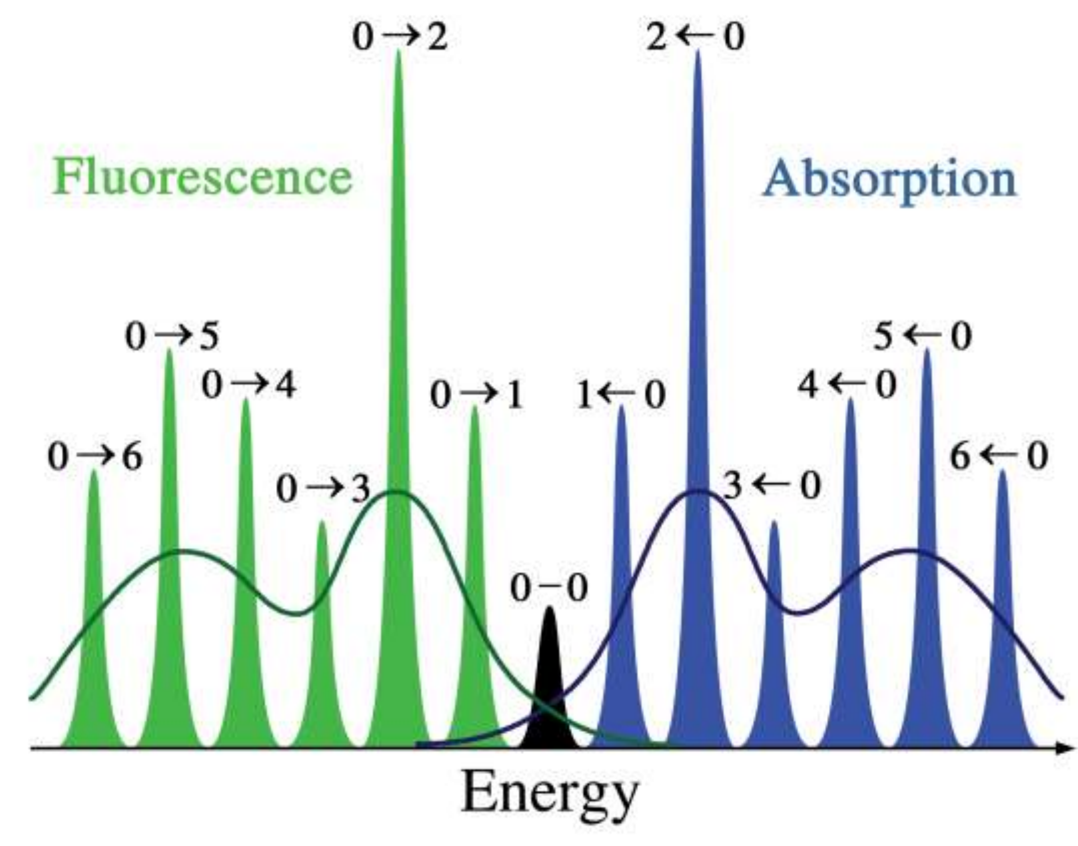
Franck-Condon Principle

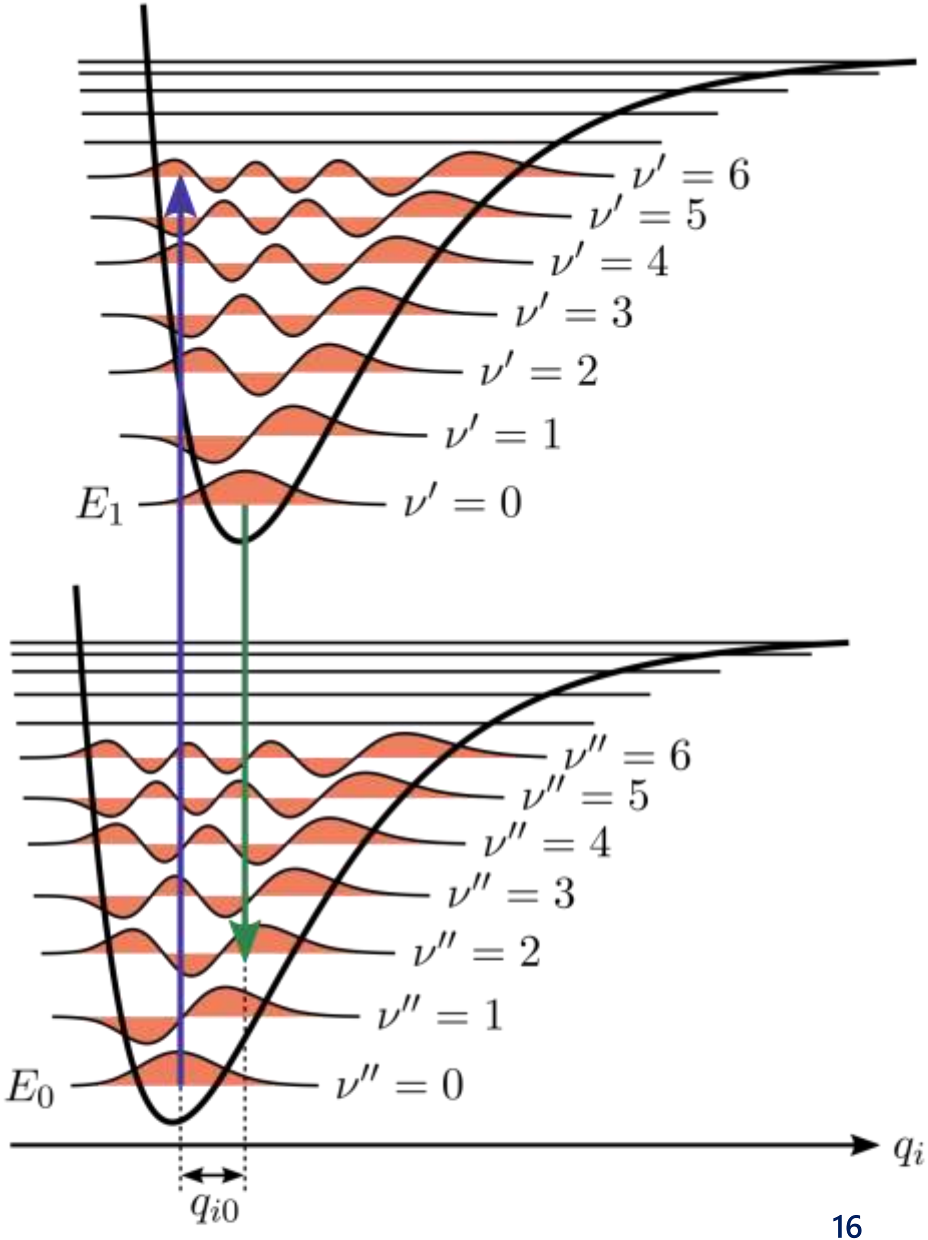
Fra

Oft on’t
sha ear
coo

Tra ion
→

He





Wikipedia/Franck-Condon principle

Some Rules for Absorption

1. Energy Conservation: $\Delta E = E_2 \; - E_1 = h\nu$
2. Transition dipole moment $|\mu_{if}|^2 > 0$ → Symmetry of orbitals matter
   $\pi \to \pi^*$ good overlap → $\varepsilon > 10\,000 \text{ M}^{-1} cm^{-1}$
   $n \to \pi^*$ poor overlap → $\varepsilon \sim 100 \; - 1000 \text{ M}^{-1} cm^{-1}$
3. Spin should be conserved
4. Vertical transitions

1st Law of Photochemistry: No Absorption, No Photochemistry

2 Intersystem Crossing

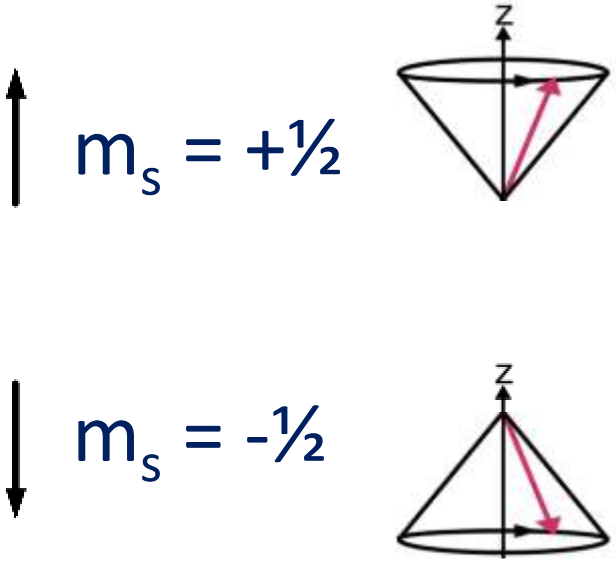
I. Singlet and triplet states

II. El-Sayed's rule

Singlet and Triplet States

Spin of an electron:
Spin magnitude: s = ½
Spin projection: m_s = +½ , -½

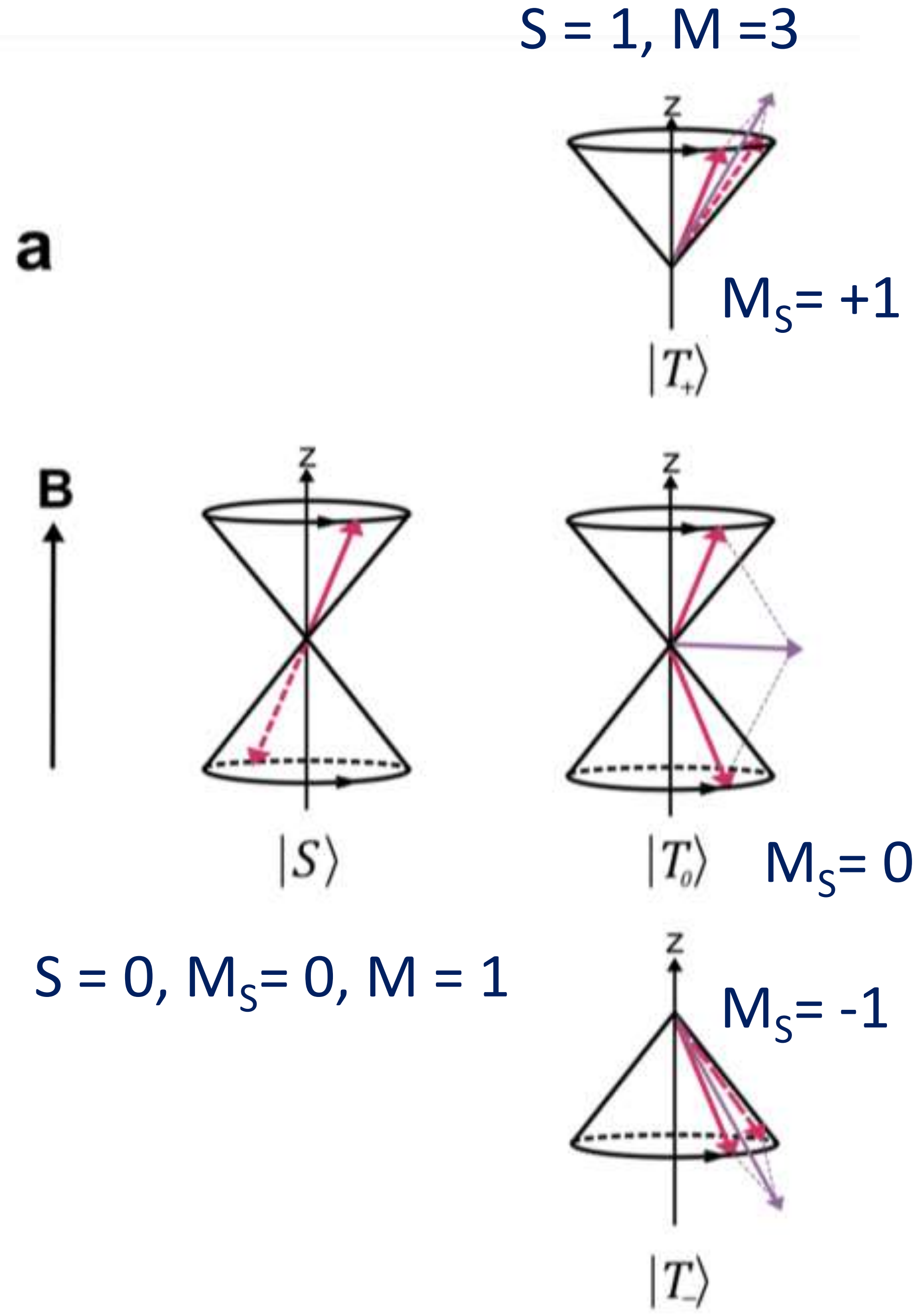
Two coupled electrons:
Total angular momentum: S = 0 (singlet), 1 (triplet)
Multiplicity: M = 2S+1 (1 singlet, 3 triplets)
Total spin projection: M_s = S, S-1,…-S
States denoted by Multiplicity: $^{M}(n,\pi^*)$



Singlet and Triplet States

Spin of an electron:
Spin magnitude: $s = ½$
Spin projection: $m_s = +½ , -½$

Two coupled electrons:
Total angular momentum: $S = 0$ (singlet), 1 (triplet)
Multiplicity: $M = 2S+1$ (1 singlet, 3 triplets)
Total spin projection: $M_s = S, S-1,…-S$
States denoted by Multiplicity: $^{M}(n, \pi^*)$



Jessica Walton, PhD Thesis

Singlet and Triplet States

D

P

s

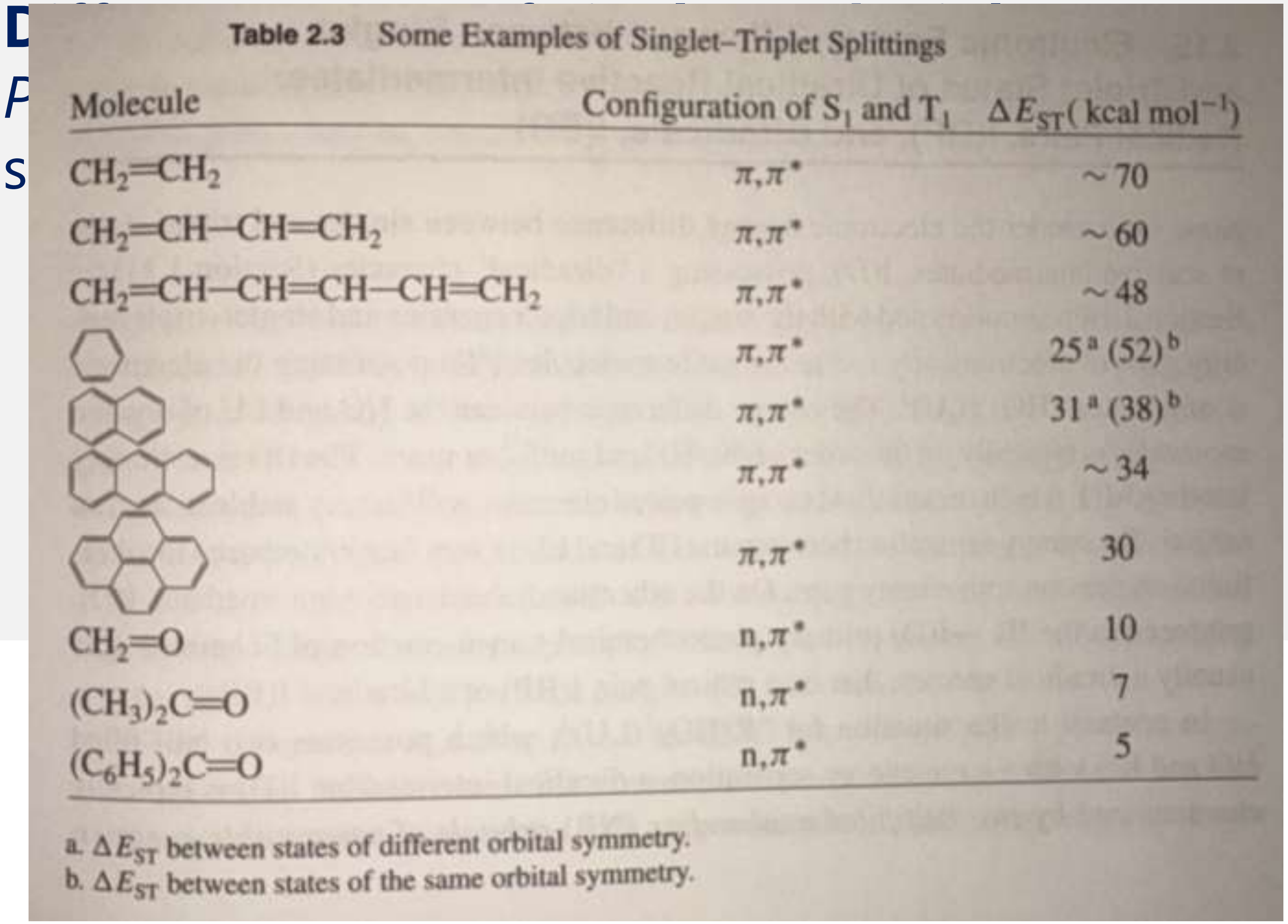
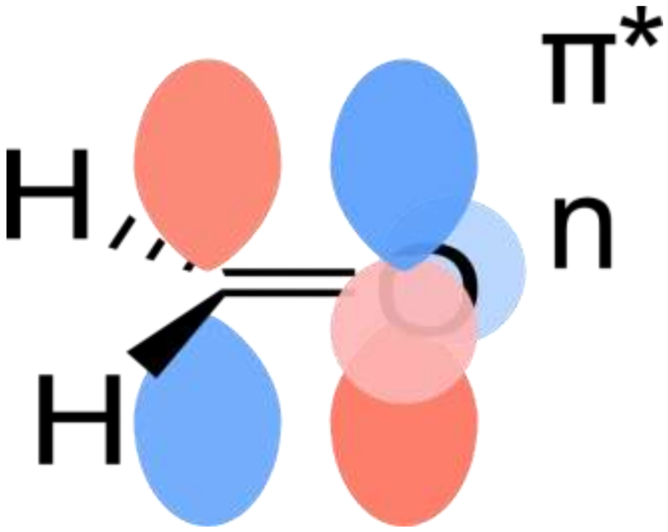


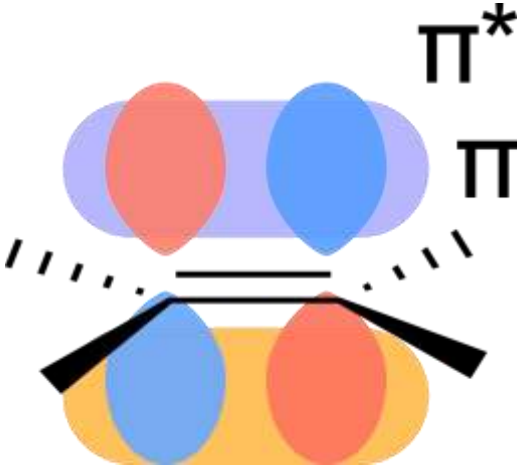
Table 2.3 Some Examples of Singlet–Triplet Splittings

Molecule	Configuration of S_1 and T_1	ΔE_{ST} (kcal mol^{-1})
$CH_2{=}CH_2$	π,π^*	~70
$CH_2{=}CH{-}CH{=}CH_2$	π,π^*	~60
$CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$	π,π^*	~48
	π,π^*	25[a] (52)[b]
	π,π^*	31[a] (38)[b]
	π,π^*	~34
	π,π^*	30
$CH_2{=}O$	n,π^*	10
$(CH_3)_2C{=}O$	n,π^*	7
$(C_6H_5)_2C{=}O$	n,π^*	5

a. ΔE_{ST} between states of different orbital symmetry.
b. ΔE_{ST} between states of the same orbital symmetry.



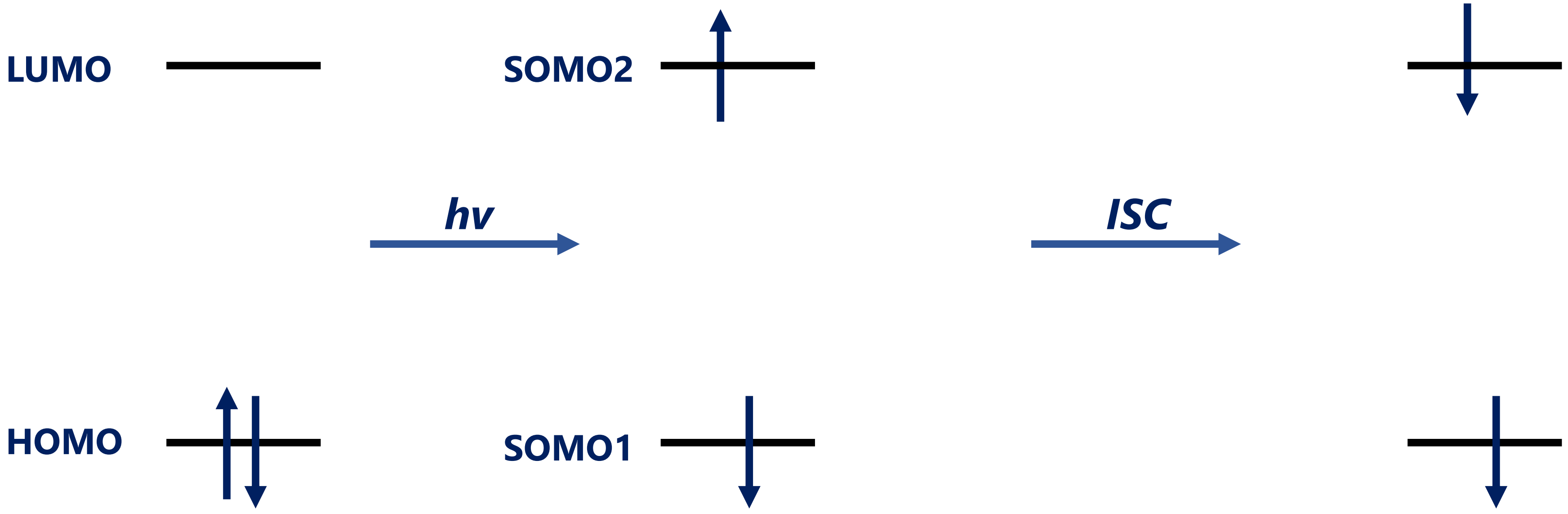
$$J(n,\pi^*) \sim \int \Psi_n^* \Psi_{\pi*} = small$$



$$J(\pi,\pi^*) \sim \int \Psi_\pi^* \Psi_{\pi*} = large$$

Singlet and Triplet States

Light carries no spin angular momentum → spin is conserved in a transition



$S = 0, M_S = 0, M = 1$ $S = 0, M_S = 0, M = 1$ $S = 1, M_S = +1,0,-1, M = 1$

Inter System Crossing (ISC)

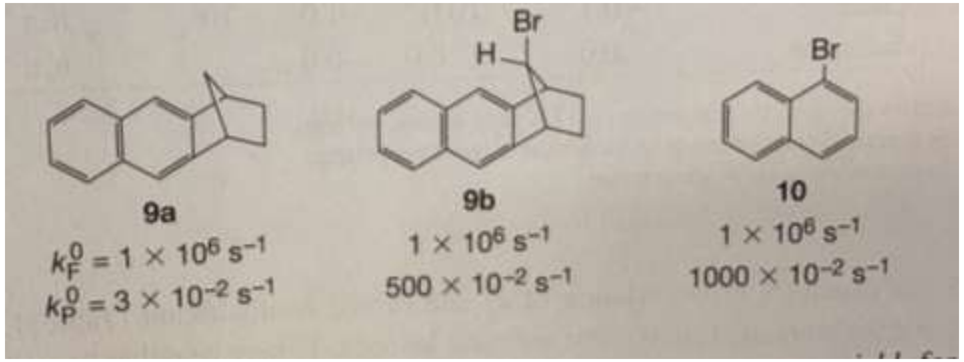
Spin-Orbit Coupling (SOC): interaction between an electron’s spin and its orbital motion around the nucleus

Consequence: the states are no longer purely singlet or triplet

$$\int \phi(s)_f^* \phi(s)_i ds \neq 0$$

Even for different spin multiplicities of final and initial state

Heavy atoms increases SOC!
SOC $\propto Z^4$



9a
$k_F^0 = 1 \times 10^6\ s^{-1}$
$k_P^0 = 3 \times 10^{-2}\ s^{-1}$

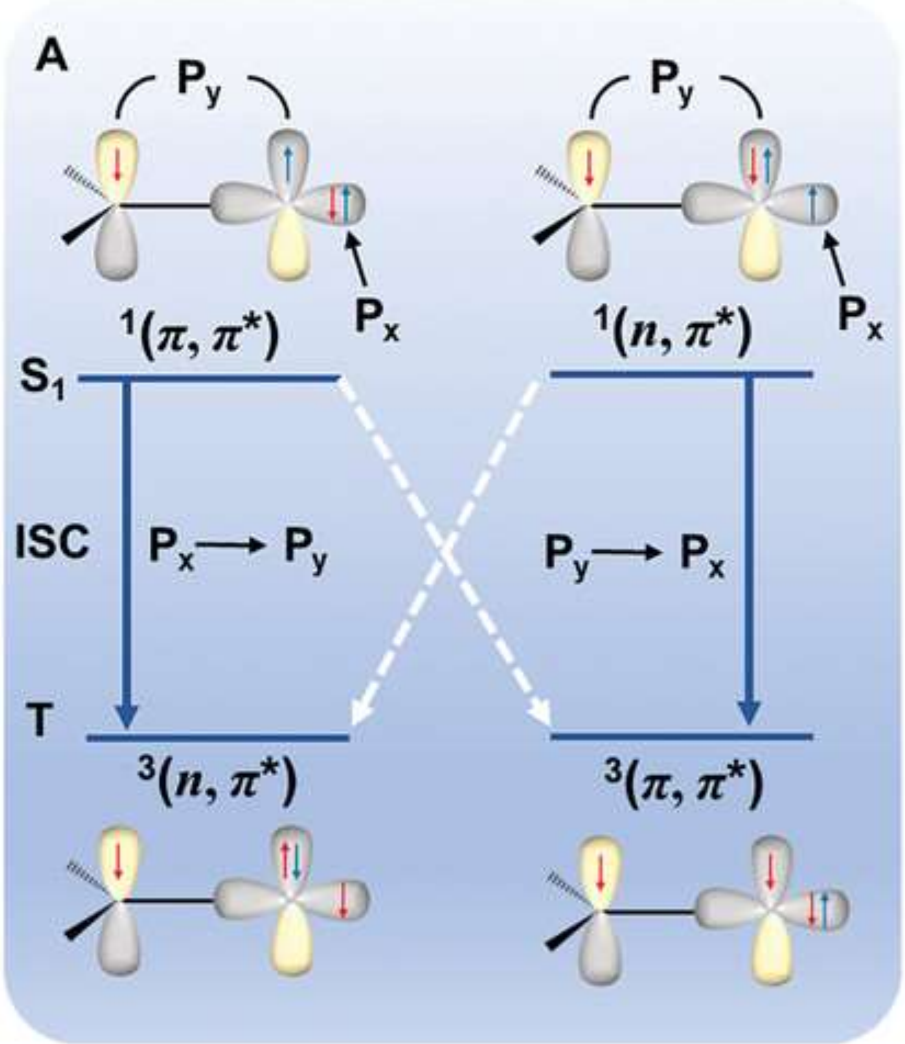
9b
$1 \times 10^6\ s^{-1}$
$500 \times 10^{-2}\ s^{-1}$

10
$1 \times 10^6\ s^{-1}$
$1000 \times 10^{-2}\ s^{-1}$

Inter System Crossing (ISC)

Change in orbital angular momentum can compensates for change in spin angular momentum

El-Sayed's Rule: Intersystem crossing is more efficient when the transition involves a change in orbital type (e.g., π,π* → nπ* or vice versa)



Adv. Funct. Mater. 2024, 34, 2315366

3

The Fate of Excited States and the Jablonski Diagram

I. Timescales of excited state processes
II. Kasha’s and Vavilov’s rule

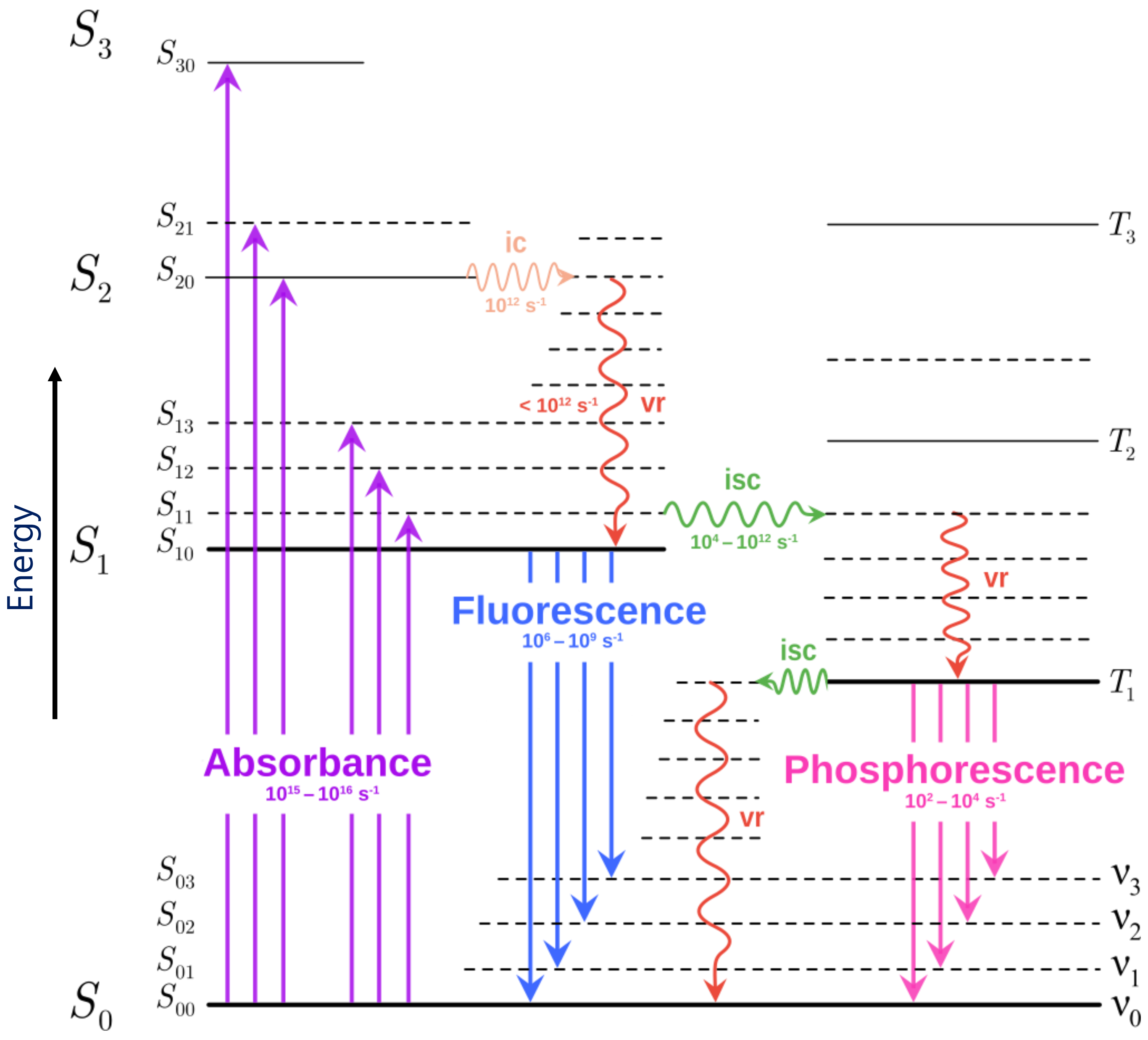
Jablonski Diagram

State diagram:
Each solid line represents an electronic state: e.g. S_1 a singlet n, π^* state.

Vibrational levels for each electronic state.

Transitions involving photons = straight arrows

Vibration mediated transitions = Wiggly arrows



Wikipedia/Jablonski diagram

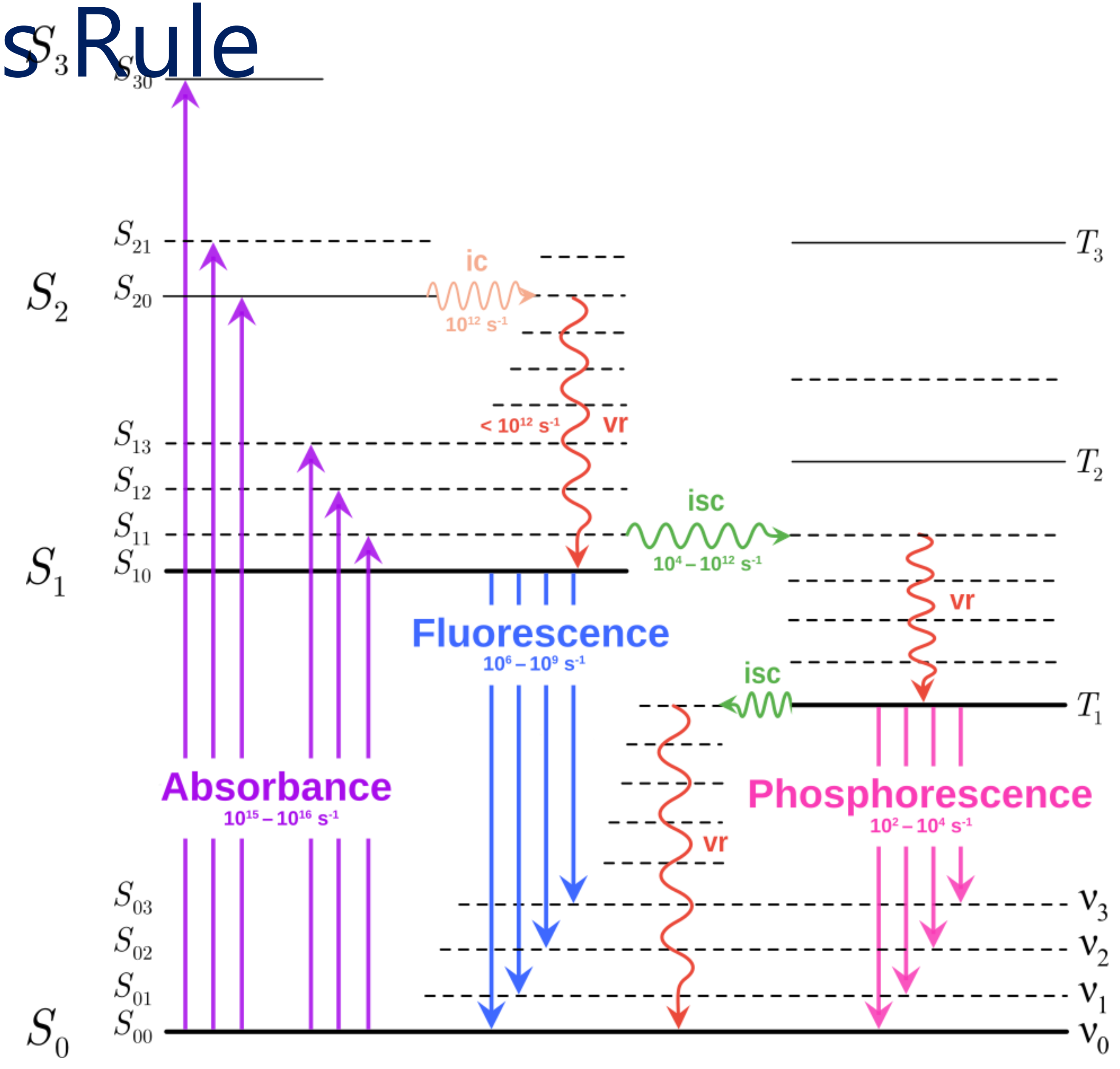
Kasha’s and Vavilov’s Rule

Transition	Time Scale (τ)
Internal Conversion	$10^{-14} - 10^{-11}$ s
Vibrational Relaxation	$10^{-14} - 10^{-11}$ s
Absorption	10^{-15} s
Phosphorescence	$10^{-4} - 10^{-1}$ s
Intersystem Crossing	$10^{-8} - 10^{-3}$ s
Fluorescence	$10^{-9} - 10^{-7}$ s

Rate of IC and VR > > rate of emission

Kasha: Photon emission occurs only from the lowest excited state of a given multiplicity

Vavilov: The quantum yield of emission is independent of excitation wavelength



Wikipedia/Jablonski diagram

Quantum Yields

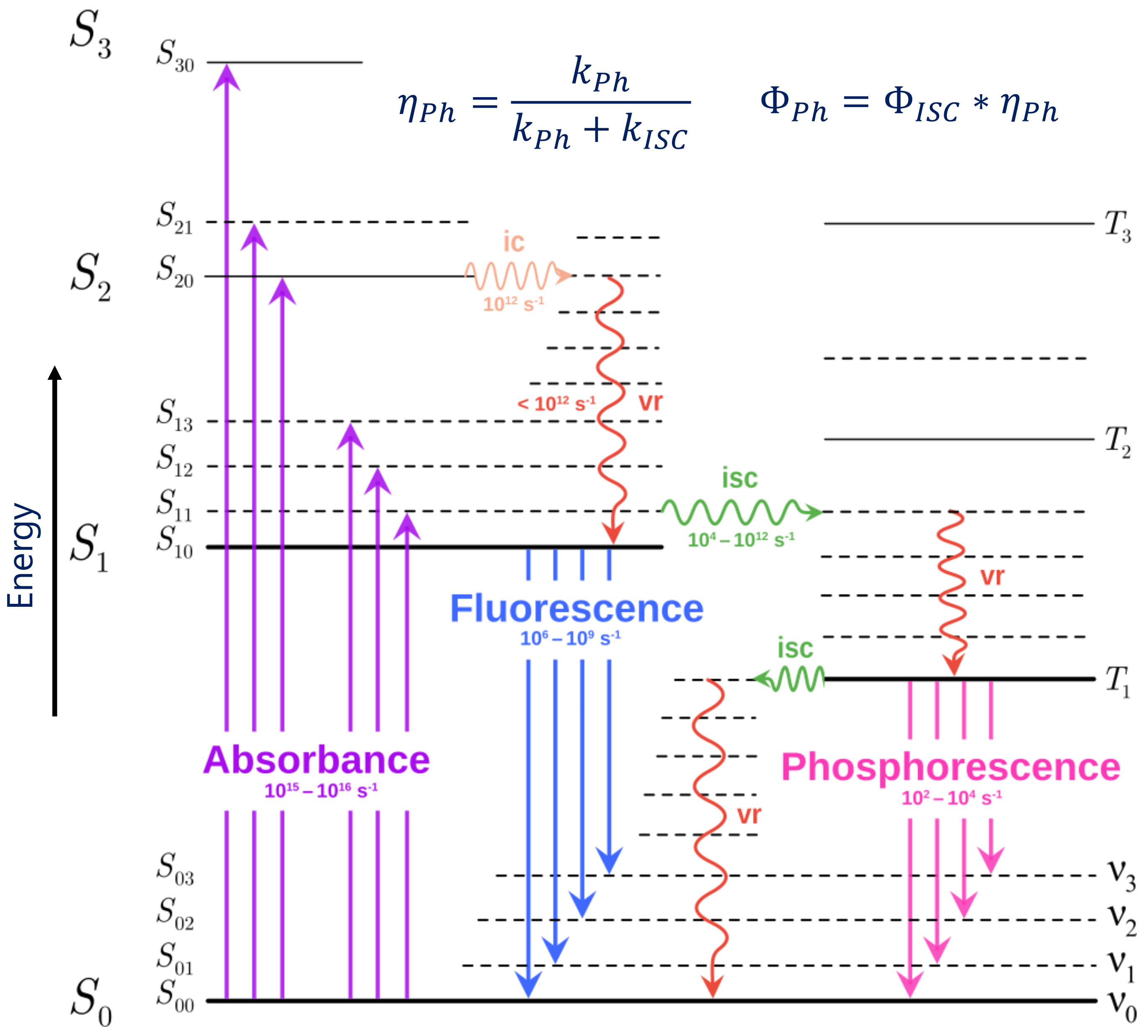
Transition	**Time Scale (τ)**
Internal Conversion	10^{-14} - 10^{-11} s
Vibrational Relaxation	10^{-14} - 10^{-11} s
Absorption	10^{-15} s
Phosphorescence	10^{-4} - 10^{-1} s
Intersystem Crossing	10^{-8} - 10^{-3} s
Fluorescence	10^{-9} - 10^{-7} s

Rate constants $k_i = 1/\tau_i$

The **quantum yield (Φ)** of a process is given by the rate of the process divided by all possible processes:

$$\Phi_{Fl} = \frac{k_r}{k_r + k_{VR} + k_{ISC}} = \frac{\#events}{\#absorbed\ photons}$$

$$\eta_{Ph} = \frac{k_{Ph}}{k_{Ph} + k_{ISC}} \qquad \Phi_{Ph} = \Phi_{ISC} * \eta_{Ph}$$



Wikipedia/Jablonski diagram

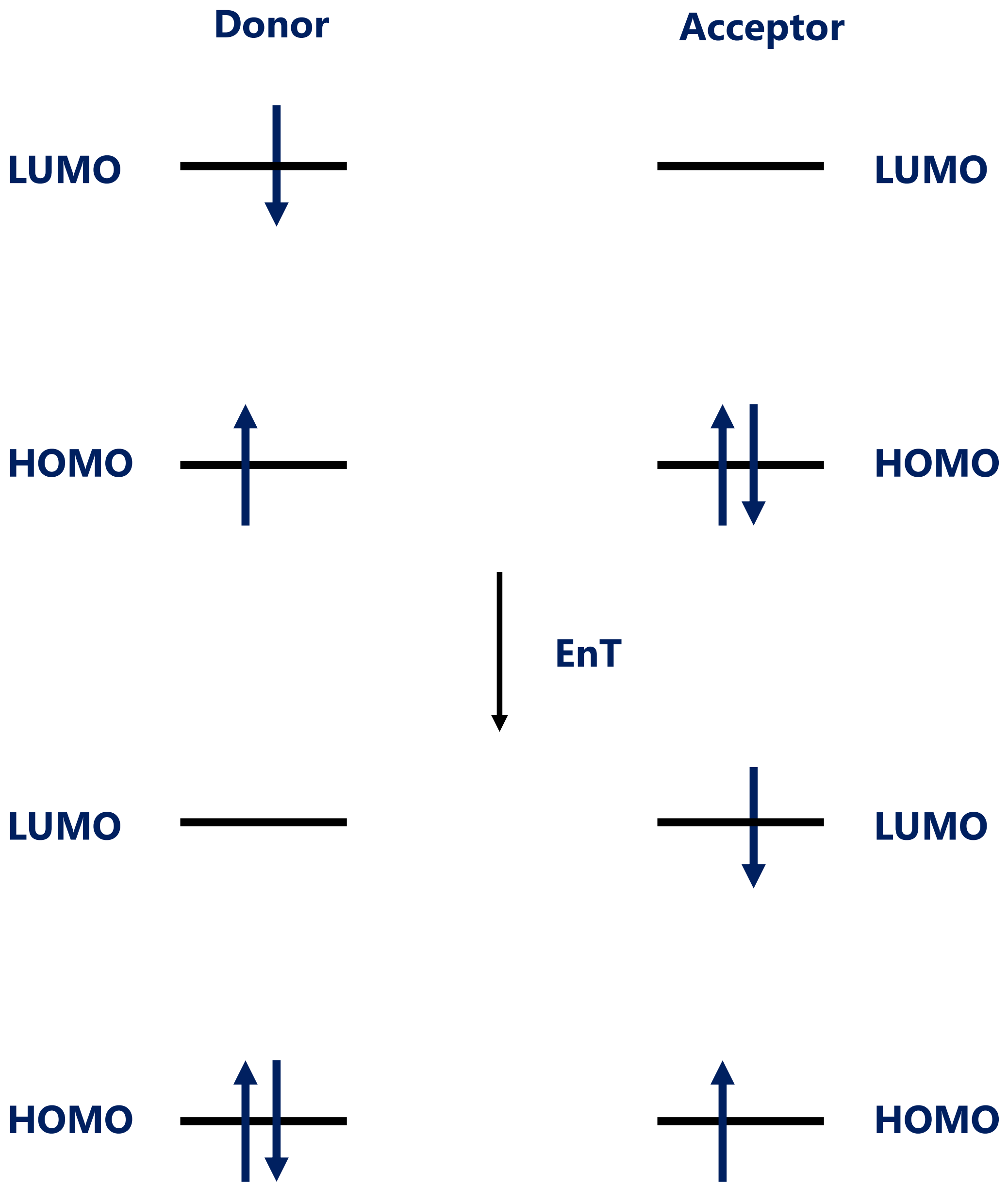
4 Energy and Electron Transfer

I. Dexter and Förster Energy transfer
II. Marcus Theory of Electron Transfer

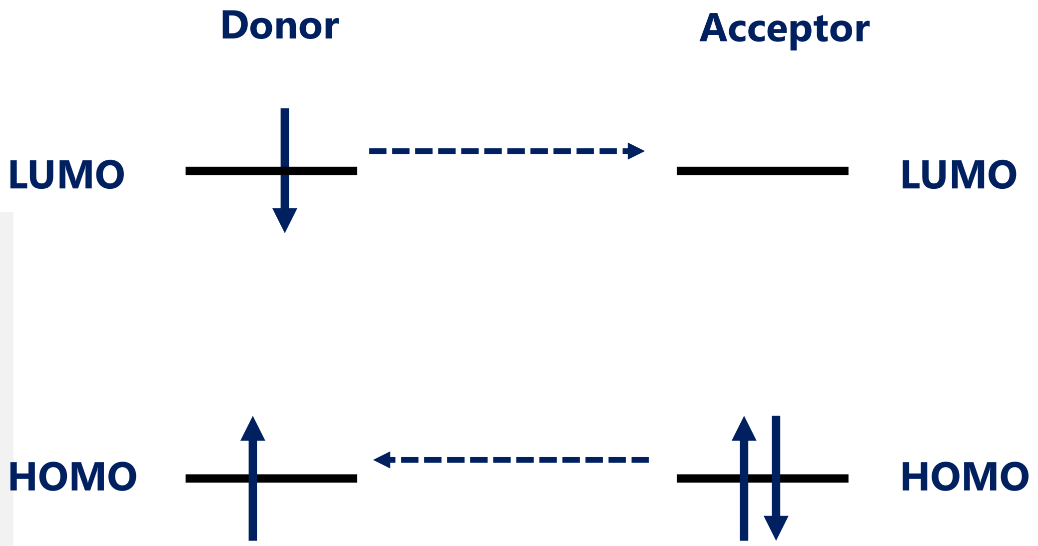
Energy Transfer

Energy from an **excited molecule** (**Donor**, **D**) is transferred to a **ground state molecule** (**Acceptor**, **A**)

There are 2 main pathways for EnT
Dexter and **Förster Energy Transfer**



Dexter vs Förster



Dexter Energy Transfer:

- Two electron exchange
- Requires orbital overlap
- $k_{EnT} \propto J\, e^{-\frac{2R}{L}}$ → short range <1nm
- Singlet and triplet EnT possible

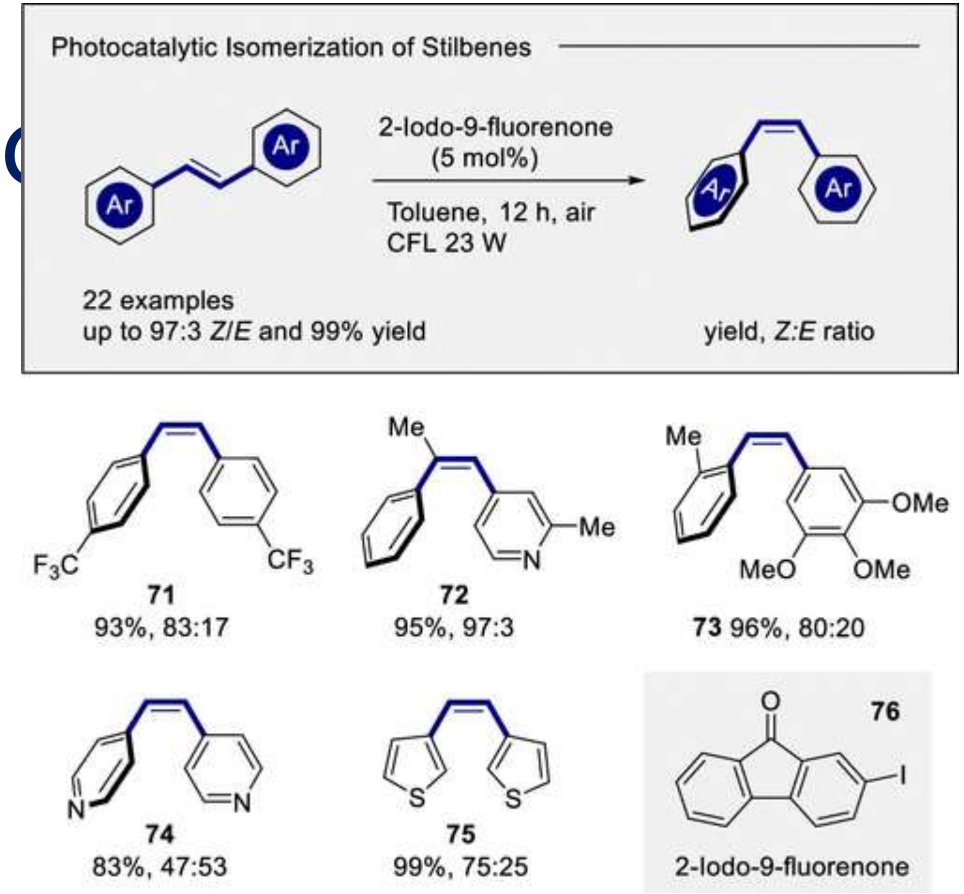
Förster Resonance Energy Transfer (FRET):

- Dipole coupling (Resonance)
- $k_{FRET} \propto \kappa^2 J \frac{1}{R^6}$ → long range 1– 10nm
- Requires large transition dipole moments triplet transfer negligible

Applications in Photoc

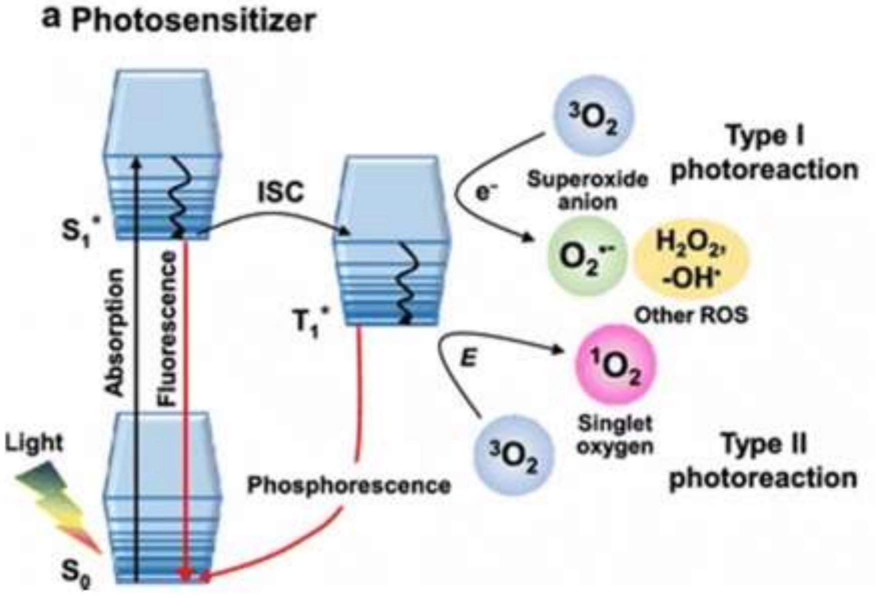
Triplet Energy Transfer:

- Triplets are longer lived than singlets → useful for photochemistry
- Can generate reactive singlet oxygen
- Can open up symmetry forbidden additions (diradical character)



Chem. Rev. 2022, 122, 2, 2650–2694

Photodynamic Therapy



Nanoscale, 2024, 16, 3243-3268

Cyclo Additions, Isomerization

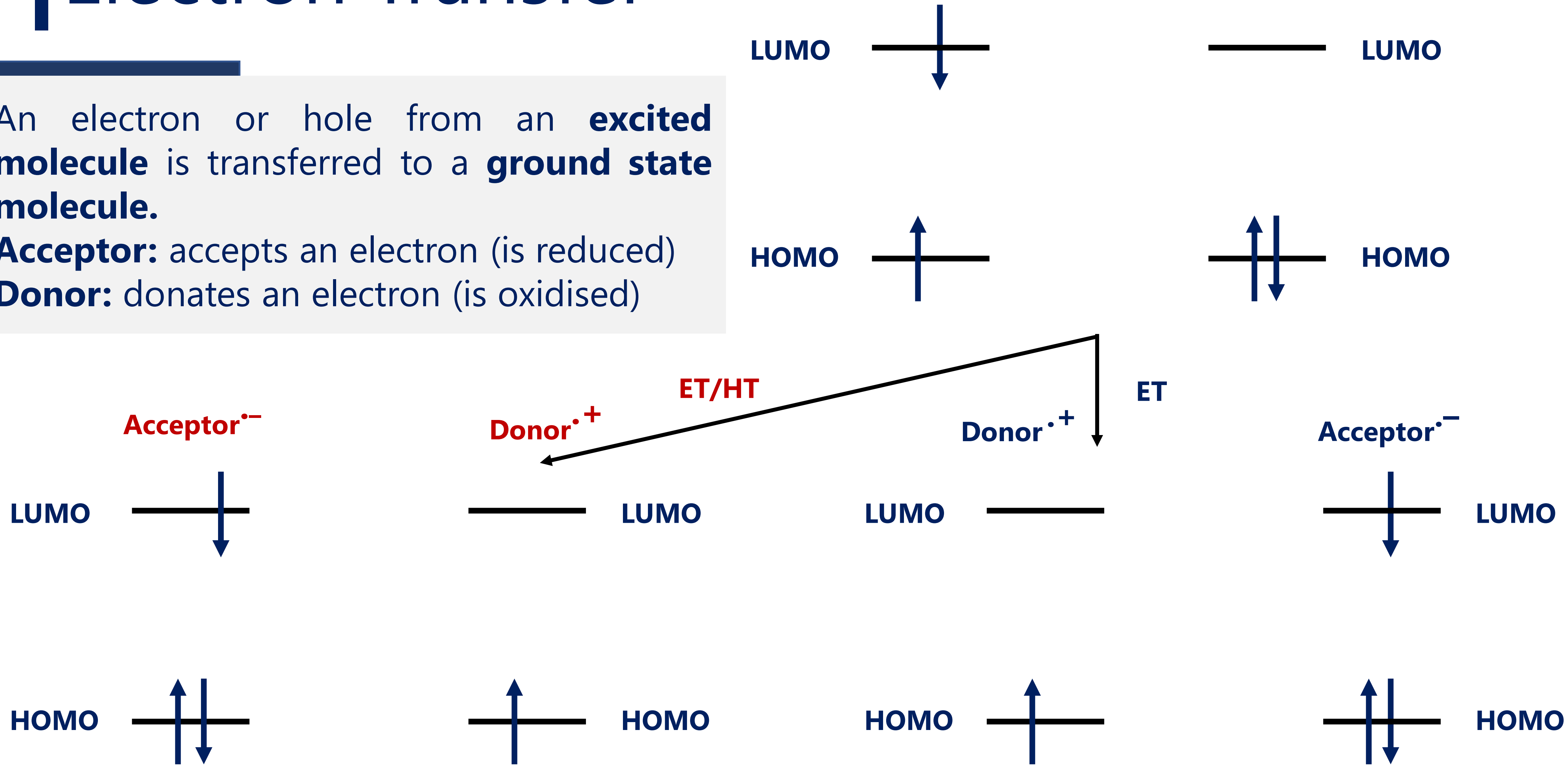
Chem. Commun., 2025, 61, 12916-12919

Electron Transfer

An electron or hole from an **excited molecule** is transferred to a **ground state molecule.**

Acceptor: accepts an electron (is reduced)

Donor: donates an electron (is oxidised)



Marcus Theory of Electron Transfer

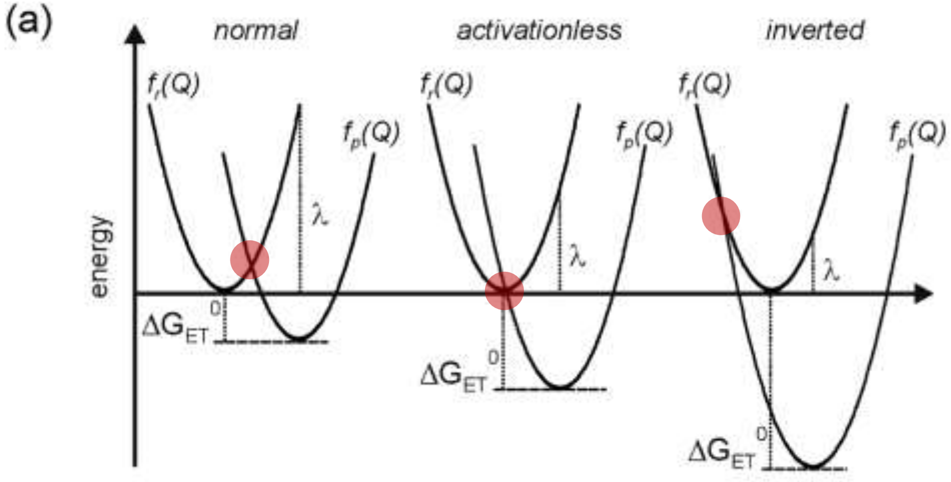
Initial (D*-A) and **final** ($D^{\cdot +}$-$A^{\cdot -}$) states expressed as two potential energy wells.

$$k_{\mathrm{ET}} = \sqrt{\frac{\pi}{\hbar^2 \cdot \lambda \cdot k_{\mathrm{B}} \cdot T}} \cdot H_{\mathrm{DA}}{}^2 \cdot \exp\left(-\frac{\left(\lambda + \Delta G^0_{\mathrm{ET}}\right)^2}{4 \cdot \lambda \cdot k_{\mathrm{B}} \cdot T}\right)$$

λ: Reorganization Energy

ΔG_{ET}^{0}: Energy difference between initial and final state (driving force)

H_{DA}^{2}: Electronic coupling



Phys. Chem. Chem. Phys., 2016, 18, 18657-18664

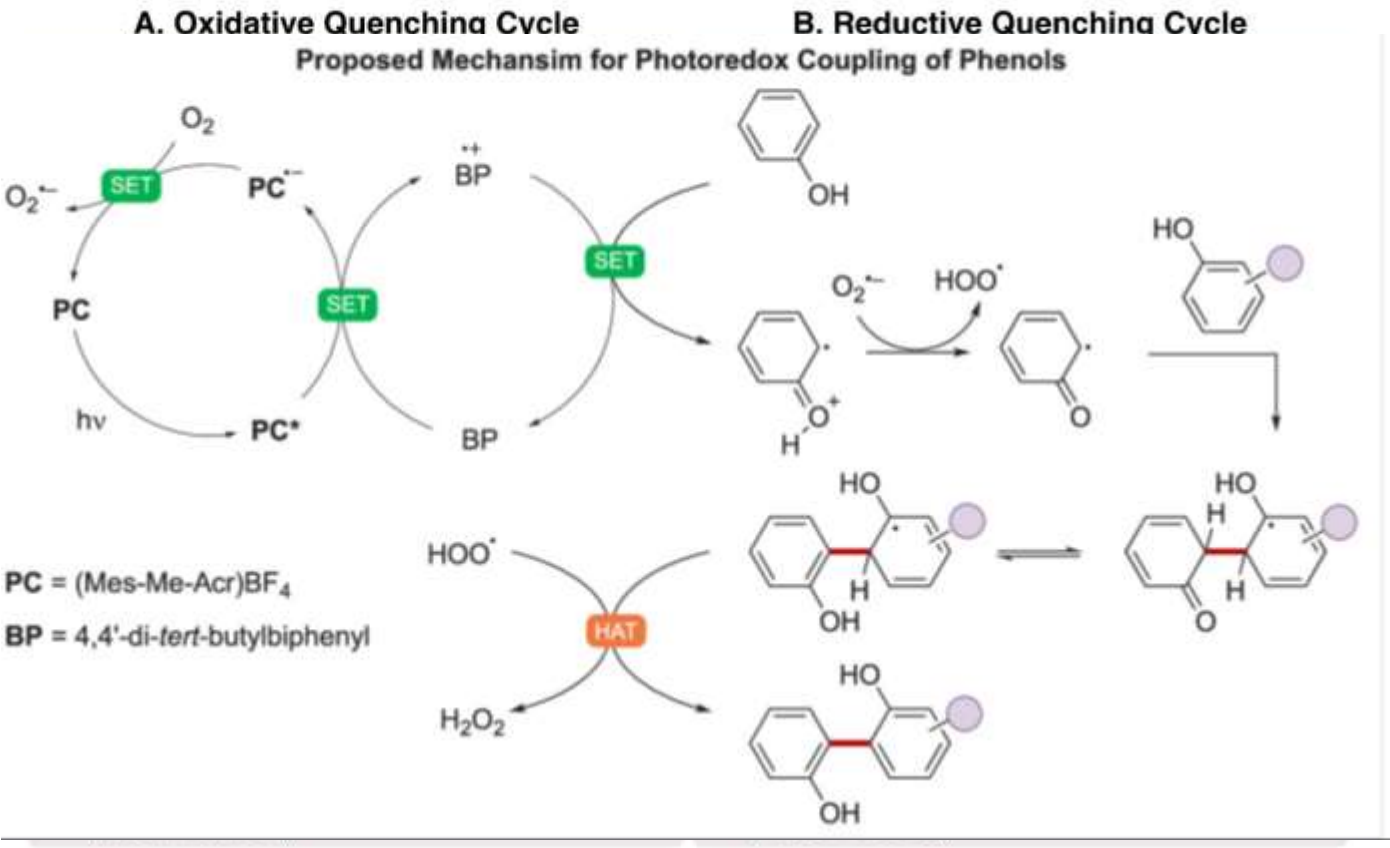
Photo Redox Catalysis

PC* can be quenched by either substrate or sacrificial donor/acceptors

PC$^{\cdot -}$ strong reductant – returns to PC by reducing substrate/sacrificial acceptor

PC$^{\cdot +}$ strong oxidant – returns to PC by oxidising substrate/sacrificial donor

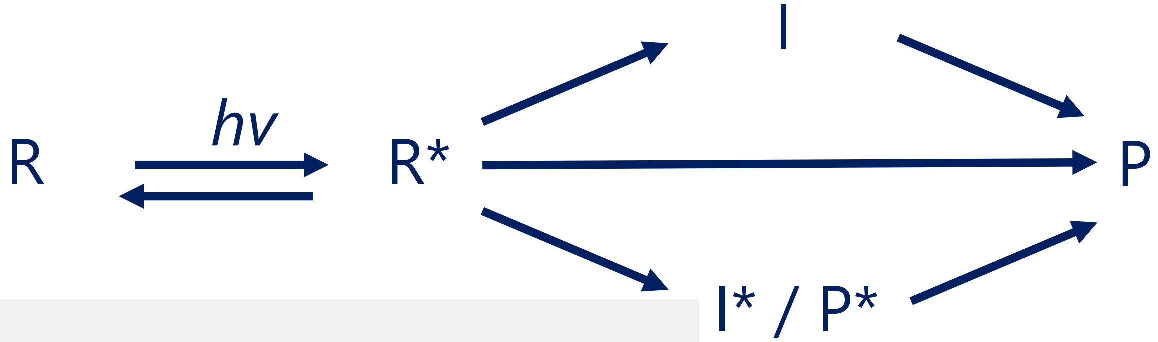
Cycles and mechanisms can be coupled in many different ways…

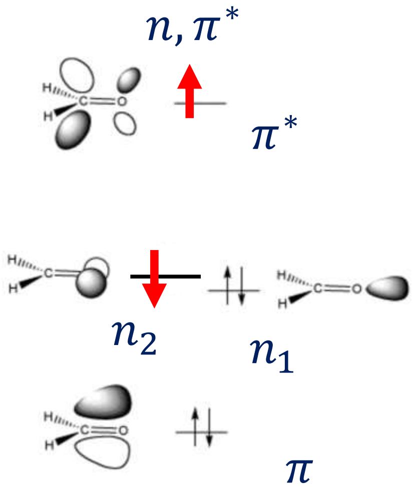


Scenario 1. Redox neutral if both A and D are used productively
Scenario 2. Net-oxidative if A is a sacrificial reducant
Scenario 3. Net-reductive if D is a sacrificial oxidant

Chem. Rev. 2022, 122, 2, 2487–2649

Summary





Probability of transition

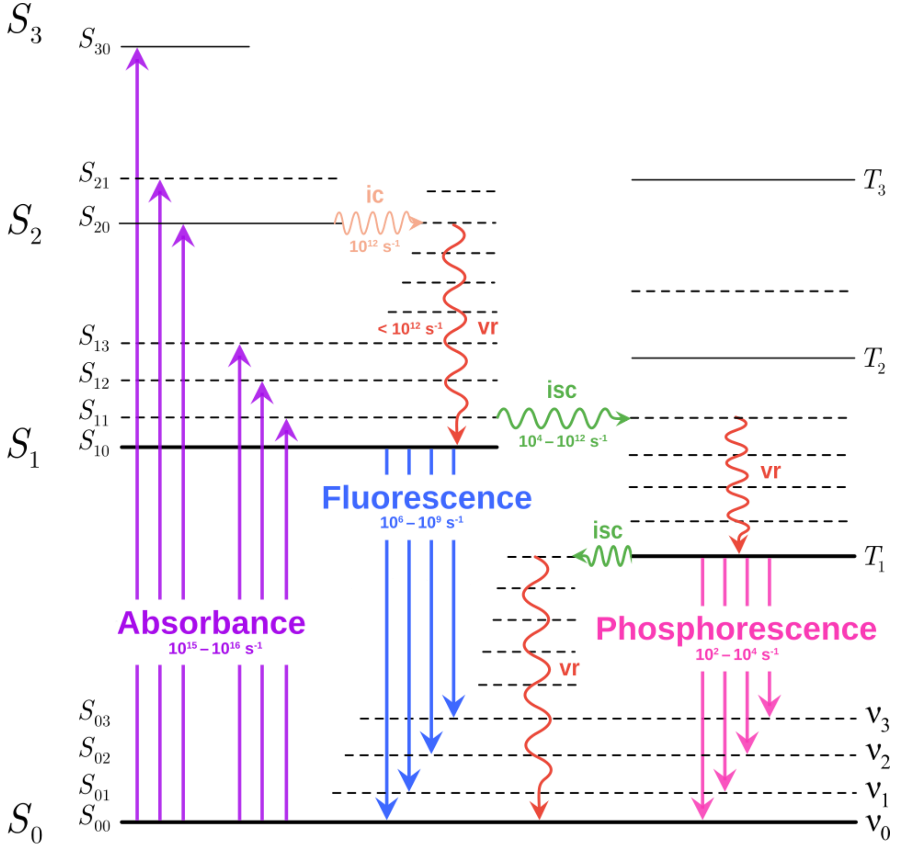
$$\propto \left|\int \psi(\mathbf{r})_f^*\hat{\mu}(\mathbf{r})\psi(\mathbf{r})_i d\mathbf{r}\right|^2 \left|\int \phi(s)_f^*\phi(s)_i ds\right|^2 \left|\int \chi(\mathbf{R})_f^*\chi(\mathbf{R})_i d\mathbf{R}\right|^2$$

Transition dipole moment   Spin Overlap ($\Delta S = 0$) Franck-Condon Factor

SOC can enable ISC – heavy atoms or change in in orbital type (e.g., π,π* → nπ*)

Kasha's rule – excited state chemistry mostly occurs from the lowest excited state of a given multiplicity

Dexter EnT, FRET, and Electron transfer are key processes to initiate photochemistry



References and Other Resources

1. Turro, Ramamurthy, Scaiano, Modern Molecular Photochemistry of Organic Molecules
2. Lakowicz, Principles of Fluorescence Spectroscopy
3. Schaller, Structure & Reactivity in Organic, Biological and Inorganic Chemistry I: Chemical Structure and Properties, ChemLibreText
4. Michael Evans, Georgia Tech, youtube series on photochemistry

ICESAA-4 Winter School (2026.1.8~2026.1.8)
IIISER Thirunanvathapuram

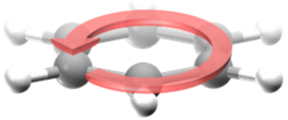
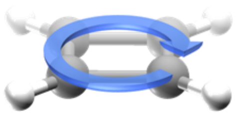
Ultrafast Spectroscopy

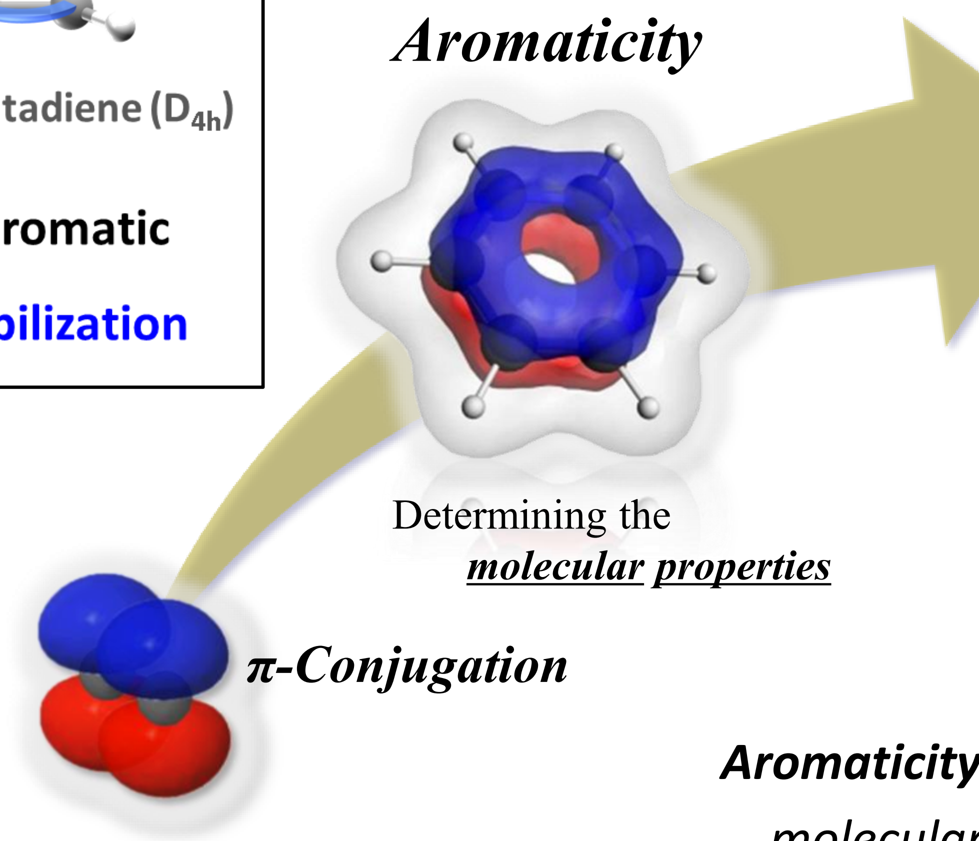
Juwon Oh

Department of Chemistry
Kyungpook National University

Aromaticity

Hückel Rule

$[4n+2]\pi$	$[4n]\pi$
	
Benzene (D_{6h})	Cyclobutadiene (D_{4h})
Aromatic	**Antiaromatic**
Stabilization	**Destabilization**



Aromaticity

Determining the
molecular properties

π-Conjugation

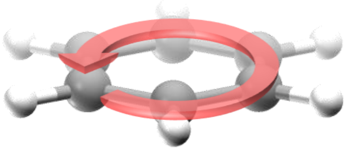
Allowing to fabricate various optoelectronic devices, such as, OLED, OFET, photovoltaic cells, and optical switches.

Aromaticity *of important factors determining molecular properties & their applications*

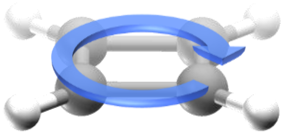
Chem. Rev. **2001**, *101*, 1385-1419

Extension of Concept to Excited States

Ground State

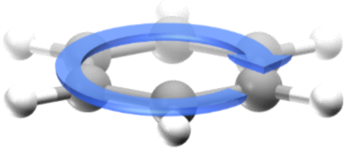


Benzene (D_{6h})
Aromatic/Stable

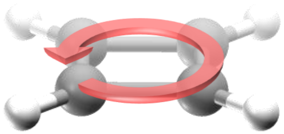


Cyclobutadiene (D_{4h})
Antiaromatic/Instable

Reversal



Benzene (D_{6h})
Antiaromatic/Instable



Cyclobutadiene (D_{4h})
Aromatic/Stable

Excited State (S_1 & T_1)

Significant Effect on Excited-State Behavior

J. Am. Chem. Soc. **1972**, *94*, 4941-4948
Chem. Soc. Rev. **2022**, *55*, 268-292

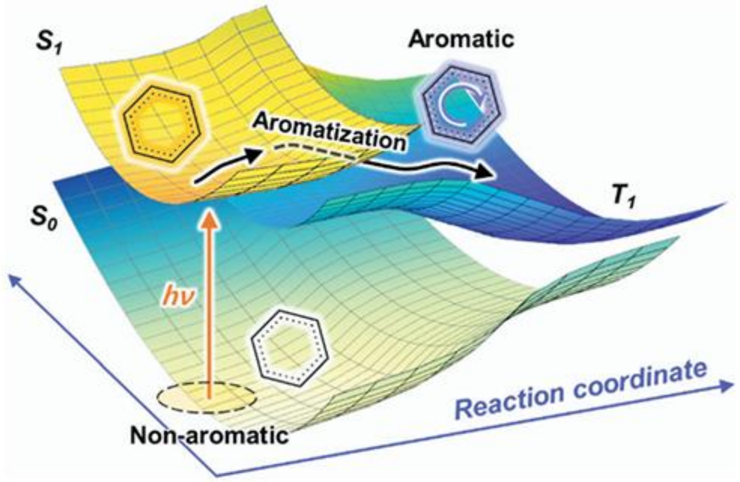
Why the Excited-State Aromaticity is important?

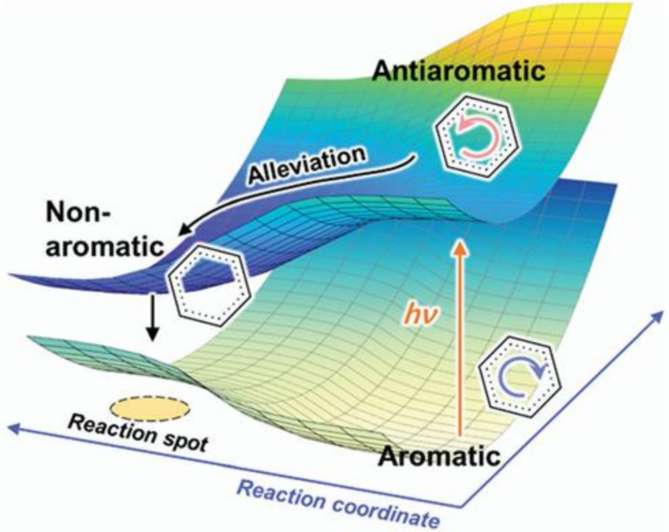
Why is the Excited State Aromaticity focused?

1. Completely reversed (anti)aromatic nature by irradiation leads to an understranding & designing of photochemical reactions

2. Potential applications in photo-active materials, organic electronics and photovoltaics as well as photosynthetic protocols

⋮



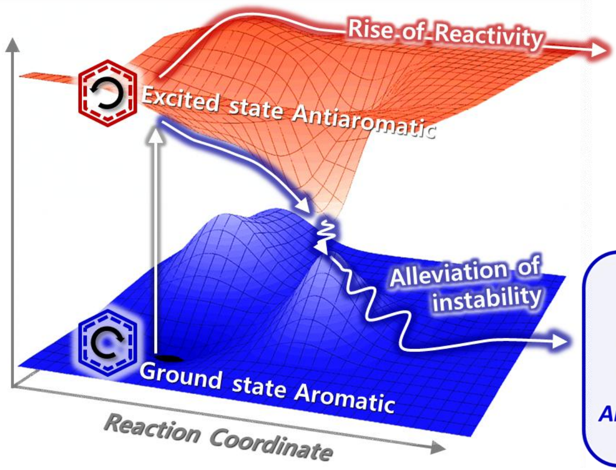


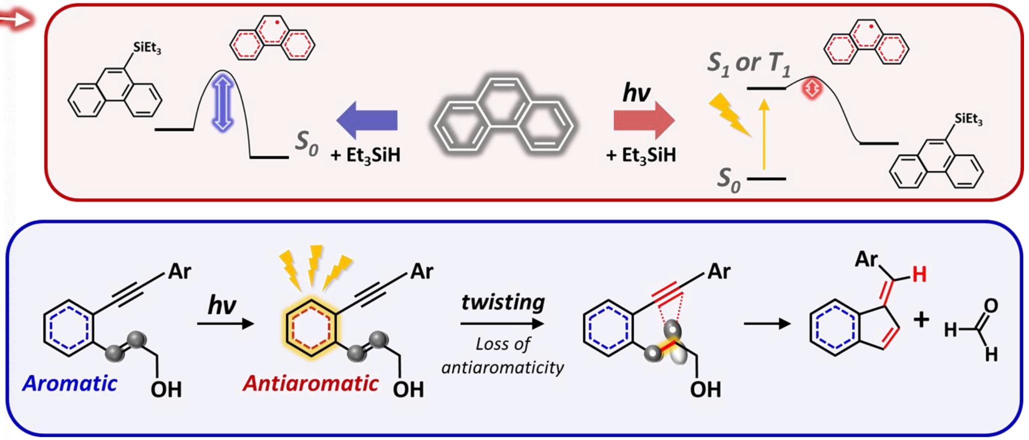
Strong Energy (de)Stabilization Effect ➔ Modulation of Photoactive Properties

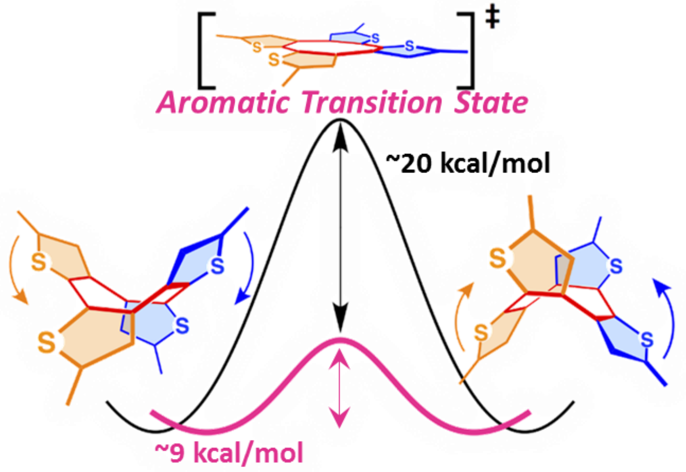
Chem. Rev. **2014**, 114, 5379-5425

Effect of Excited-State (anti)Aromaticity

Photosynthetic Protocols







Organo-Spin

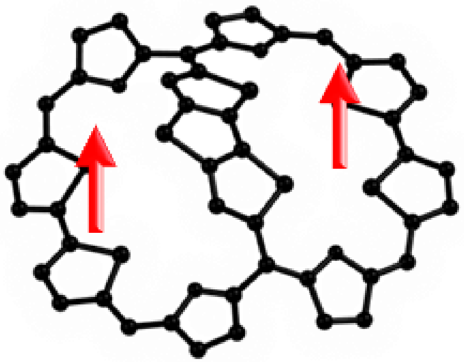
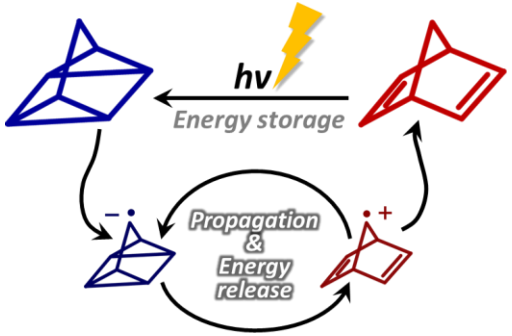
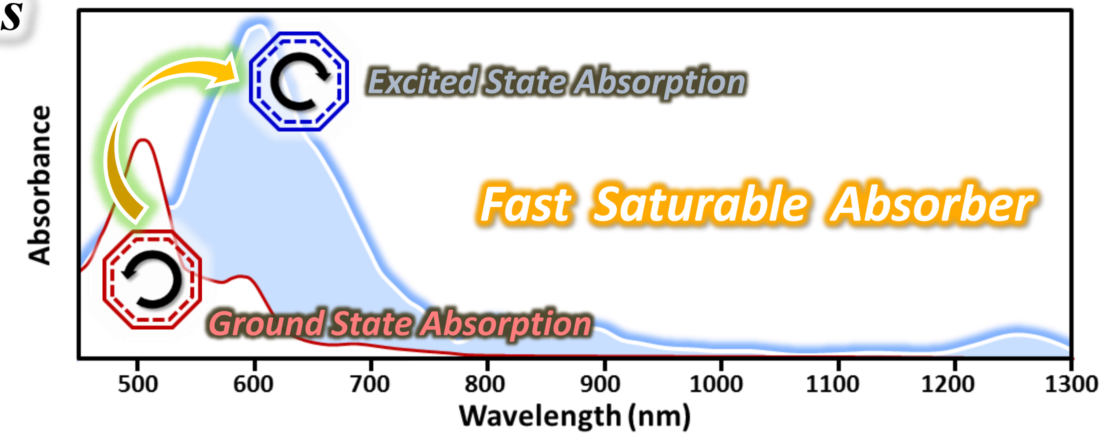


Photo-active materials



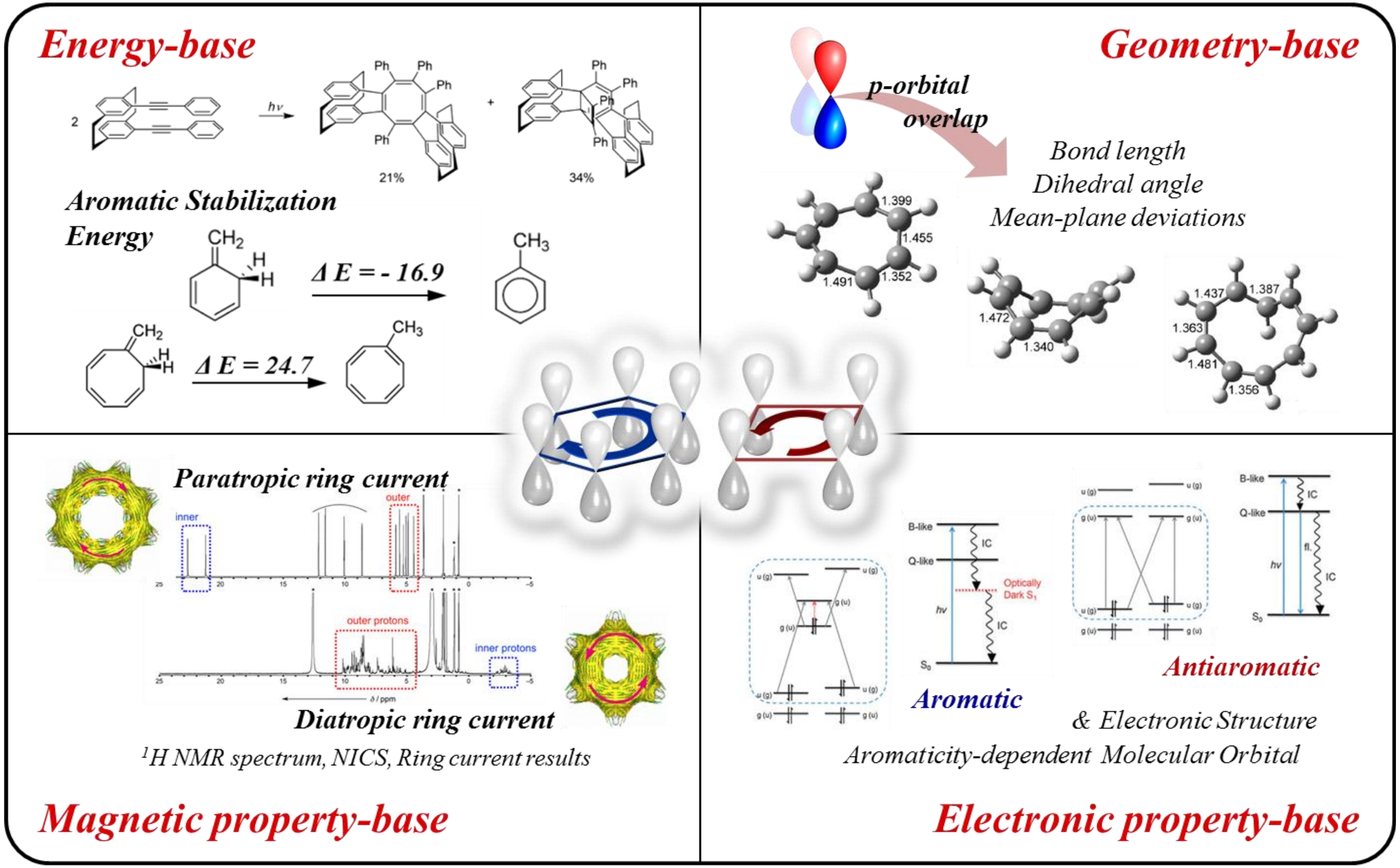
Photochemical Energy-storage



Chem. Soc. Rev. **2015**, *44*, 6472-6493
Chem. Soc. Rev. **2022**, *55*, 268-292

How to Reveal Excited-State Aromaticity

Evalution of Aromaticity



Energy-base

Aromatic Stabilization Energy

$\Delta E = -16.9$

$\Delta E = 24.7$

Geometry-base

p-orbital overlap

Bond length
Dihedral angle
Mean-plane deviations

Paratropic ring current

Diatropic ring current

^{1}H NMR spectrum, NICS, Ring current results

Magnetic property-base

Aromatic

Antiaromatic

& Electronic Structure
Aromaticity-dependent Molecular Orbital

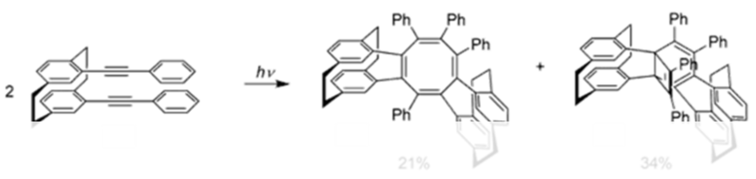
Electronic property-base

Chem. Rev. **2005**, 105, 3773-3811

How to Reveal Excited-State Aromaticity

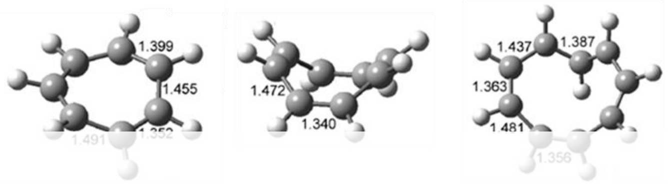
Experimental Evalution of Aromaticity

Energy-base



Synthetic Product Analyses

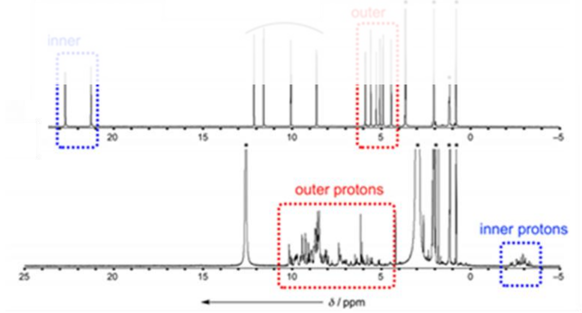
Geometry-base



X-ray Single Crystallography

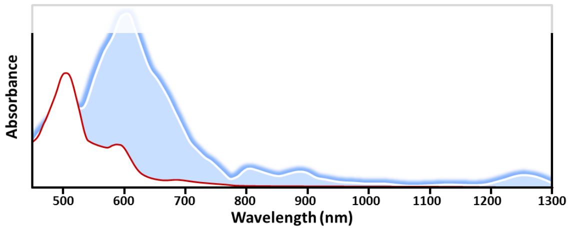
How about applying these methods to excited state?

^{1}H NMR



Magnetic property-base

UV-Vis Absorption

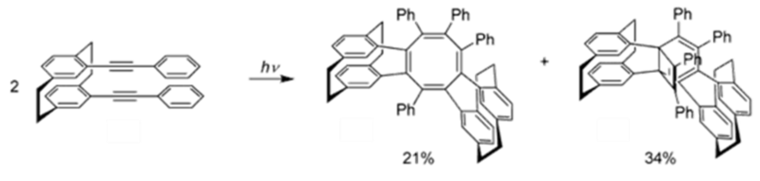


Electronic property-base

How to Reveal Excited-State Aromaticity

Applicability to Excited-State Aromaticity Analyses

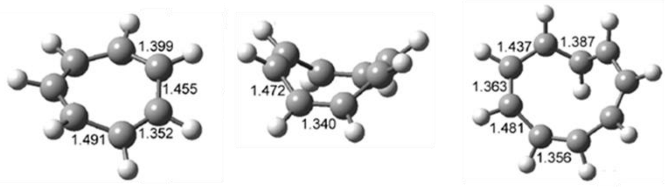
Energy-base



Synthetic Product Analyses

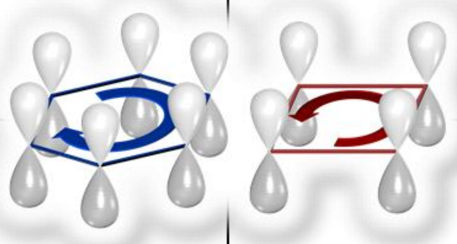
Impossible

Geometry-base

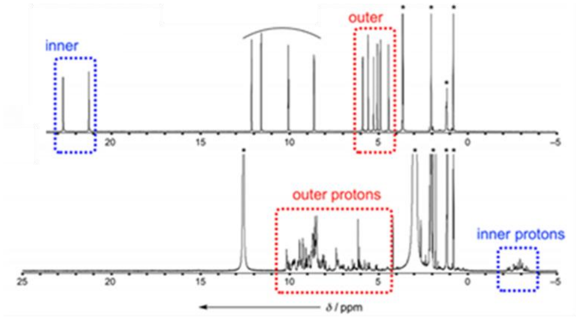


X-ray Single Crystallography

Impossible



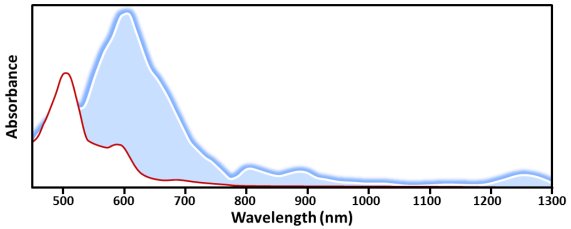
^{1}H NMR



Magnetic property-base

Impossible

UV-Vis Absorption



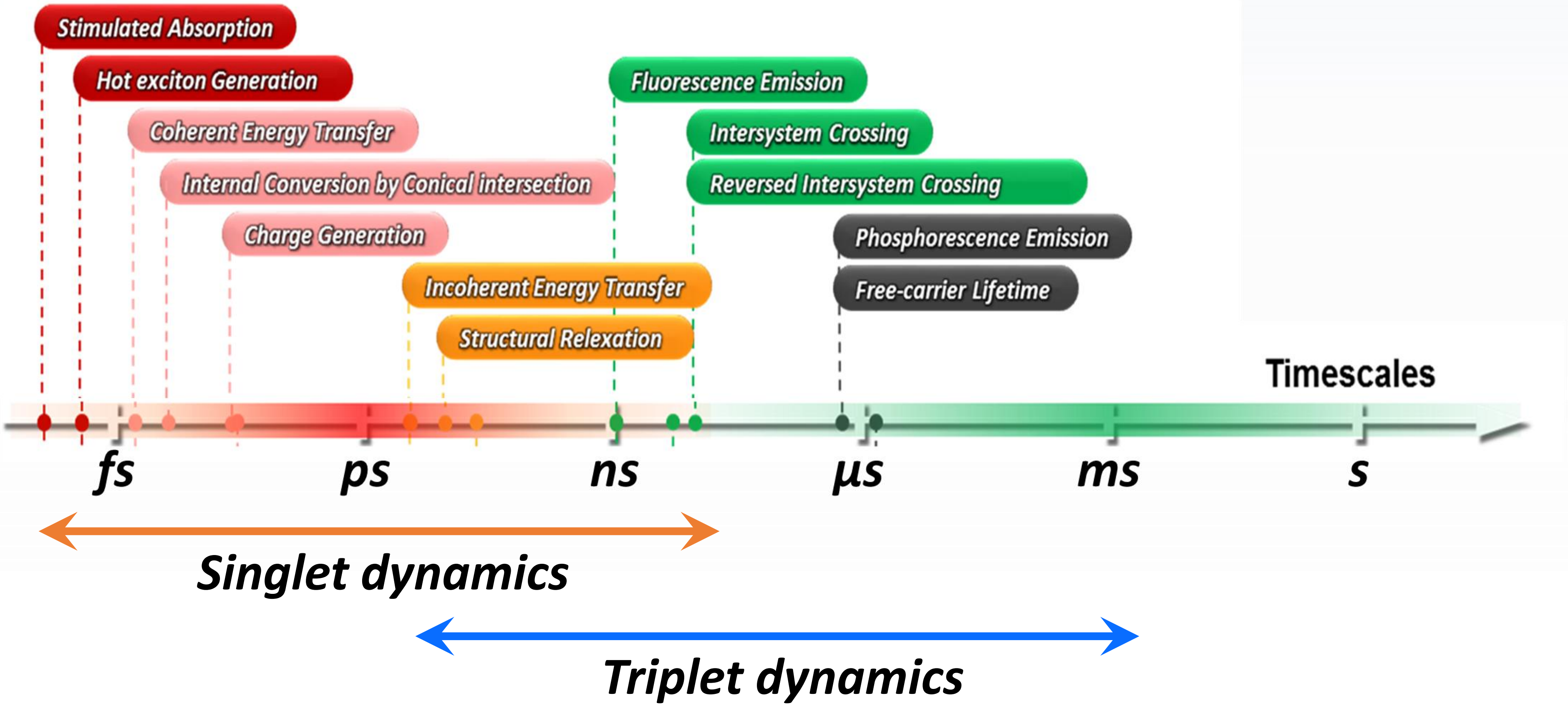
Electronic property-base

Possible

How to Reveal Excited-State Aromaticity

Applicability to Excited-State Aromaticity Analyses

Excited-State Dynamics



➔ *For Observing Excited States, we need **shorter time resolution than their whole lifetime***

How to Reveal Excited-State Aromaticity

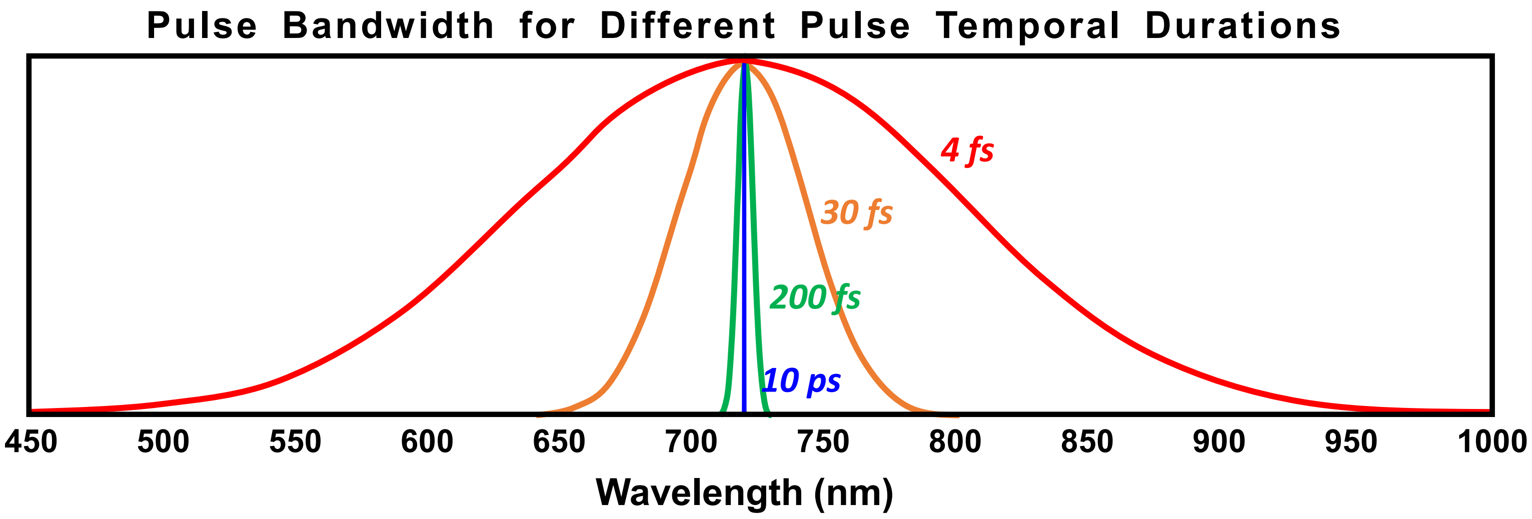
Applicability to Excited-State Aromaticity Analyses

Heisenberg's Principle

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

Time *Energy*

We cannot know both the position and speed of a particle, such as a photon or electron, with perfect accuracy

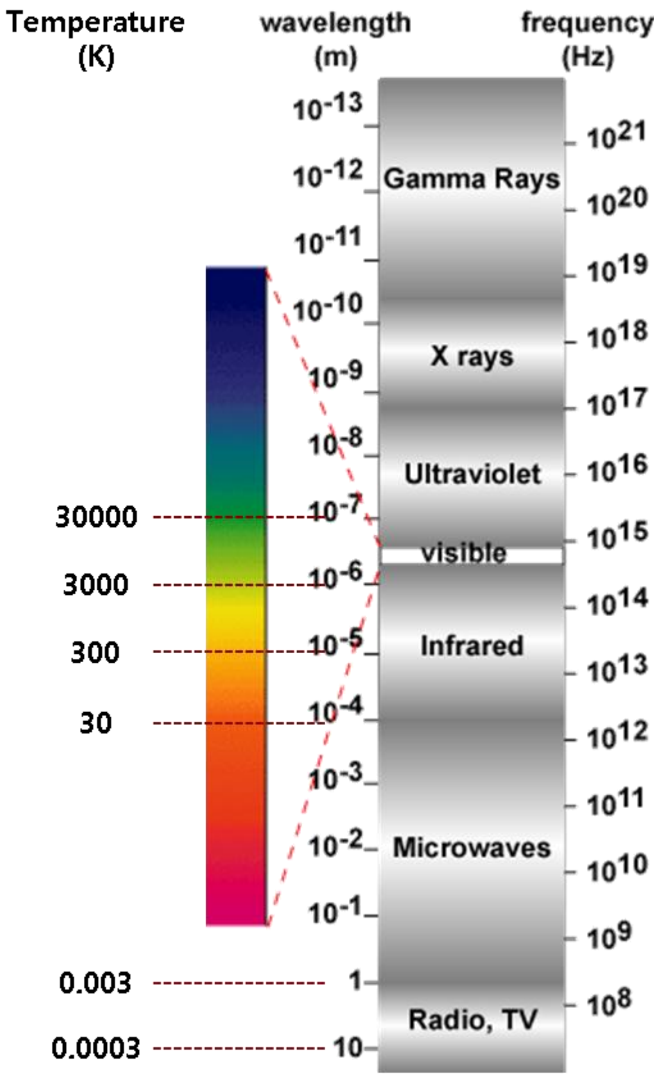


How to Reveal Excited-State Aromaticity

Applicability to Excited-State Aromaticity Analyses

Heisenberg's Principle

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$



Time resolution limit

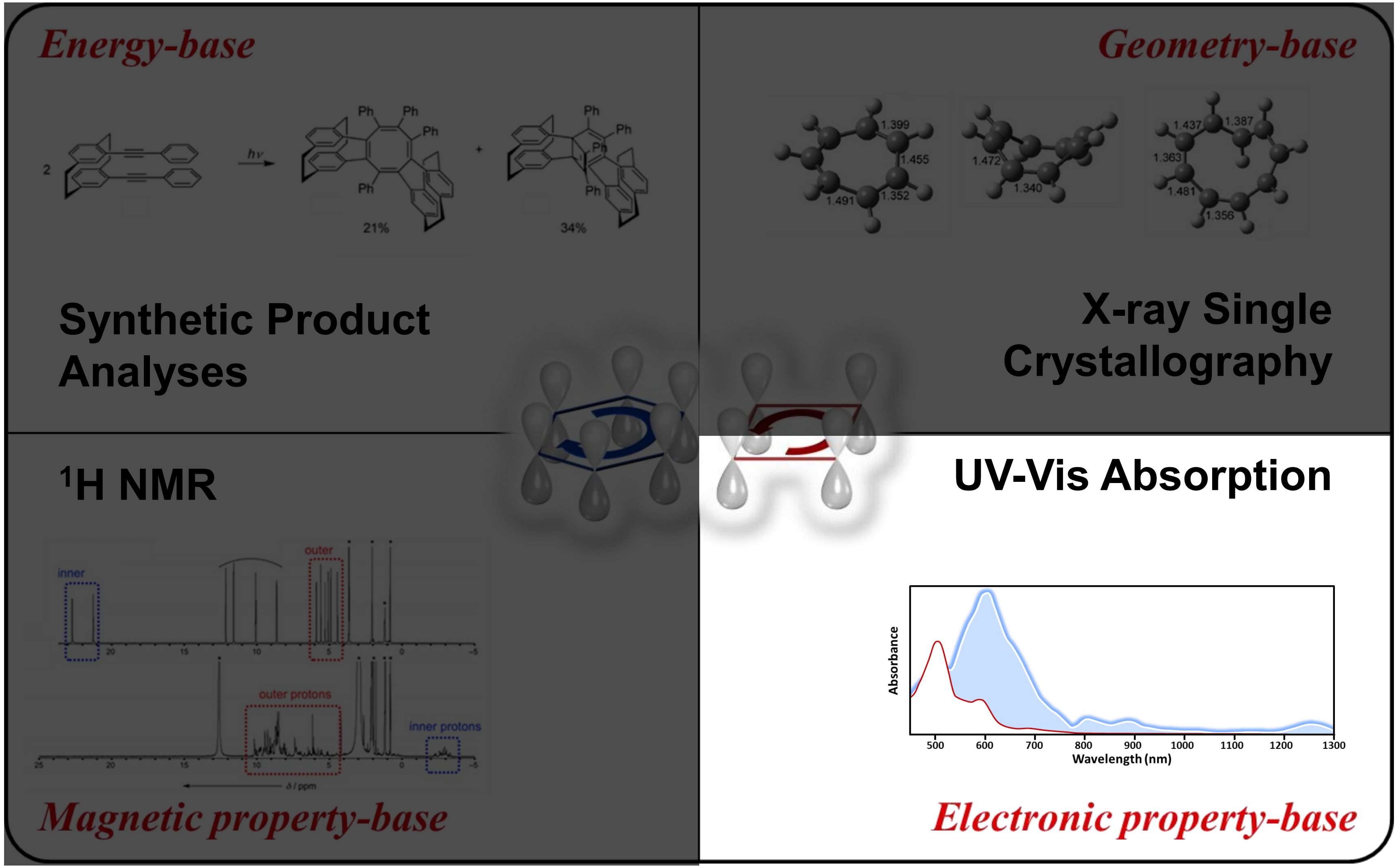
➡ *Attosecond*

➡ *femtosecond*

➡ *sub-millisecond*

How to Reveal Excited-State Aromaticity

Applicability to Excited-State Aromaticity Analyses



Energy-base

Synthetic Product Analyses

Geometry-base

X-ray Single Crystallography

^{1}H NMR

Magnetic property-base

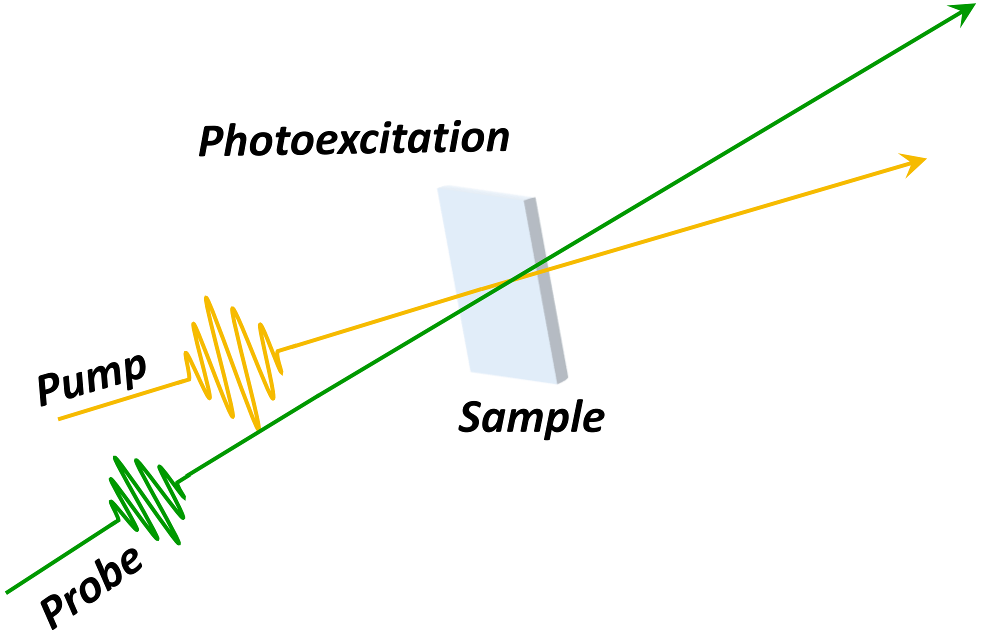
UV-Vis Absorption

Electronic property-base

Pump-Probe Methods

Pump-Probe Spectroscopies

Most well-known Methods to observing Excited-State Dynamics



X-ray : *Core-electron transition*
+ Atomic Scattering

UV-Vis-NIR : *Valence electron transition*

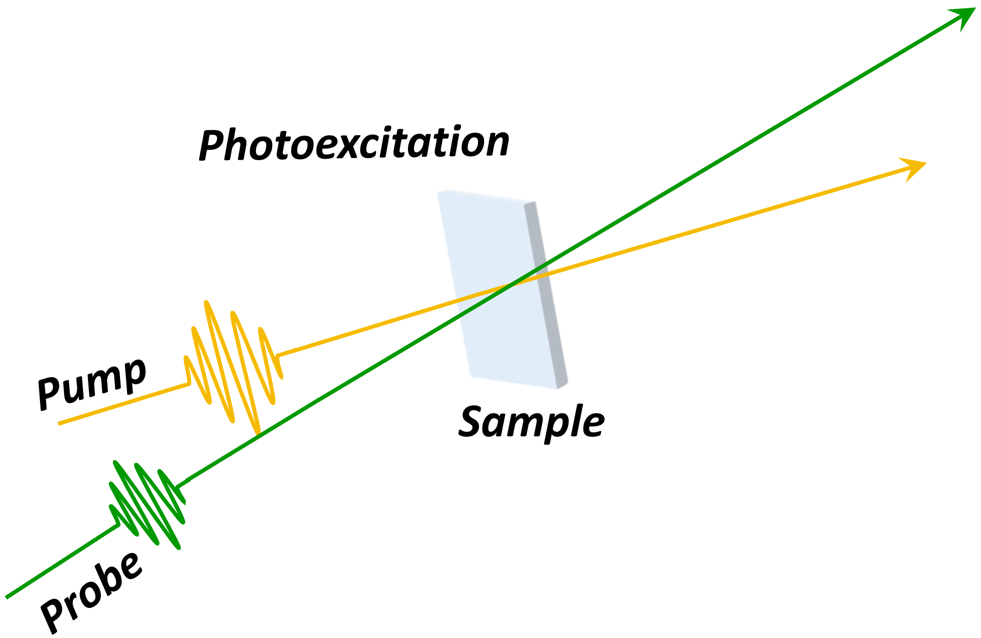
Mid-IR : *Vibrational Transition*

Terahertz : *Free electron resonance absorption*

E-beam : *Atomic Scattering*
+ Elemental information

⋮

Transient Absorption Spectroscopy



X-ray *: Core-electron transition*

+ Atomic Scattering

UV-Vis-NIR *: Valence electron transition*

Mid-IR *: Vibrational Transition*

Terahertz *: Free electron resonance absorption*

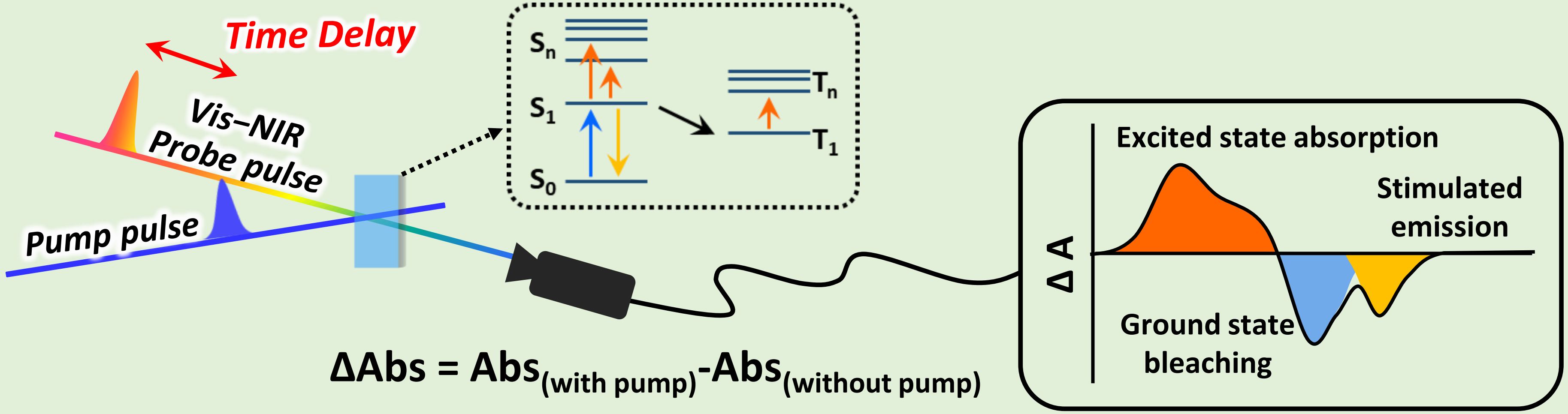
E-beam *: Atomic Scattering*

+ Elemental information

⋮

Transient Absorption Spectroscopy

Transient Absorption Spectroscopy



Time Delay

Vis–NIR Probe pulse

Pump pulse

S_n, S_1, S_0, T_n, T_1

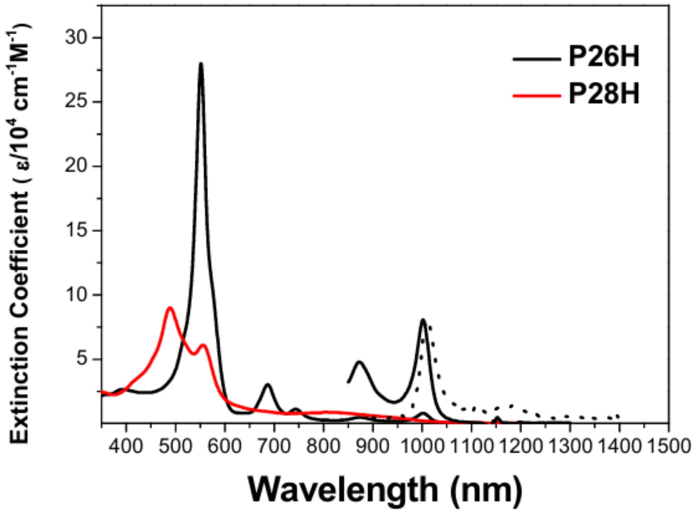
Excited state absorption

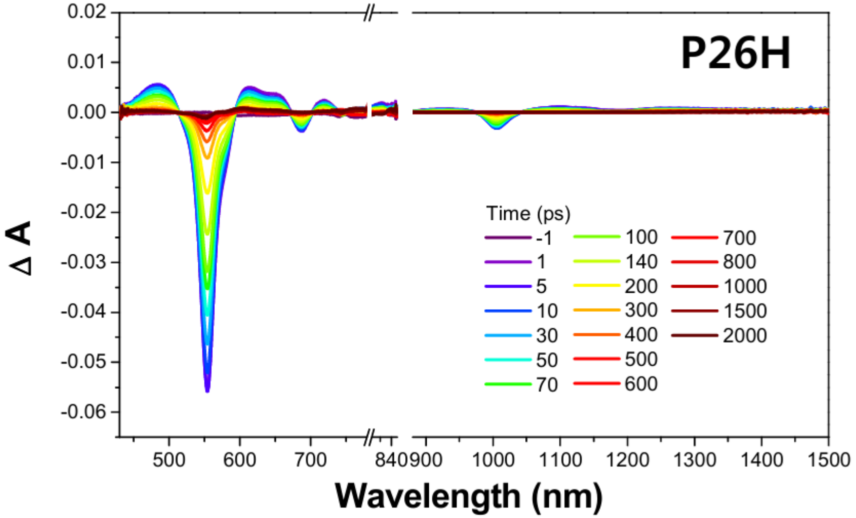
Stimulated emission

Ground state bleaching

ΔA

$$\Delta Abs = Abs_{(with\ pump)} - Abs_{(without\ pump)}$$

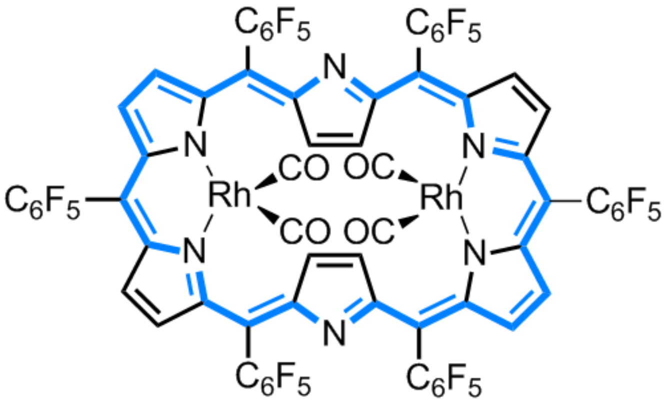




J. Am. Chem. Soc.. **2015**, 137, 11856

T_1-State Aromaticity with Transient Absorption Spectroscopy

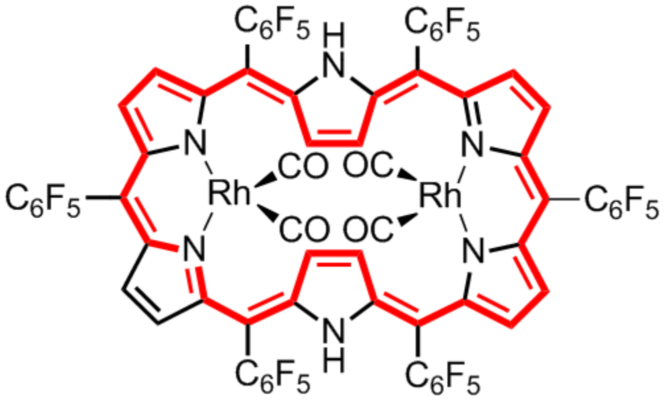
Reversal of Aromaticity in the Excited T_1 State



R26H

[26]π electrons

Aromatic



R28H

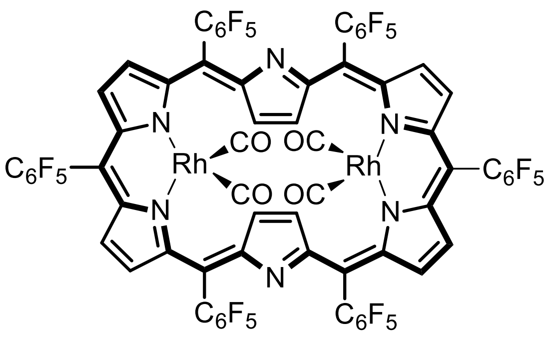
[28]π electrons

Antiaromatic

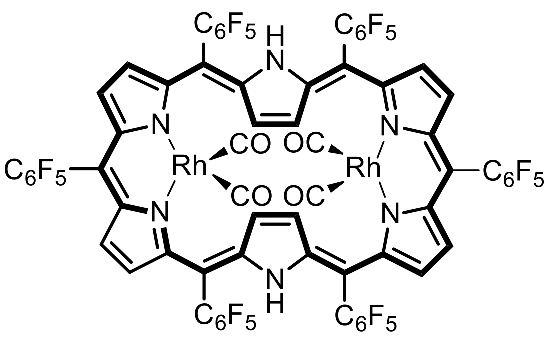
Aromatic/Antiaromatic Molecular Congeners

Nat. Chem. **2015**, 7, 418

T_1-State Aromaticity with Transient Absorption Spectroscopy

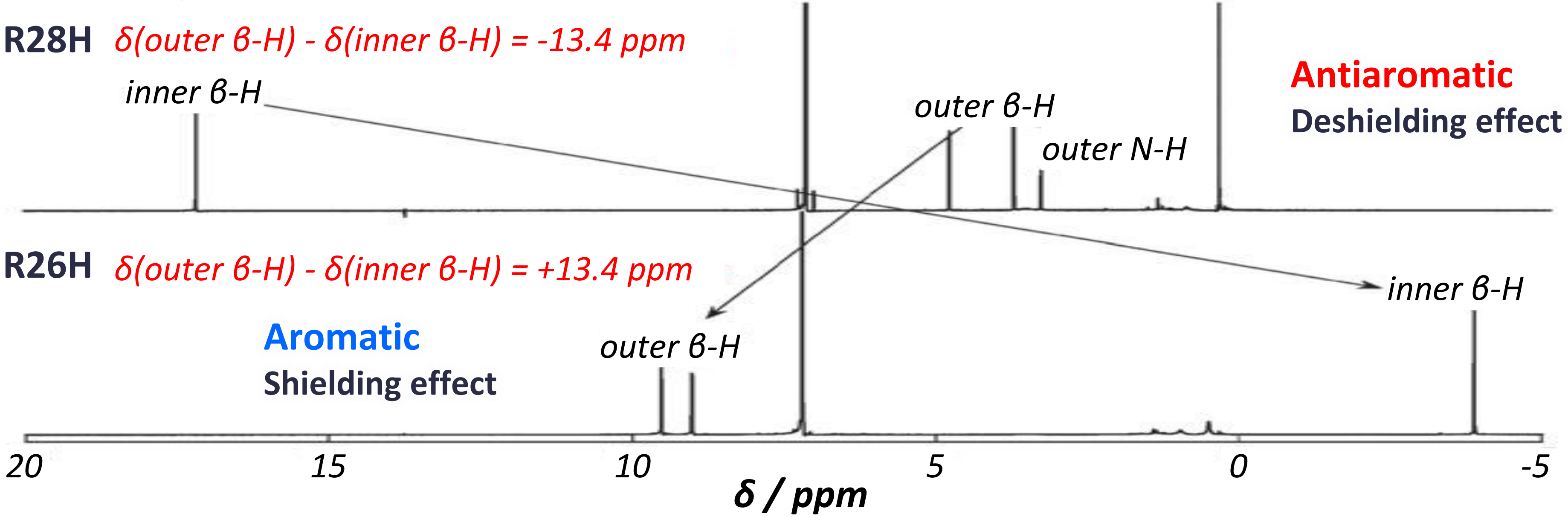


R26H



R28H

^{1}H-NMR spectra



R28H *δ(outer β-H) - δ(inner β-H) = -13.4 ppm*

Antiaromatic
Deshielding effect

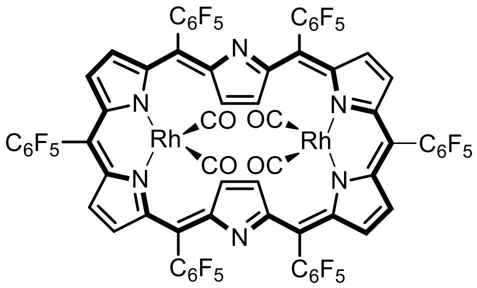
R26H *δ(outer β-H) - δ(inner β-H) = +13.4 ppm*

Aromatic
Shielding effect

Aromaticity-dependent NMR Spectral Features

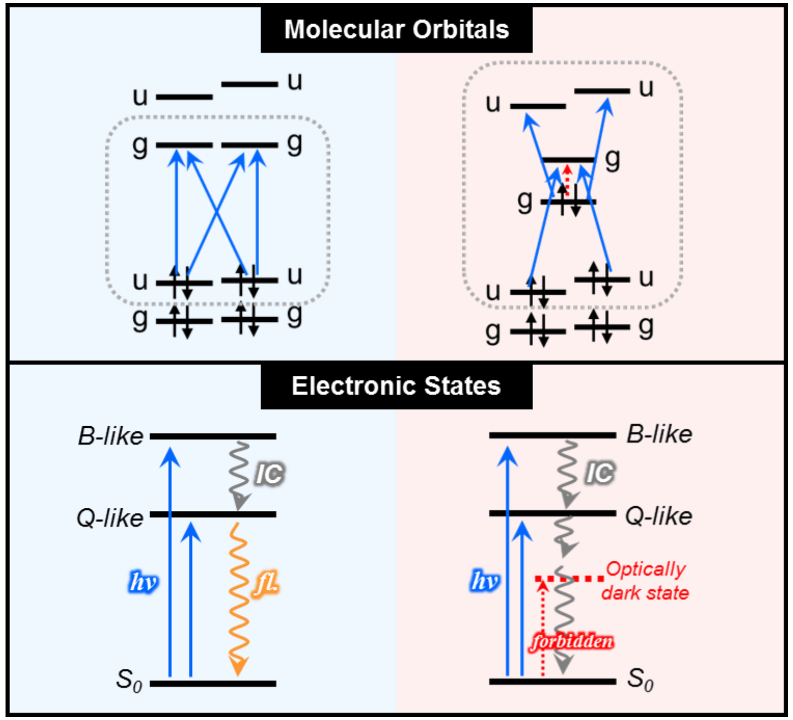
T_1-State Aromaticity with Transient Absorption Spectroscopy

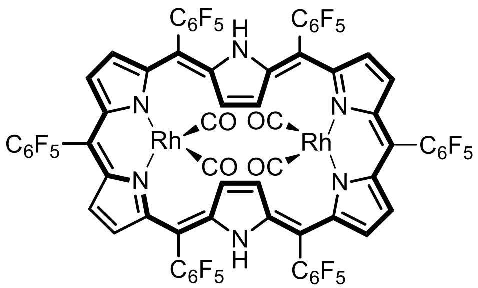
Aromaticity-Dependent Absorption Spectral Features



R26H

Aromatic

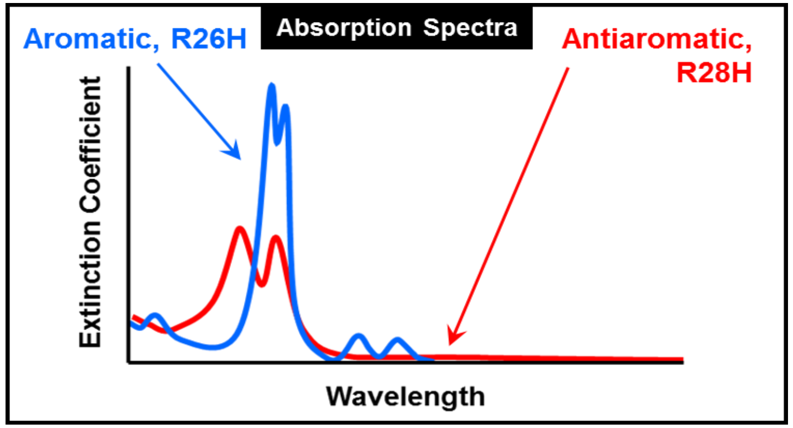




R28H

Antiaromatic

__Aromatic:__ sharp and distint spectral features from intense B- and weak Q-bands

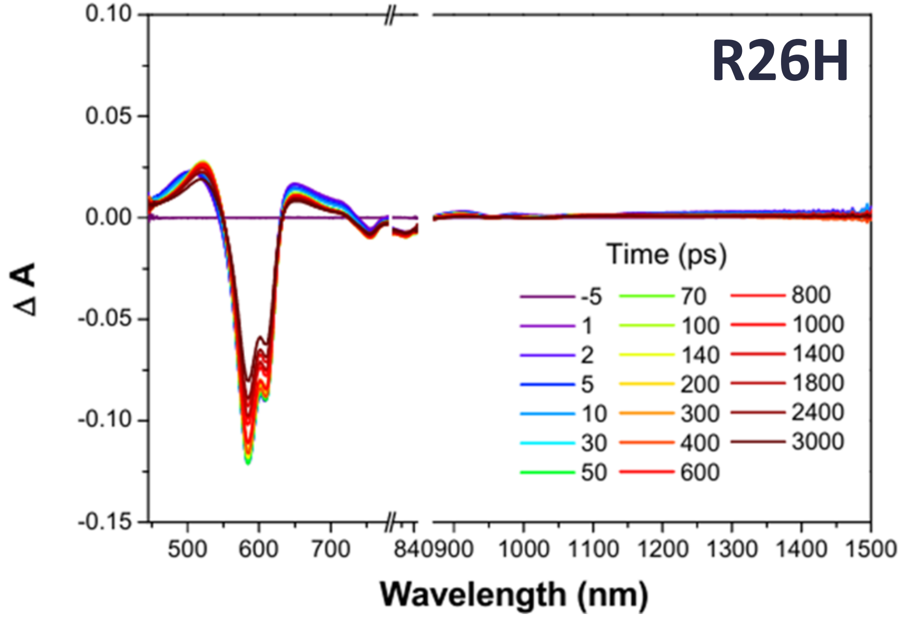


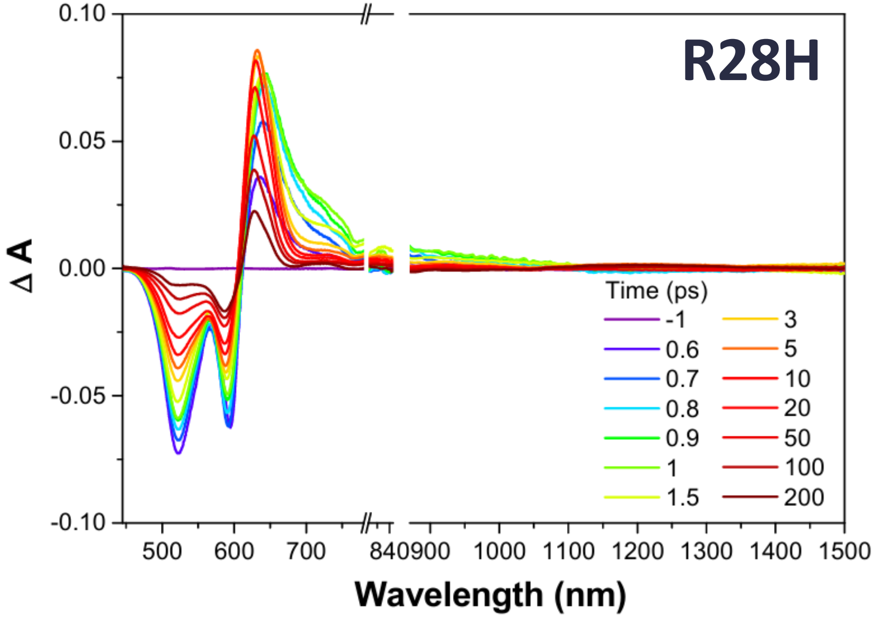
__Antiaromatic:__ broad and weak spectral features with a tail in the NIR region

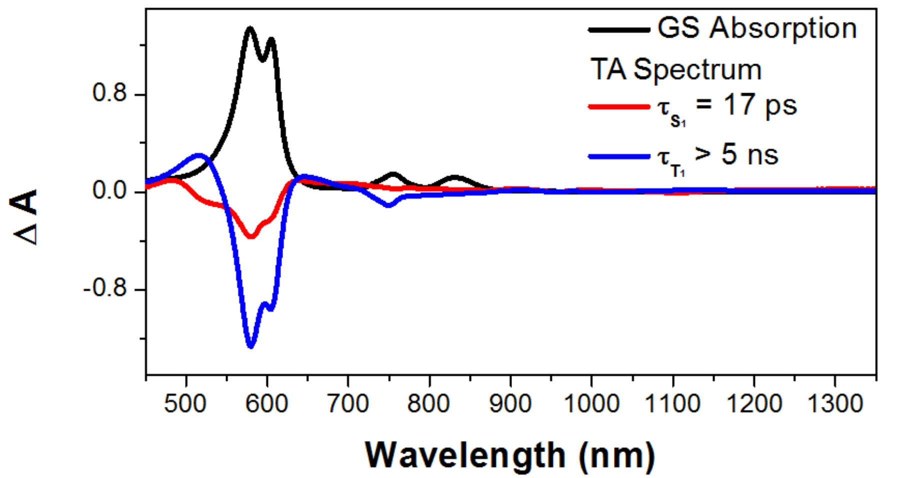
Chem. Rev. **2017**, 117, 2257

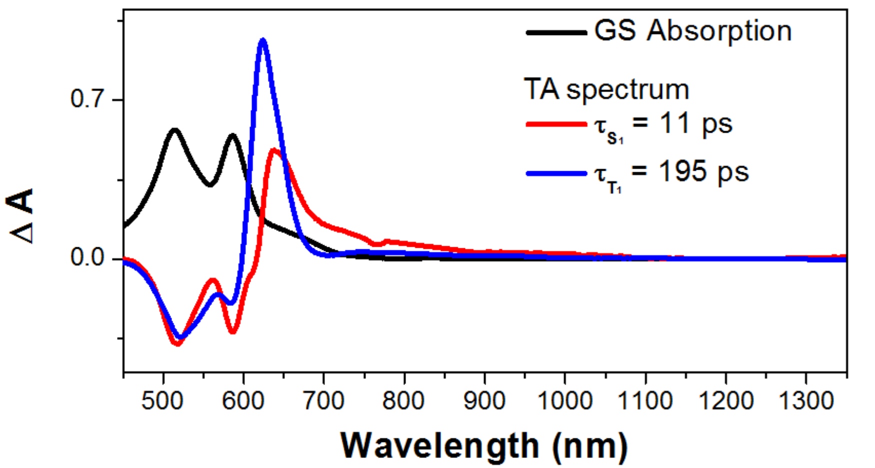
T_1-State Aromaticity with Transient Absorption Spectroscopy

Transient Absorption measurement





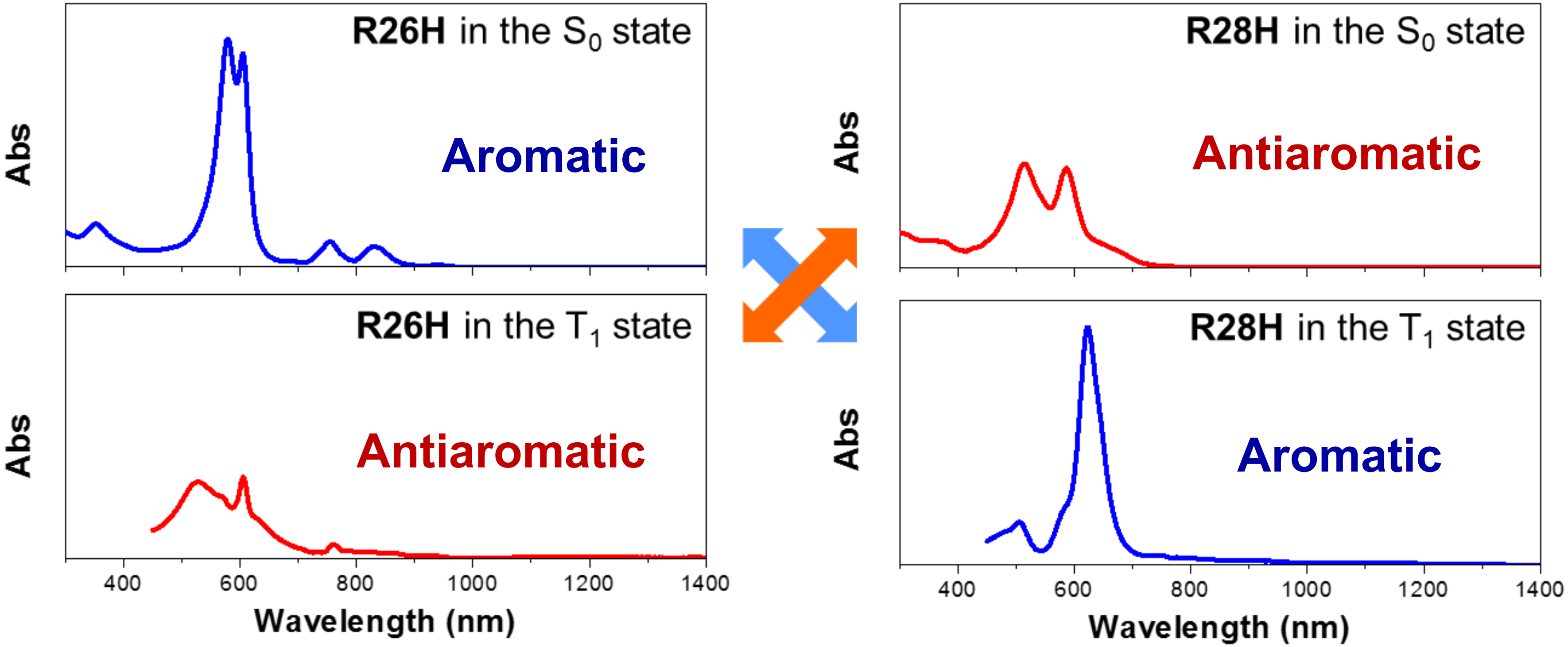




T_1-State Aromaticity with Transient Absorption Spectroscopy

Extraction of T_1-State Absorption Spectra

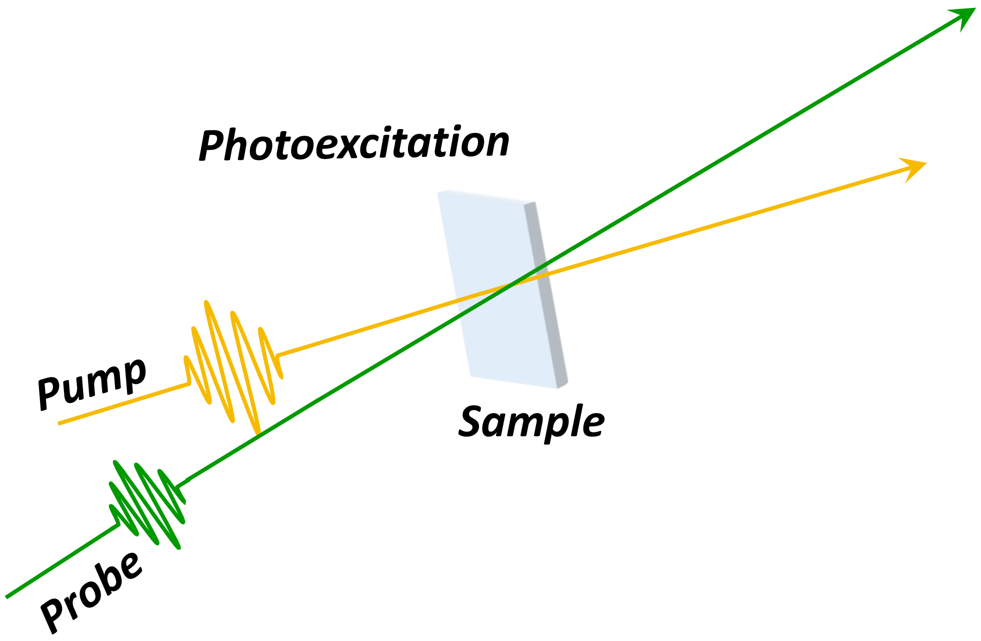
Interconvertible spectral features



➔ Aromaticity Reversal in T_1 state based on Baird's rule

Nat. Chem. **2015**, 7, 418

Transient IR Spectroscopy



X-ray *: Core-electron transition*
+ Atomic Scattering

UV-Vis-NIR *: Valence electron transition*

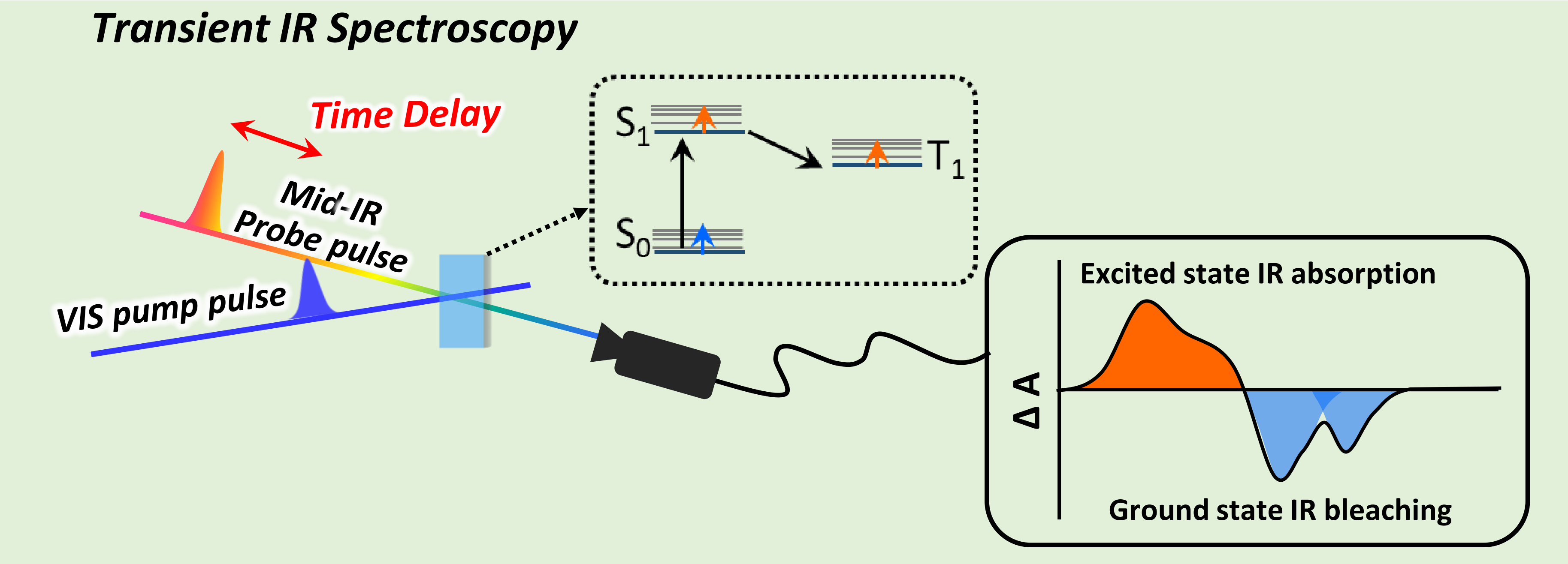
Mid-IR *: Vibrational Transition*
(carries structural information)

Terahertz *: Free electron resonance absorption*

E-beam *: Atomic Scattering*
+ Elemental information

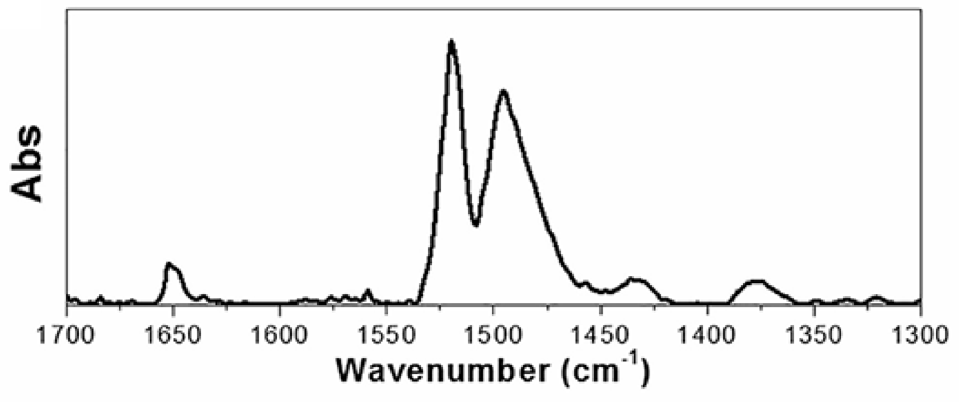
⋮

Transient IR Spectroscopy

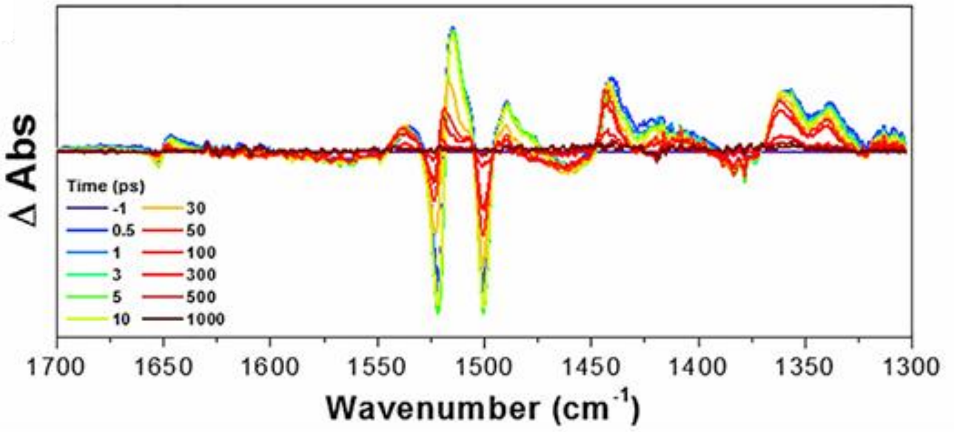


Transient IR Spectroscopy

FT-IR Spectrum



Transient IR Spectra



IR Spectroscopy and Molecular Structure

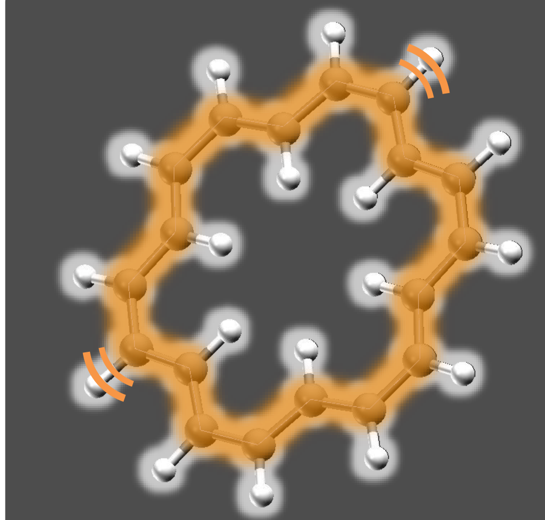
Vibrational modes

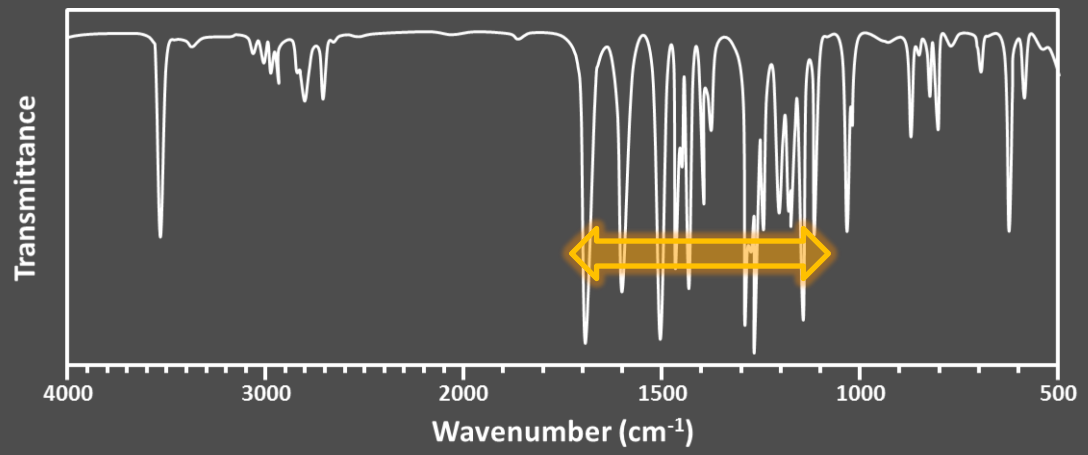
IR active → *dipole moment change*

$$M(\nu \to \nu') = \int_{-\infty}^{\infty} \psi^*(\nu)\mu\psi(\nu)dx$$

Raman active → *polarizability change*

$$M(\nu \to \nu') = \int_{-\infty}^{\infty} \psi^*(\nu)\alpha\psi(\nu)dx$$



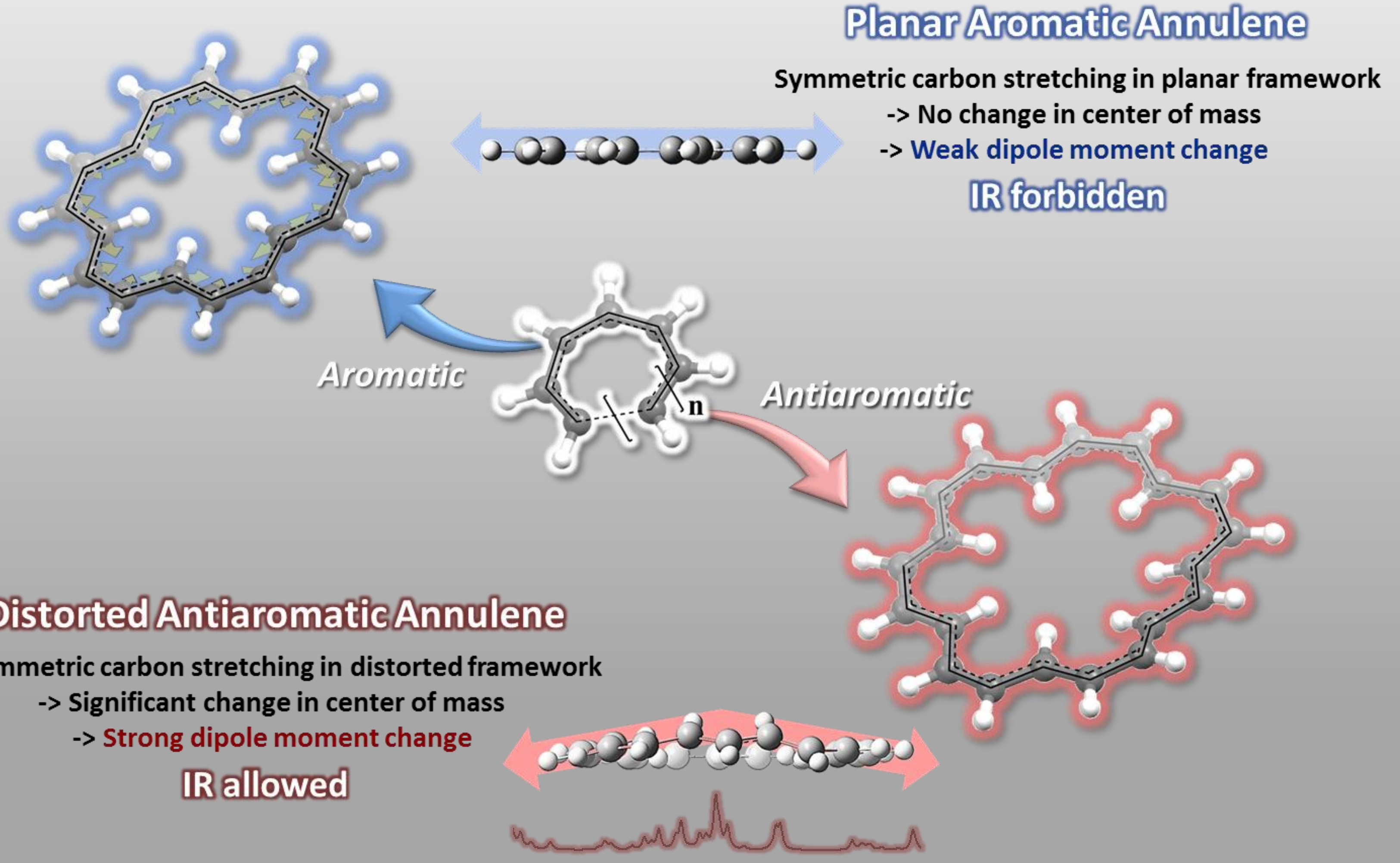


C=C stretching modes from whole cyclic conjugation

IR activity of C=C stretching modes are sensitive to structural change

IR Spectroscopy and Molecular Structure

Aromaticity-dependence of Structures & IR-Activities



Planar Aromatic Annulene

Symmetric carbon stretching in planar framework
-> No change in center of mass
-> Weak dipole moment change

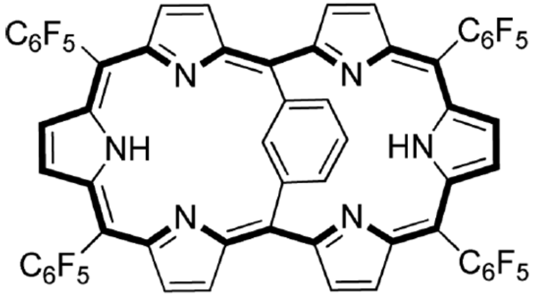
IR forbidden

Distorted Antiaromatic Annulene

Asymmetric carbon stretching in distorted framework
-> Significant change in center of mass
-> Strong dipole moment change

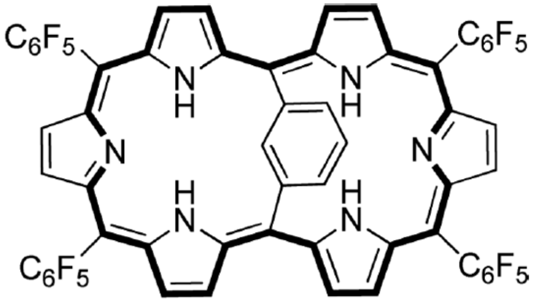
IR allowed

S_1-State Aromaticity with Transient IR Spectroscopy



P26H

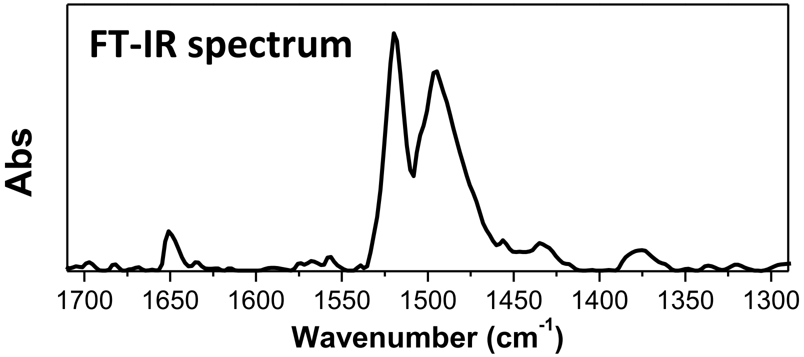
Aromatic

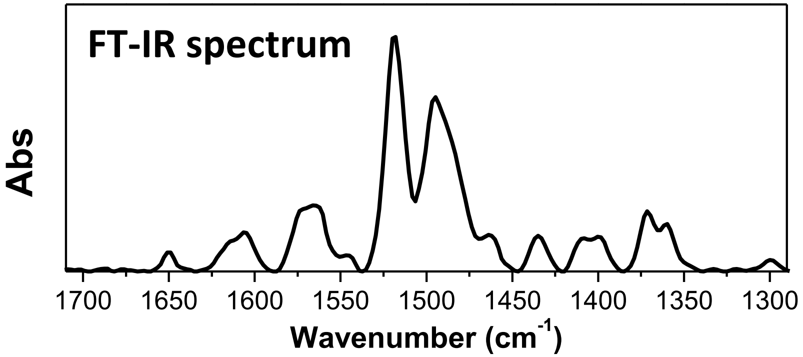


P28H

Antiaromatic

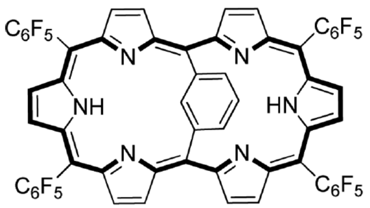
Aromatic/Antiaromatic Molecular Congeners



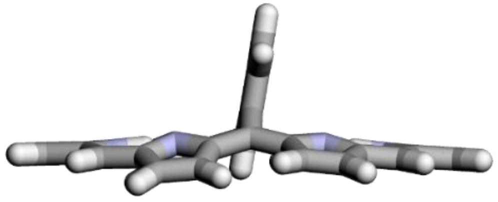


Chem **2017**, 3, 870

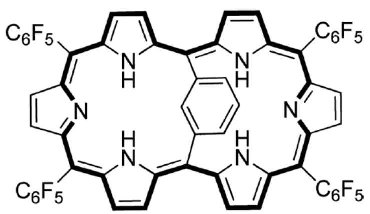
S_1-State Aromaticity with Transient IR Spectroscopy



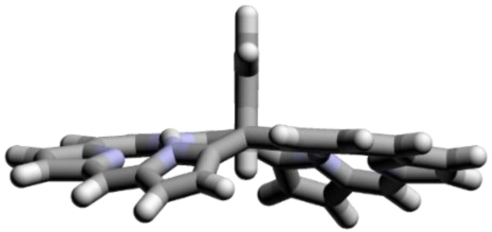
P26H



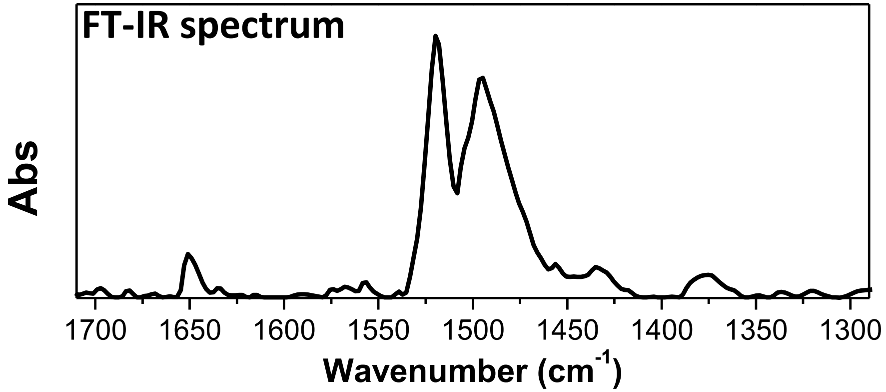
Planar



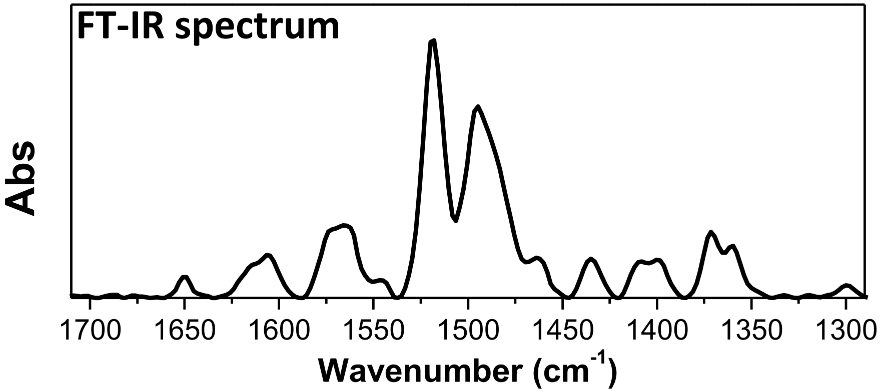
P28H



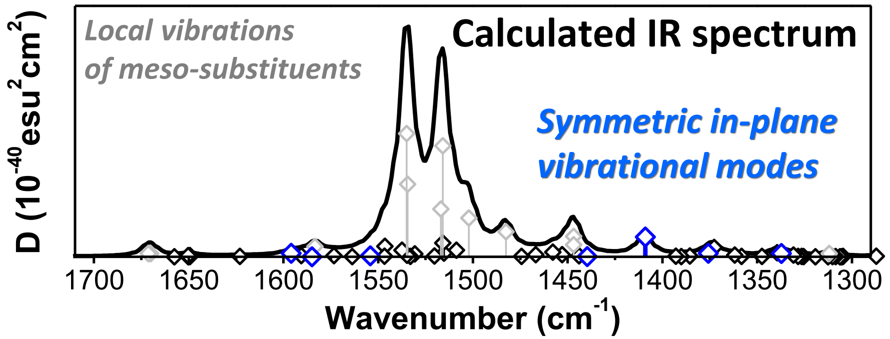
Distorted



FT-IR spectrum



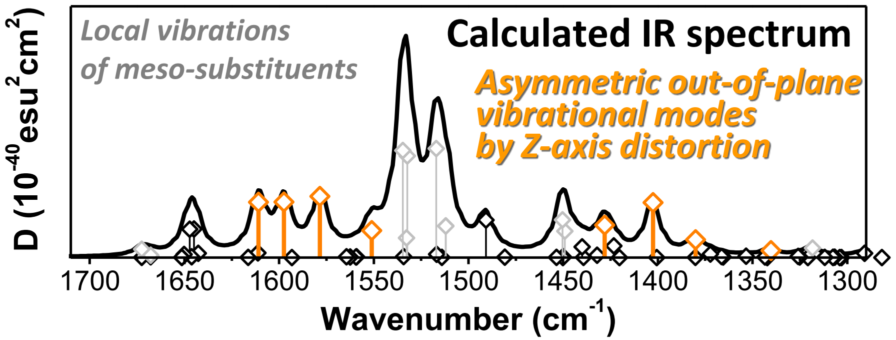
FT-IR spectrum



Calculated IR spectrum

Local vibrations of meso-substituents

Symmetric in-plane vibrational modes



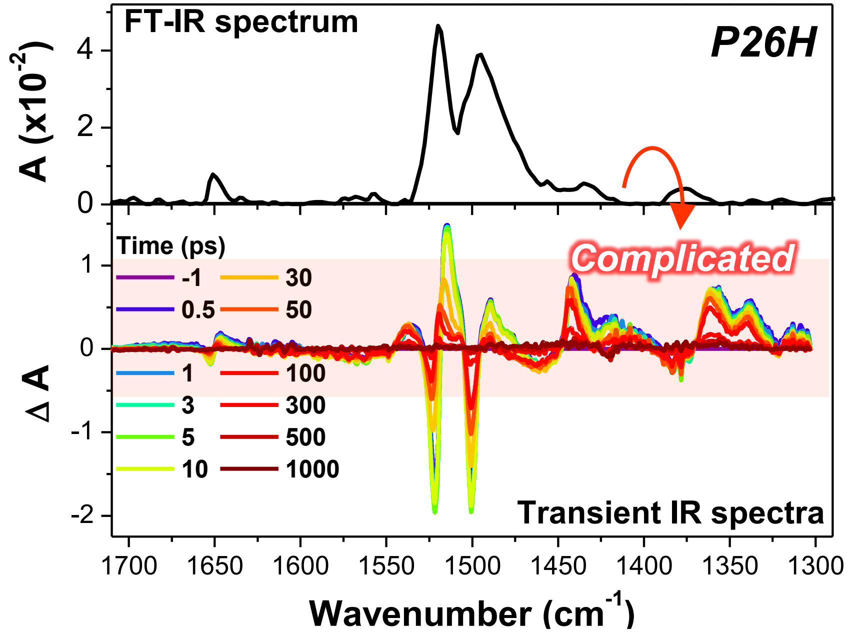
Calculated IR spectrum

Local vibrations of meso-substituents

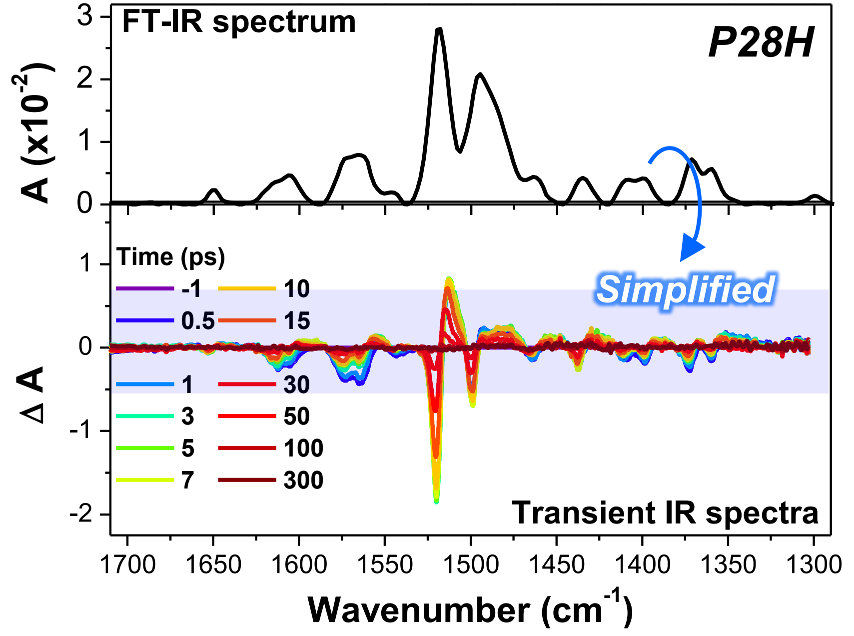
Asymmetric out-of-plane vibrational modes by Z-axis distortion

Distorted structure of *Antiaromatic* hexaphyrins → Enhanced C=C stretching IR modes

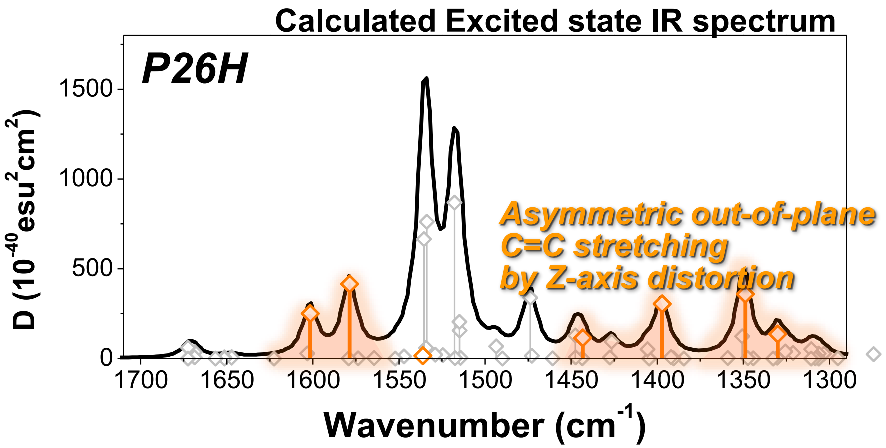
S_1-State Aromaticity with Transient IR Spectroscopy


P26H

Complicated

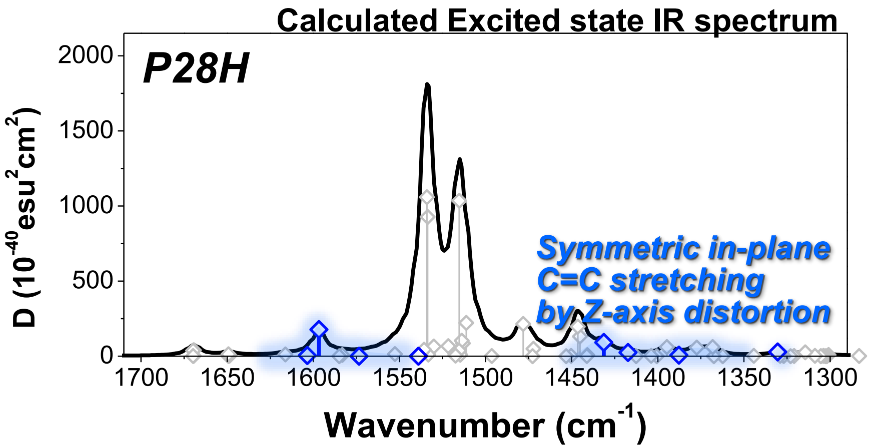

P28H

Simplified


Calculated Excited state IR spectrum

P26H

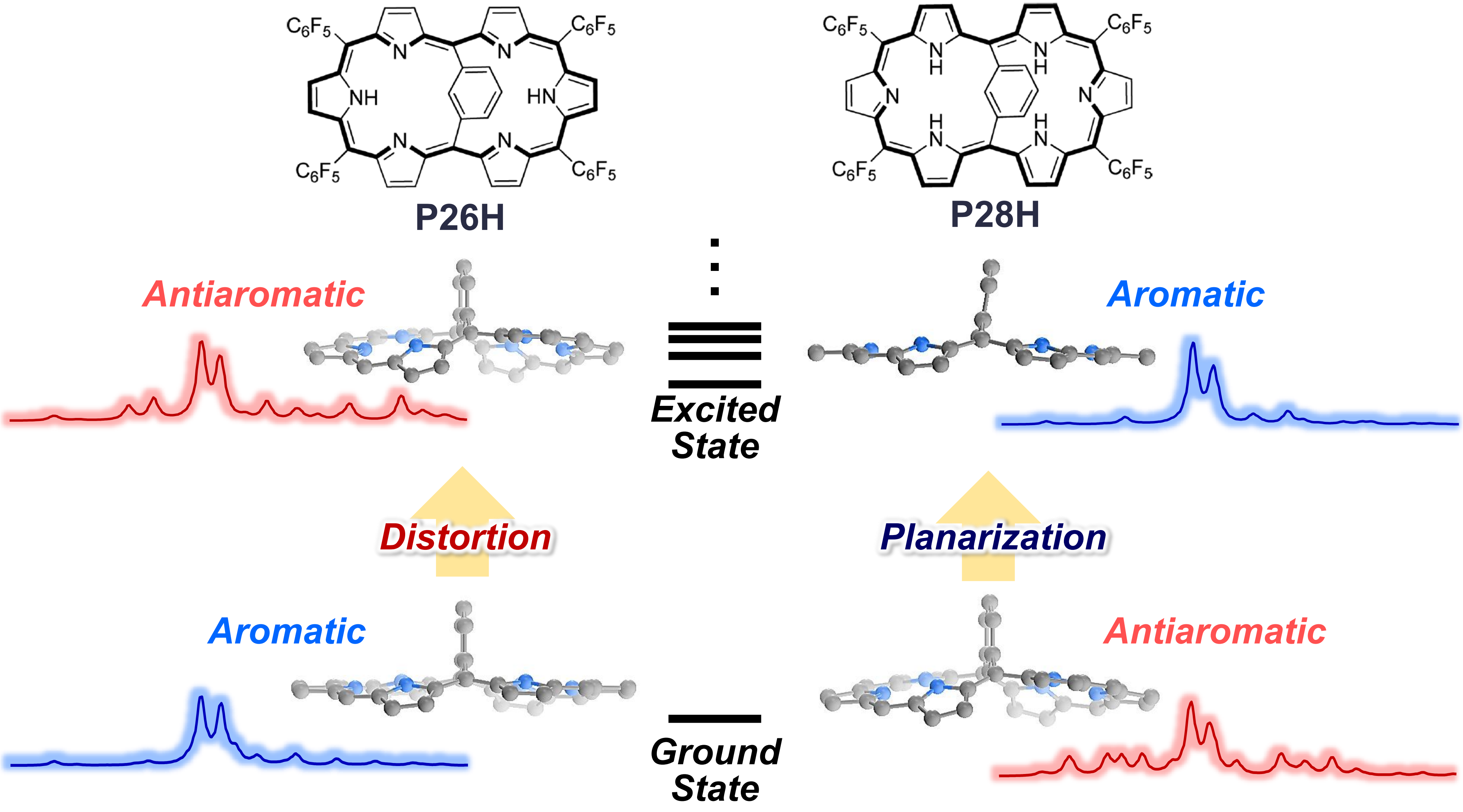
Asymmetric out-of-plane C=C stretching by Z-axis distortion


Calculated Excited state IR spectrum

P28H

Symmetric in-plane C=C stretching by Z-axis distortion

S_1-State Aromaticity with Transient IR Spectroscopy



P26H

P28H

Antiaromatic

Aromatic

Excited State

Distortion

Planarization

Aromatic

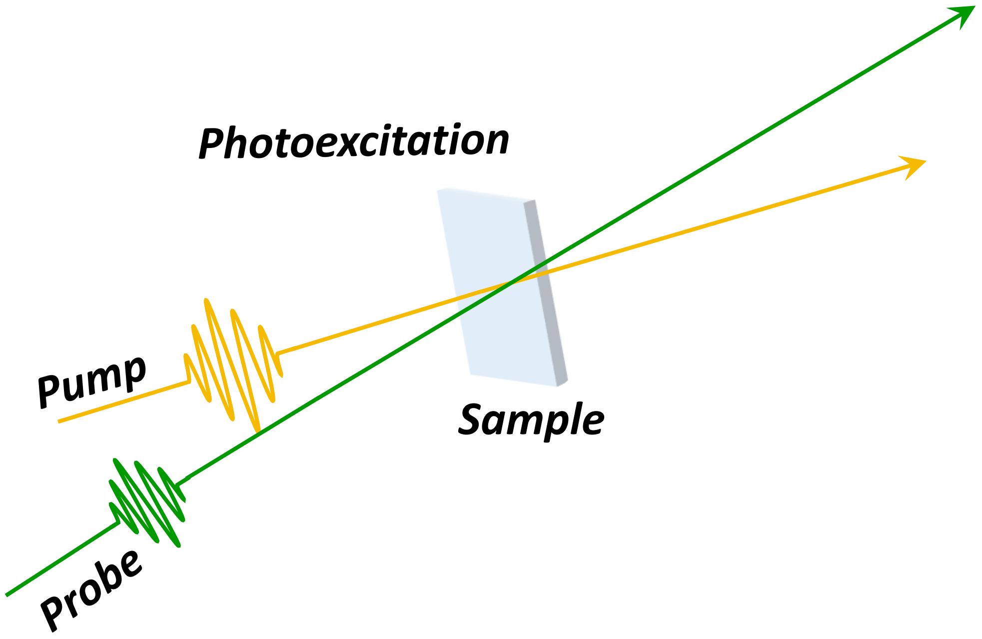
Antiaromatic

Ground State

Capturing Aromaticity-driven Structural Change by Transient IR method

Chem **2017**, 3, 870

Time-resolved Electron Diffraction Spectroscopy



X-ray *: Core-electron transition*

+ Atomic Scattering

UV-Vis-NIR *: Valence electron transition*

Mid-IR *: Vibrational Transition*

(carries structural information)

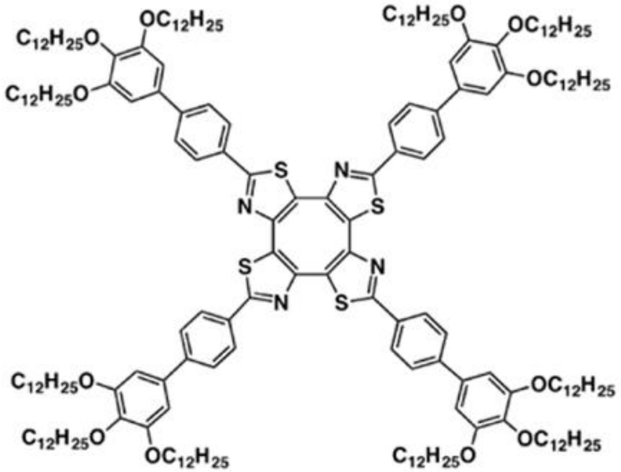
Terahertz *: Free electron resonance absorption*

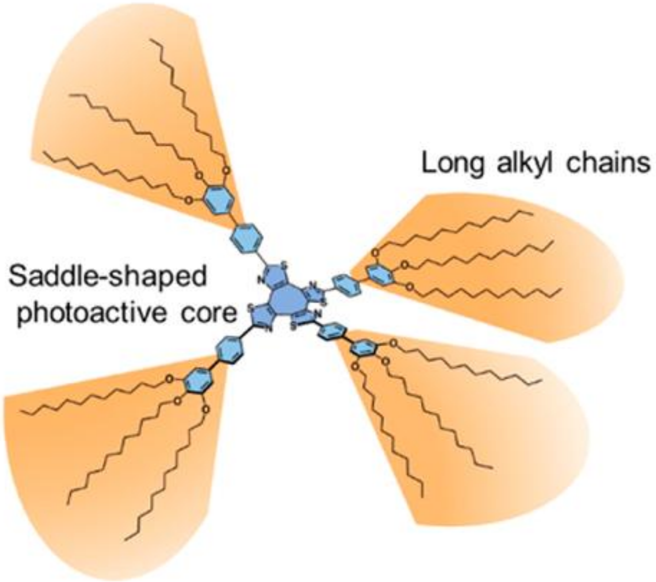
E-beam *: Atomic Scattering*

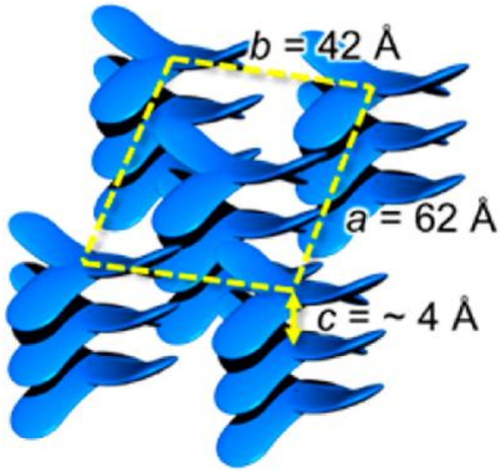
+ Elemental information

⋮

S_1-State Aromatization with Time-resolved Electron Diffraction





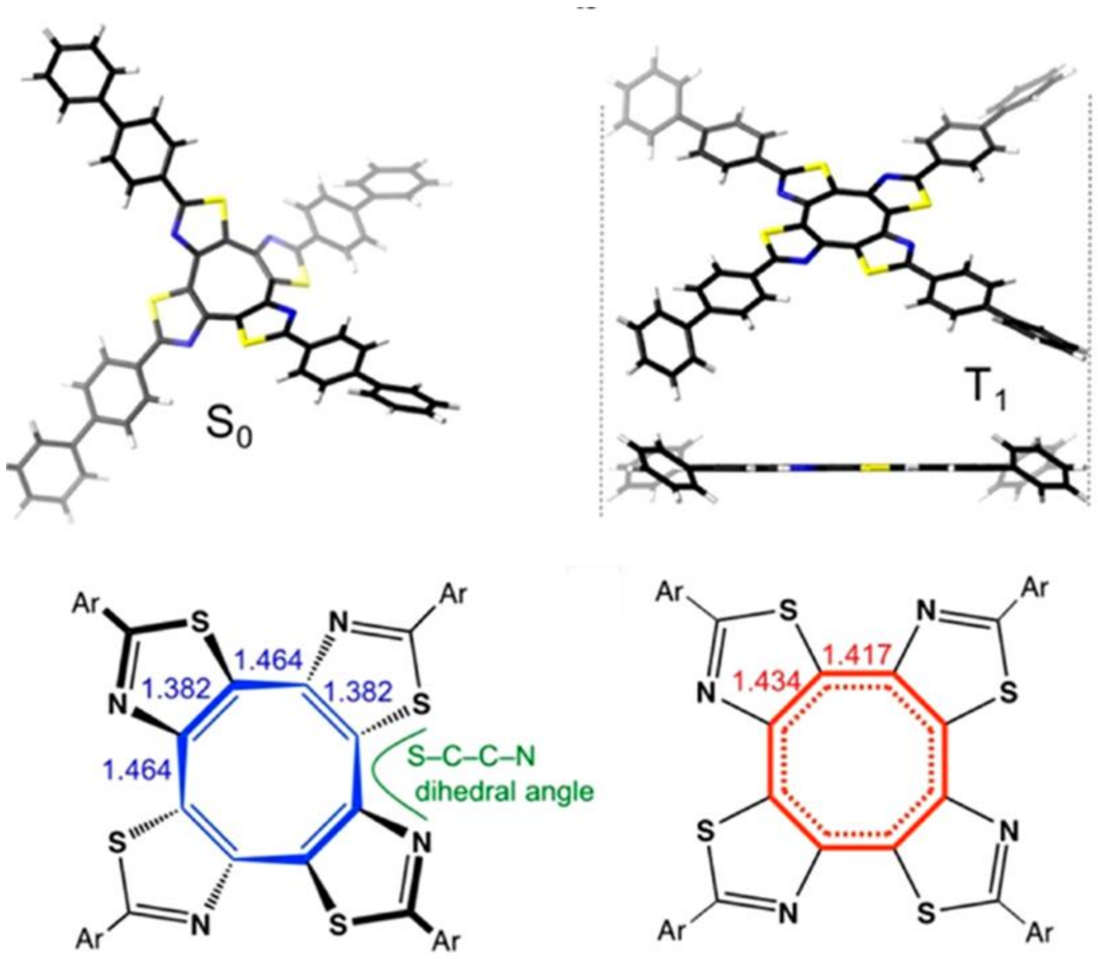


Rectangular columnar phase (*C*2/*m*)

Liquid Crystal

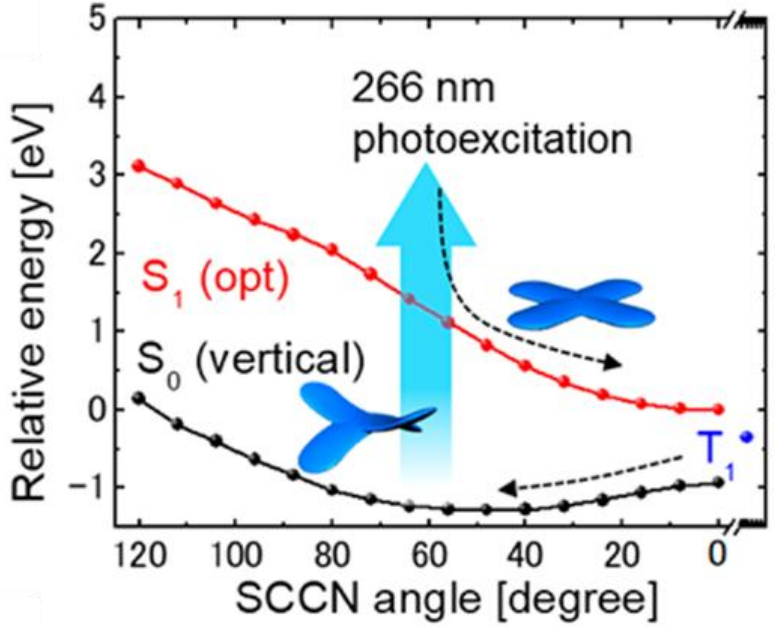
J. Am. Chem. Soc.. **2017**, 139, 15792

S_1-State Aromatization with Time-resolved Electron Diffraction



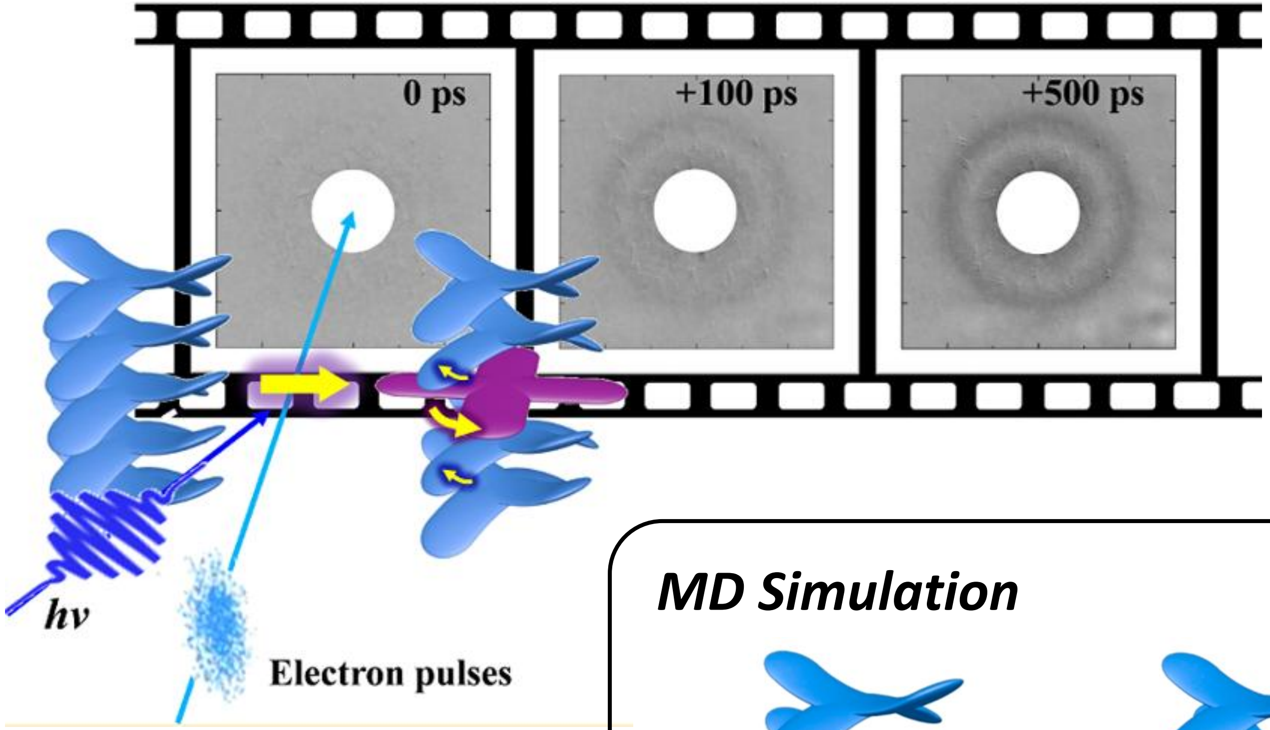
NICS(1) 2.76
NICS(1)$_{zz}$ 18.31
HOMA$_{COT}$ 0.25
Nonaromatic

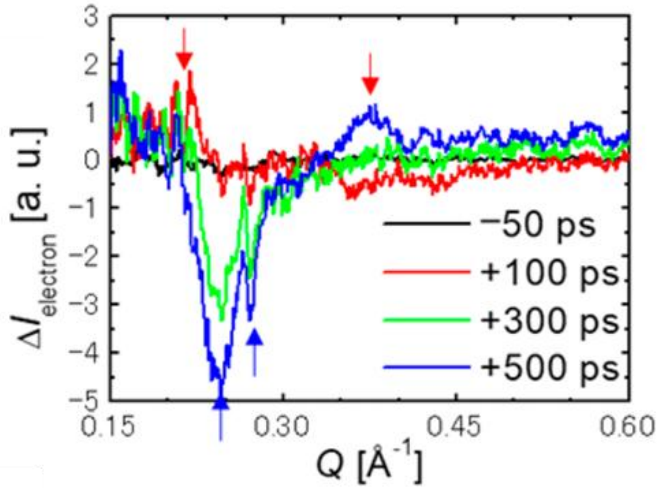
NICS(1) –8.04
NICS(1)$_{zz}$ –18.24
HOMA$_{COT}$ 0.63
Aromatic



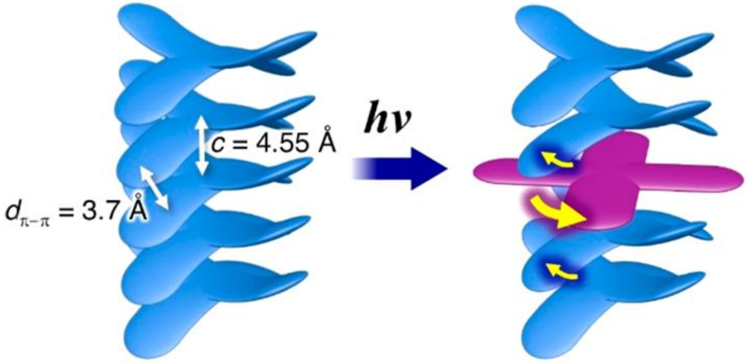
S_1-State Aromatization with Time-resolved Electron Diffraction

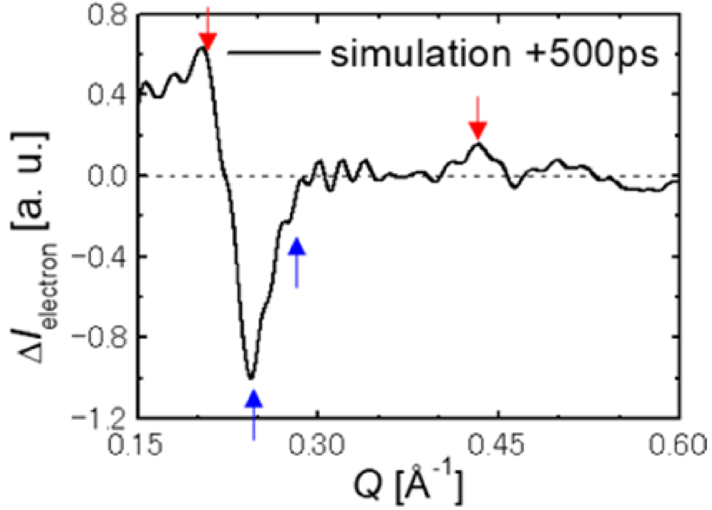
Time-resolved Electron Diffraction Pattern





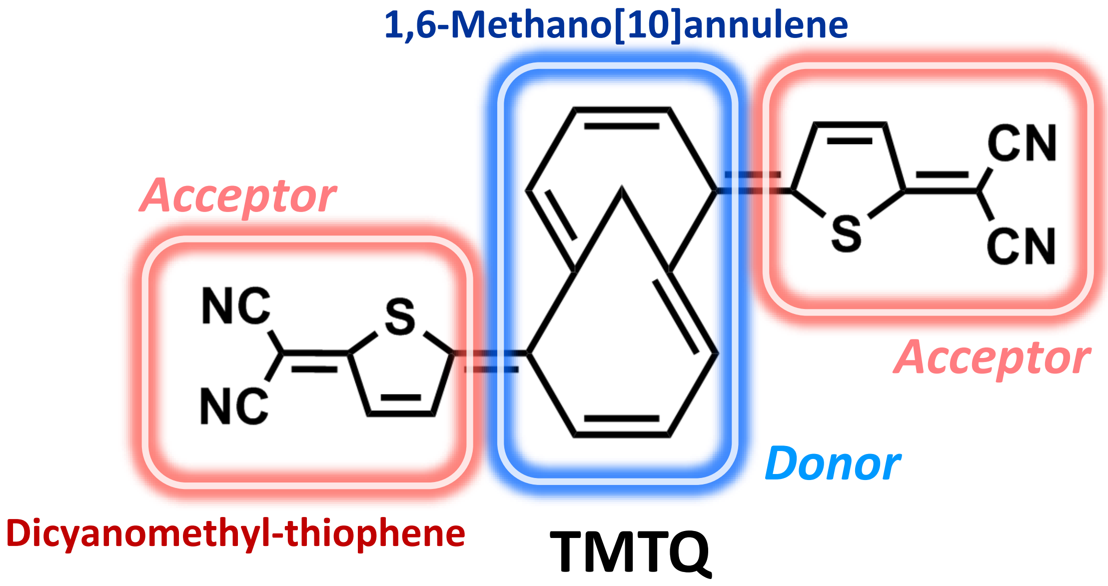
MD Simulation





Verification of Excited-State Aromatization with pump-probe methods

Acceptor-Donor-Acceptor Conjugated Oligomer

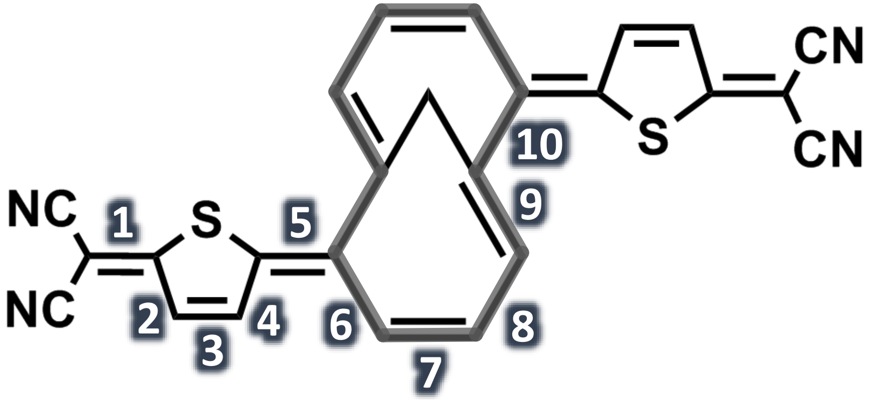


Nat. Commun **2019**, 10, 4983

Verification of Excited-State Aromatization with pump-probe methods

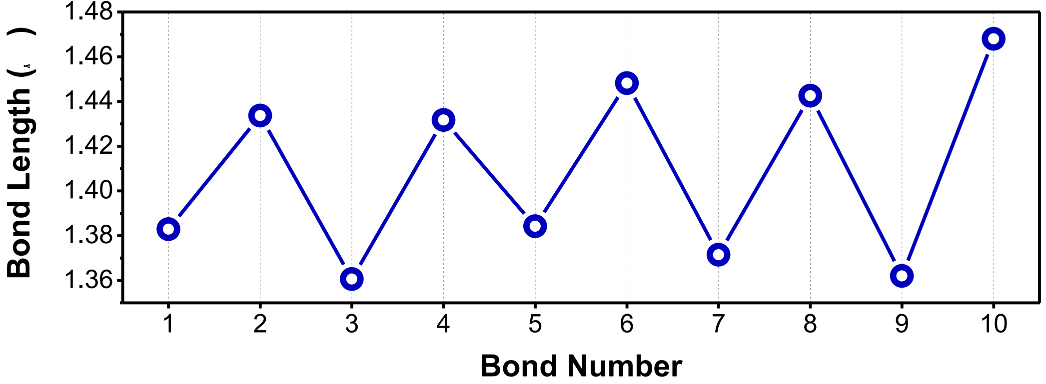
Acceptor-Donor-Acceptor Conjugated Oligomer

Non-aromatic [10] annulene



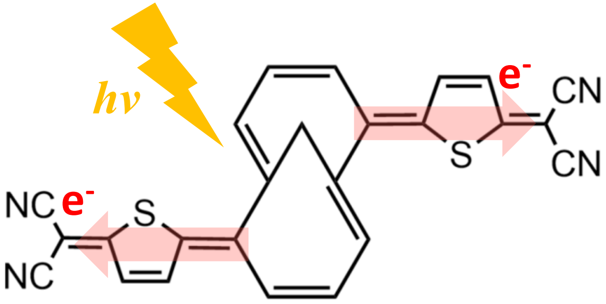
TMTQ

Discrete π-conjugation

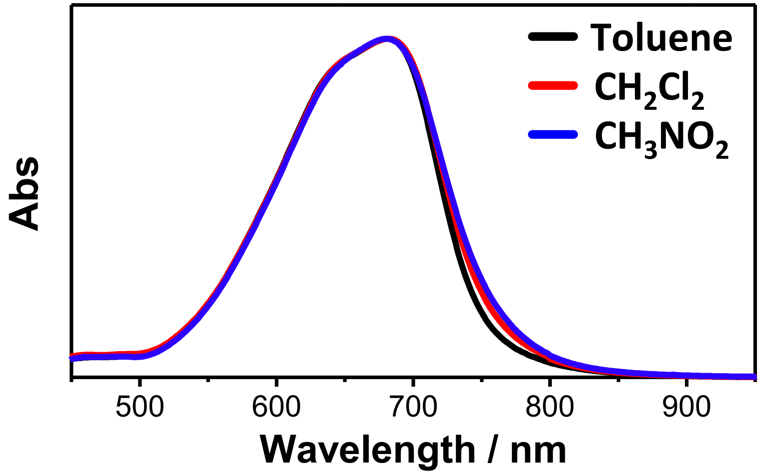


Nat. Commun **2019**, 10, 4983

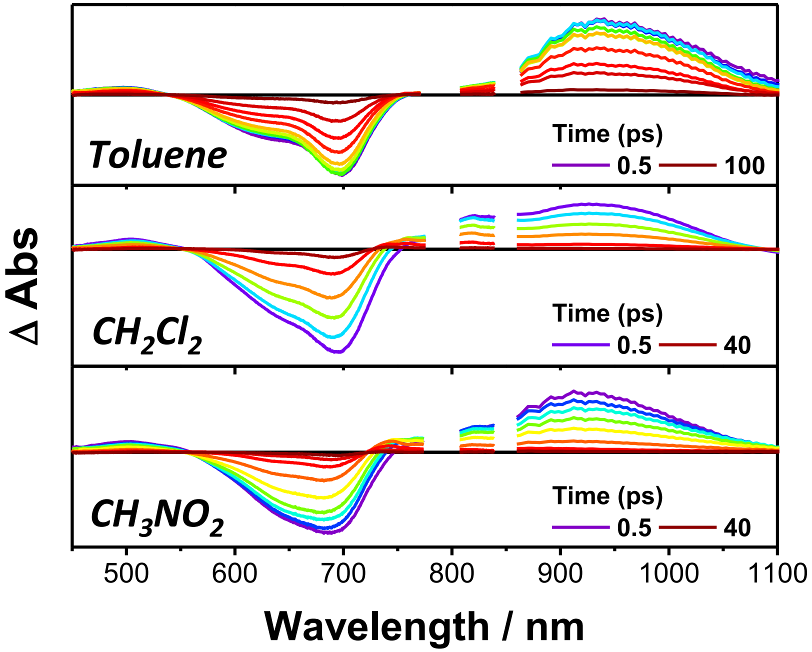
Verification of Excited-State Aromatization with pump-probe methods

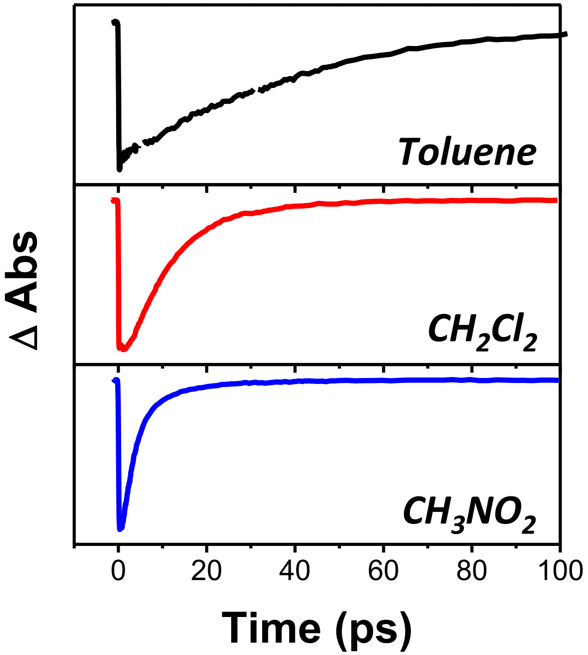


Intramolecular CT process



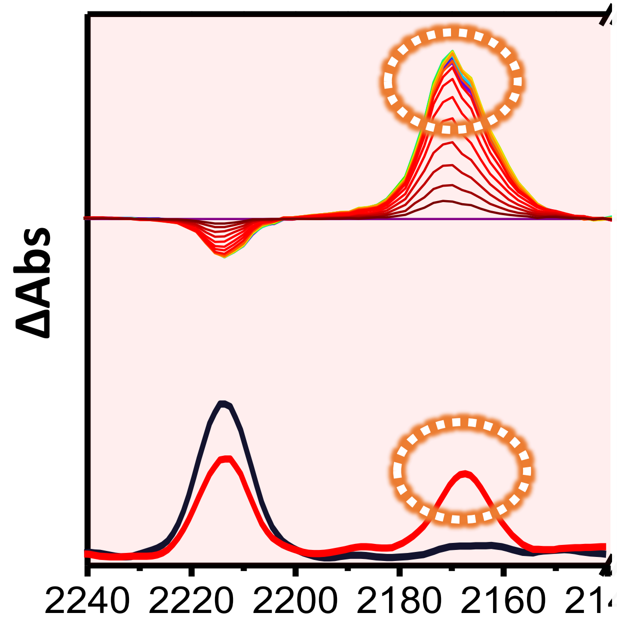
Transient Absorption results



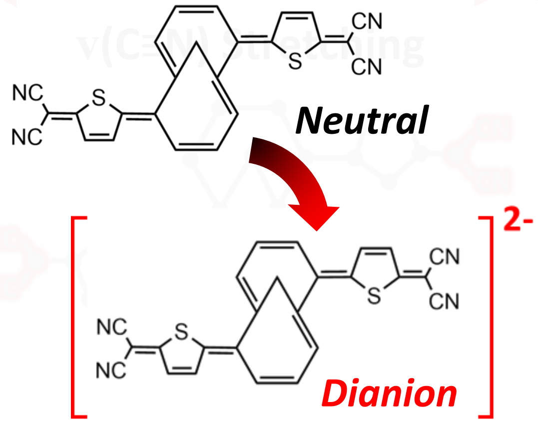


Acceleration of Decay
Upon an increase of Polarity

Verification of Excited-State Aromatization with pump-probe methods

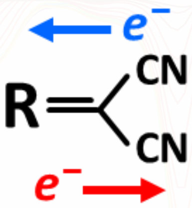


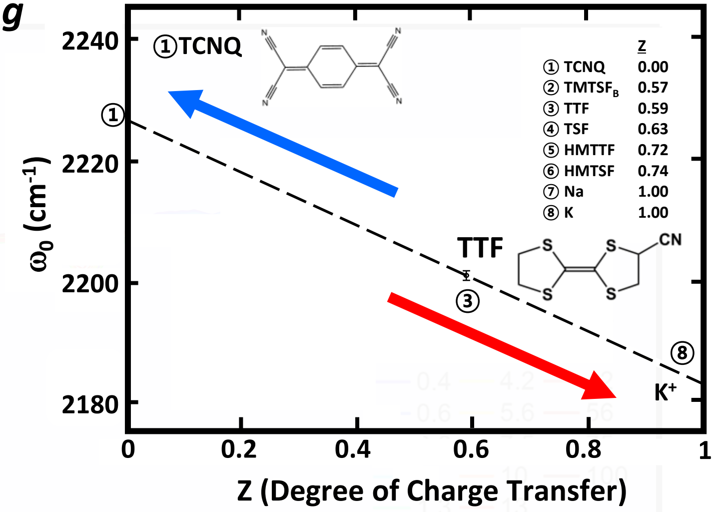
Electrochemical Reduction



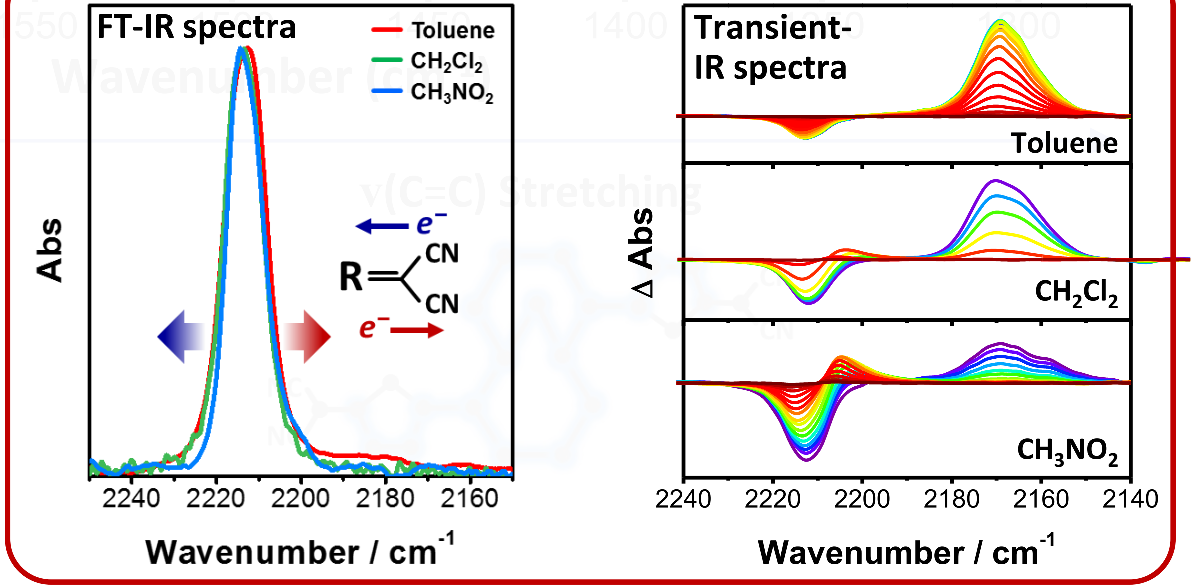
IR frequency of CN stretching

Effective marker *for electron density on dicyano group*



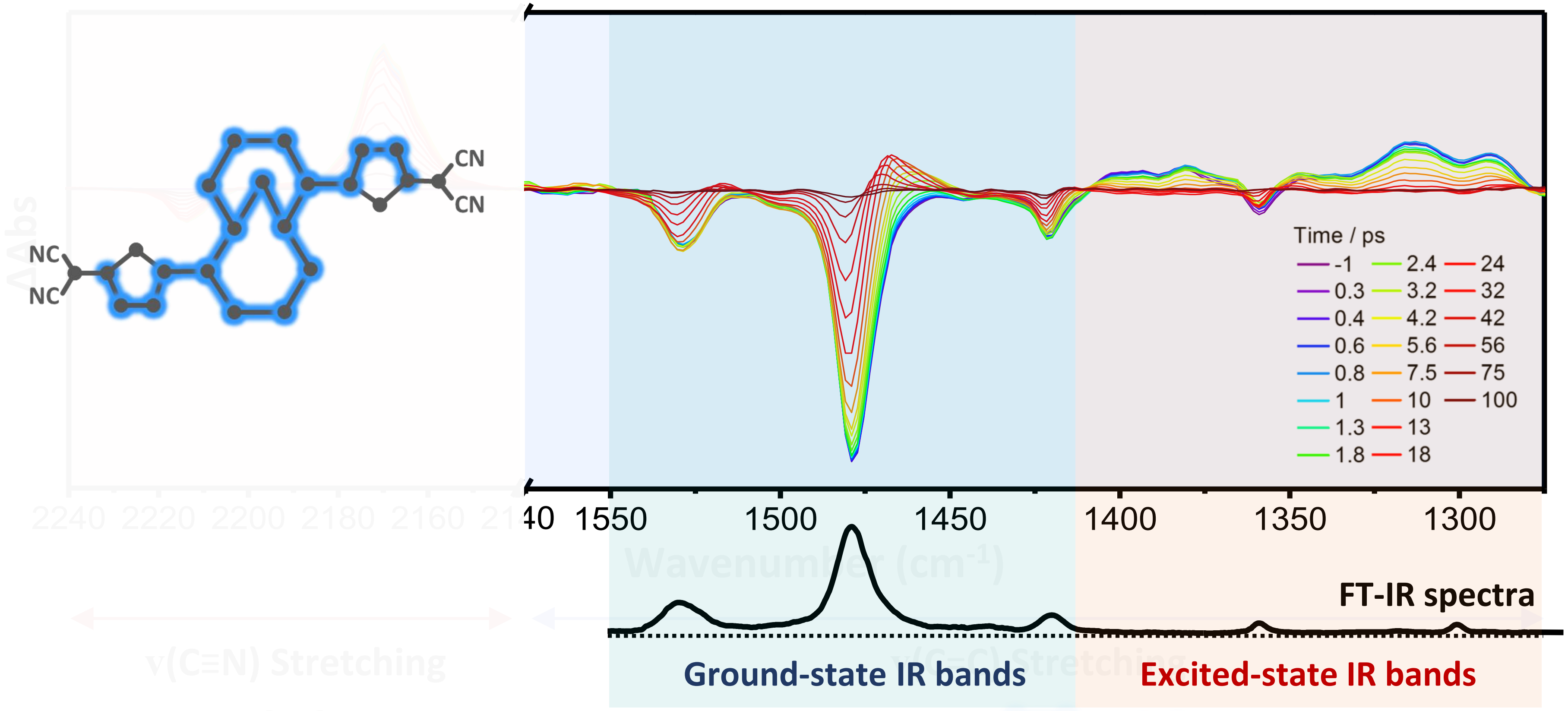


Intramolecular CT Process in the Excited State



J. Am. Chem. Soc. **1981**, *103*, 2442.

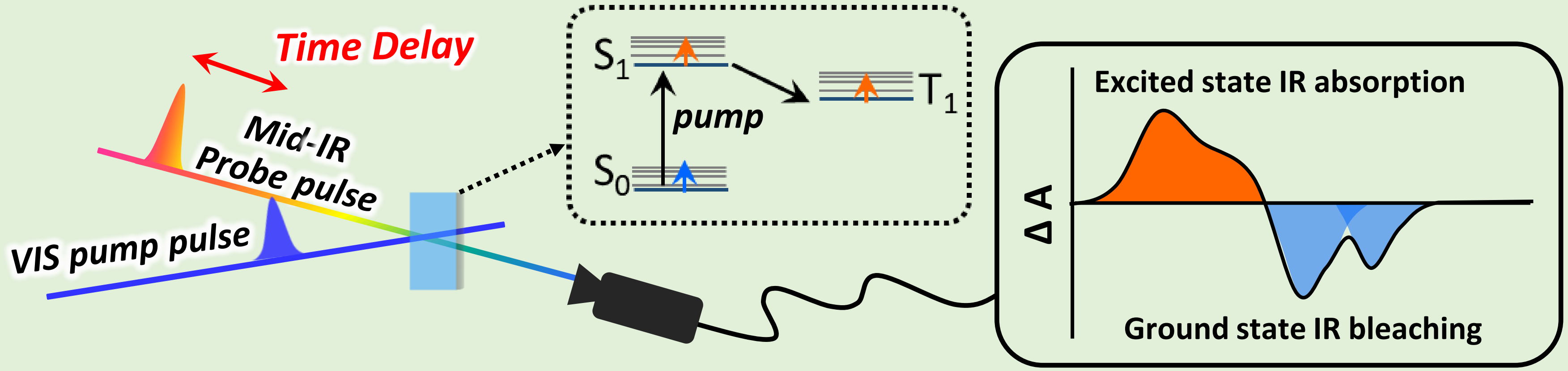
Verification of Excited-State Aromatization with pump-probe methods



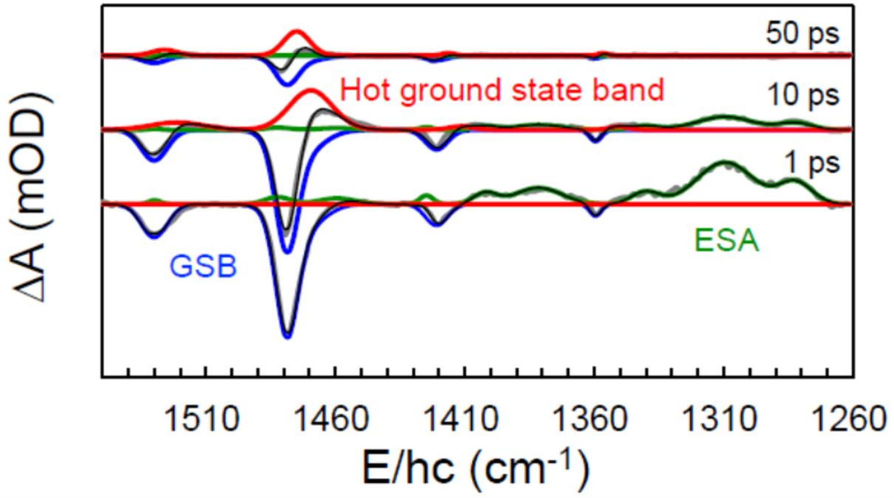
Substantial IR Spectral Change
between Ground & Excited States

Verification of Excited-State Aromatization with pump-probe methods

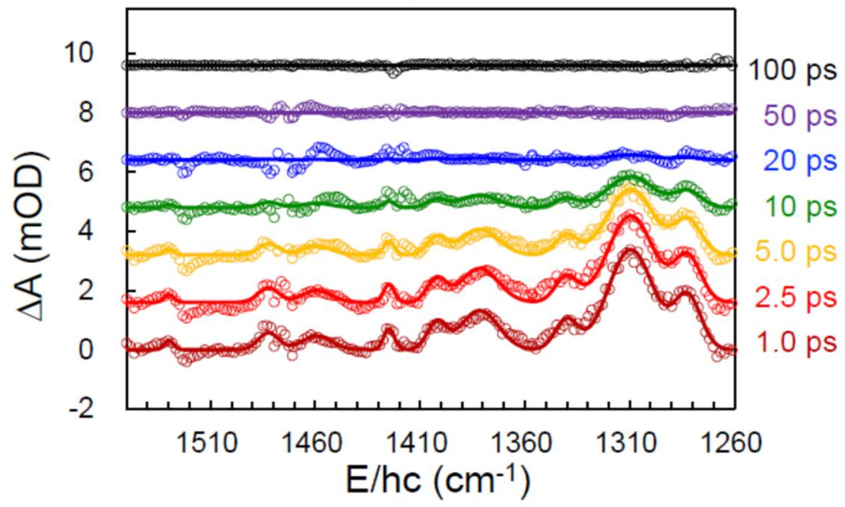
Transient IR Spectroscopy



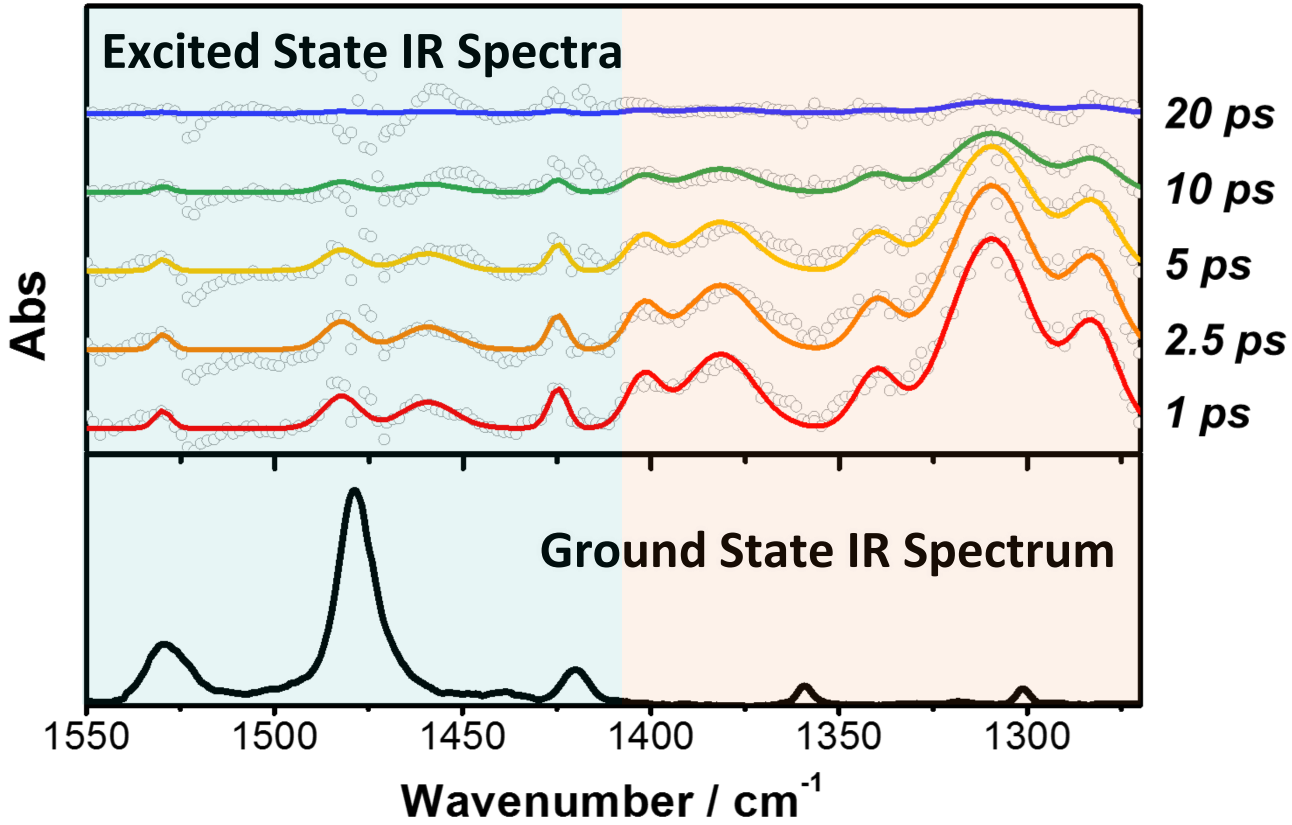
Time-resolved IR spctra fitting



Extrated ESA bands in TRIR spectra

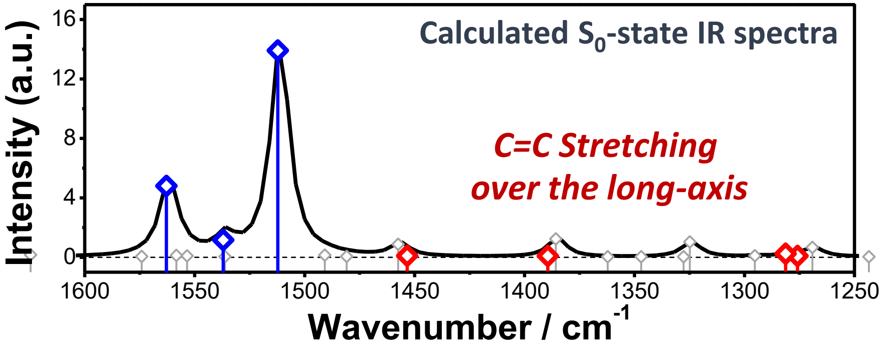


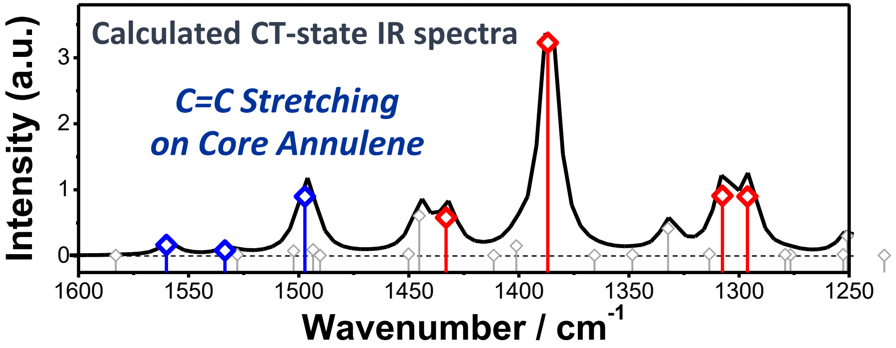
Verification of Excited-State Aromatization with pump-probe methods

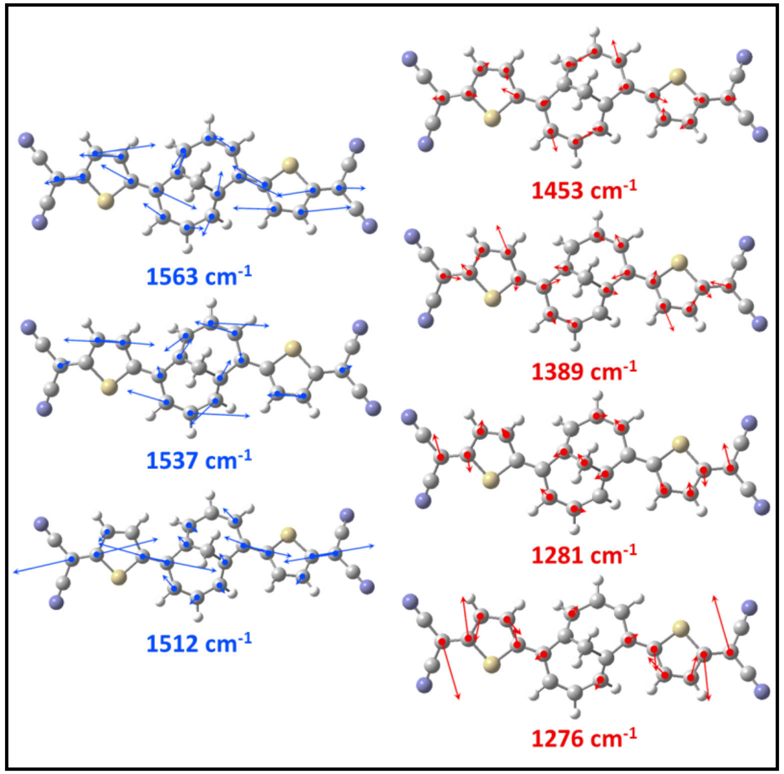


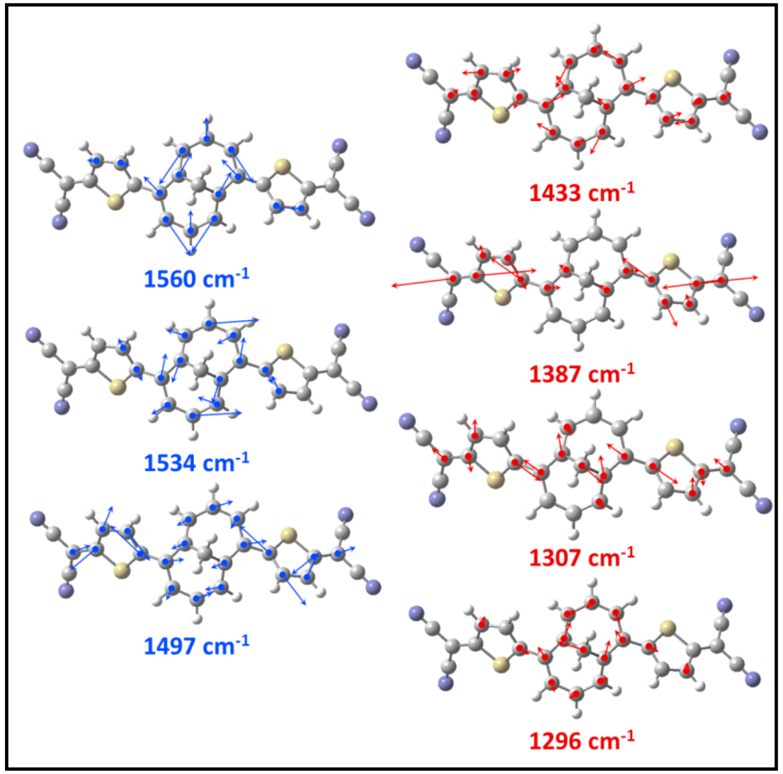
Substantial IR Spectral Change between Ground & Excited States

Verification of Excited-State Aromatization with pump-probe methods

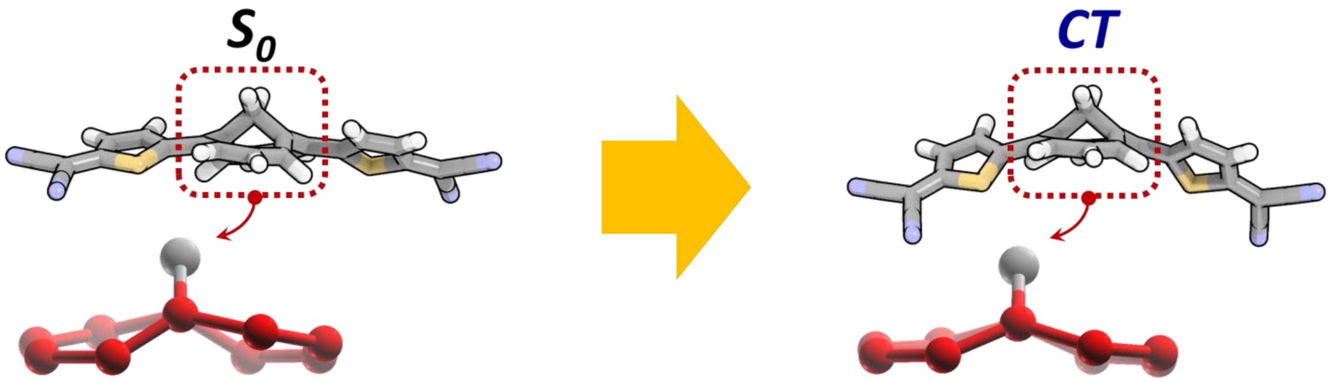






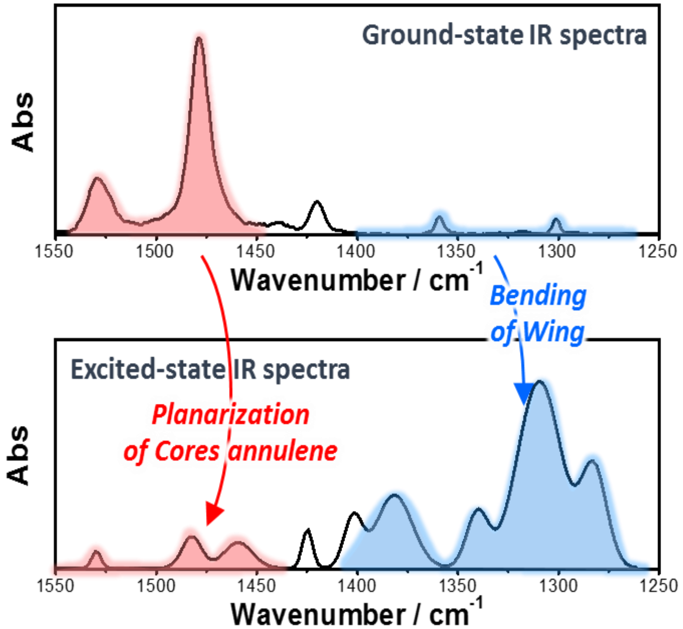


Verification of Excited-State Aromatization with pump-probe methods



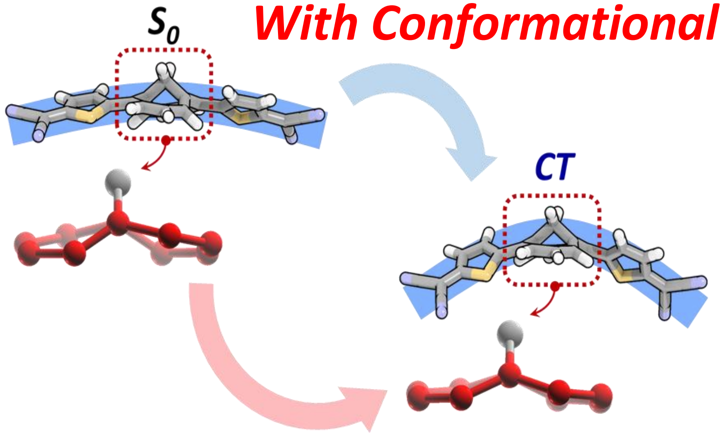
Core : distorted + Overall : Linear

Core : planar + Overall : Bent



CT-induced Excited-State Aromatization

With Conformational change



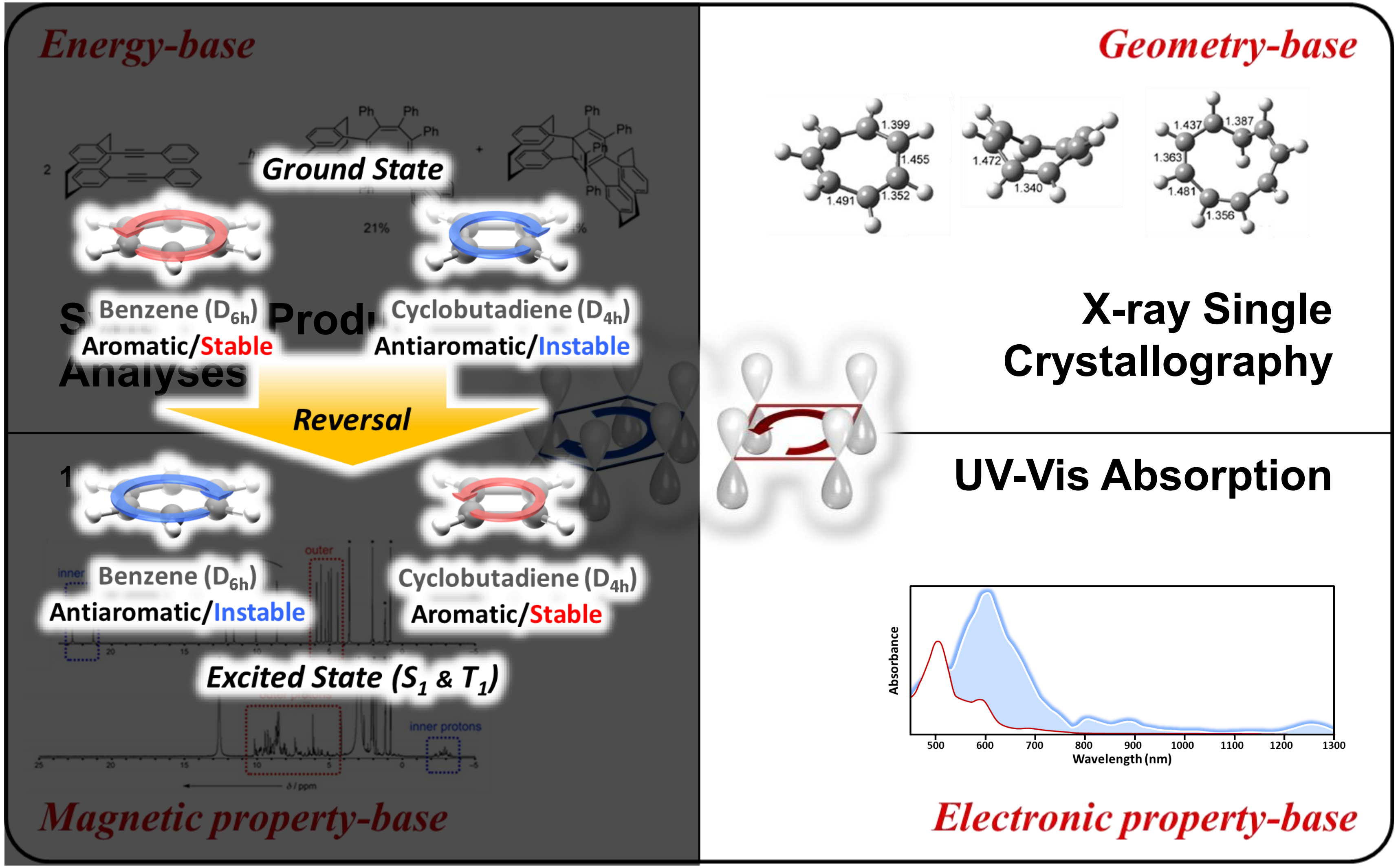
Nat. Commun **2019**, 10, 4983

How to Reveal Excited-State Aromaticity

Applicability to Excited-State Aromaticity Analyses

Impossible

Impossible



Transient IR & Electron Scattering

Transient Absorption

Thank you for your kind attention

4th International Conference on
Excited State Aromaticity and Anti-Aromaticity
8-11 January, 2026. IISER Thiruvananthapuram, Kerala, India.

Excited State features

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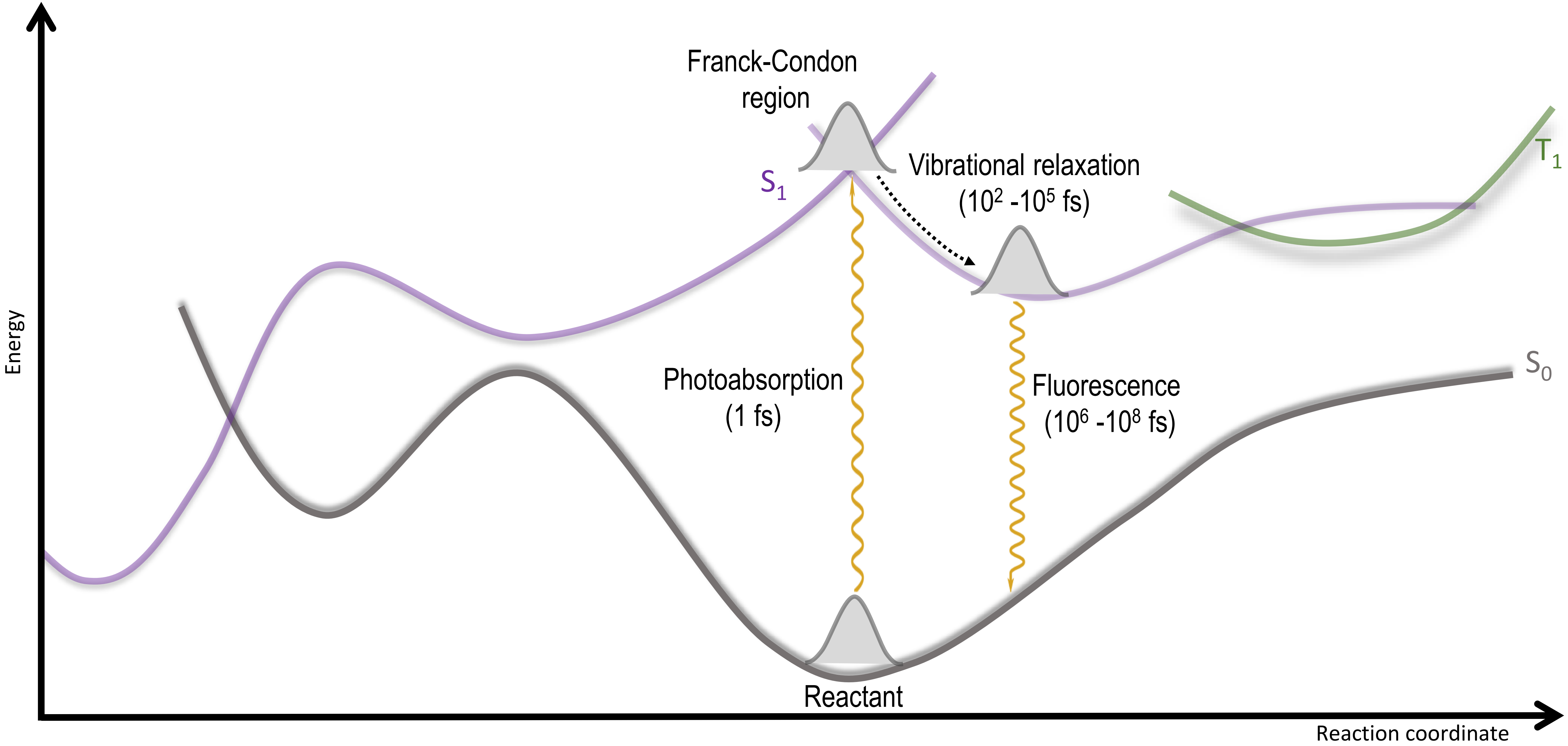
LABORATOIRE
DE CHIMIE
ENS DE LYON

Université Claude Bernard Lyon 1

Potential Energy Surface (PES): the key concept

Photochemical and photophysical behavior is encoded in the excited-state potential energy surfaces.



Potential Energy Surface (PES): the key concept

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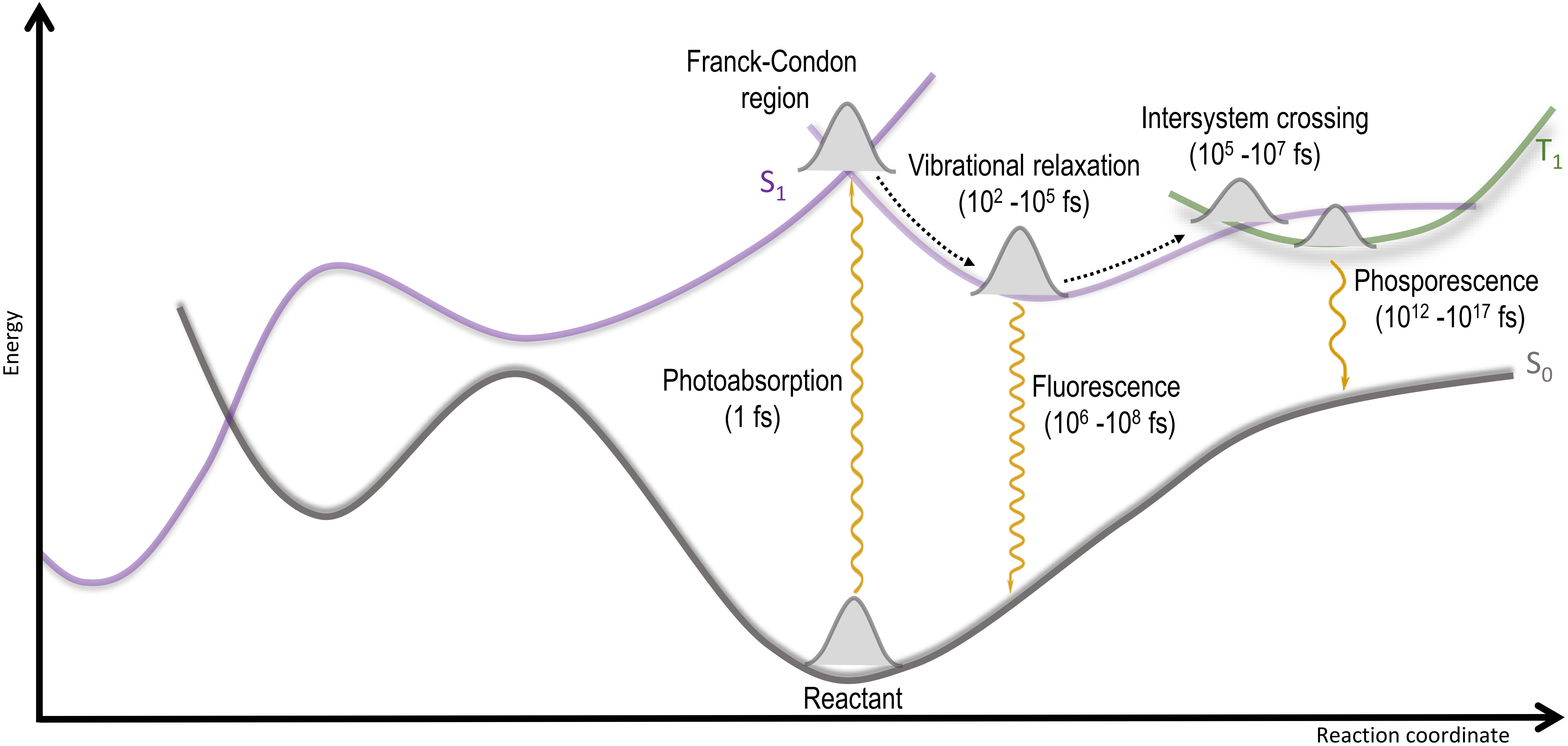
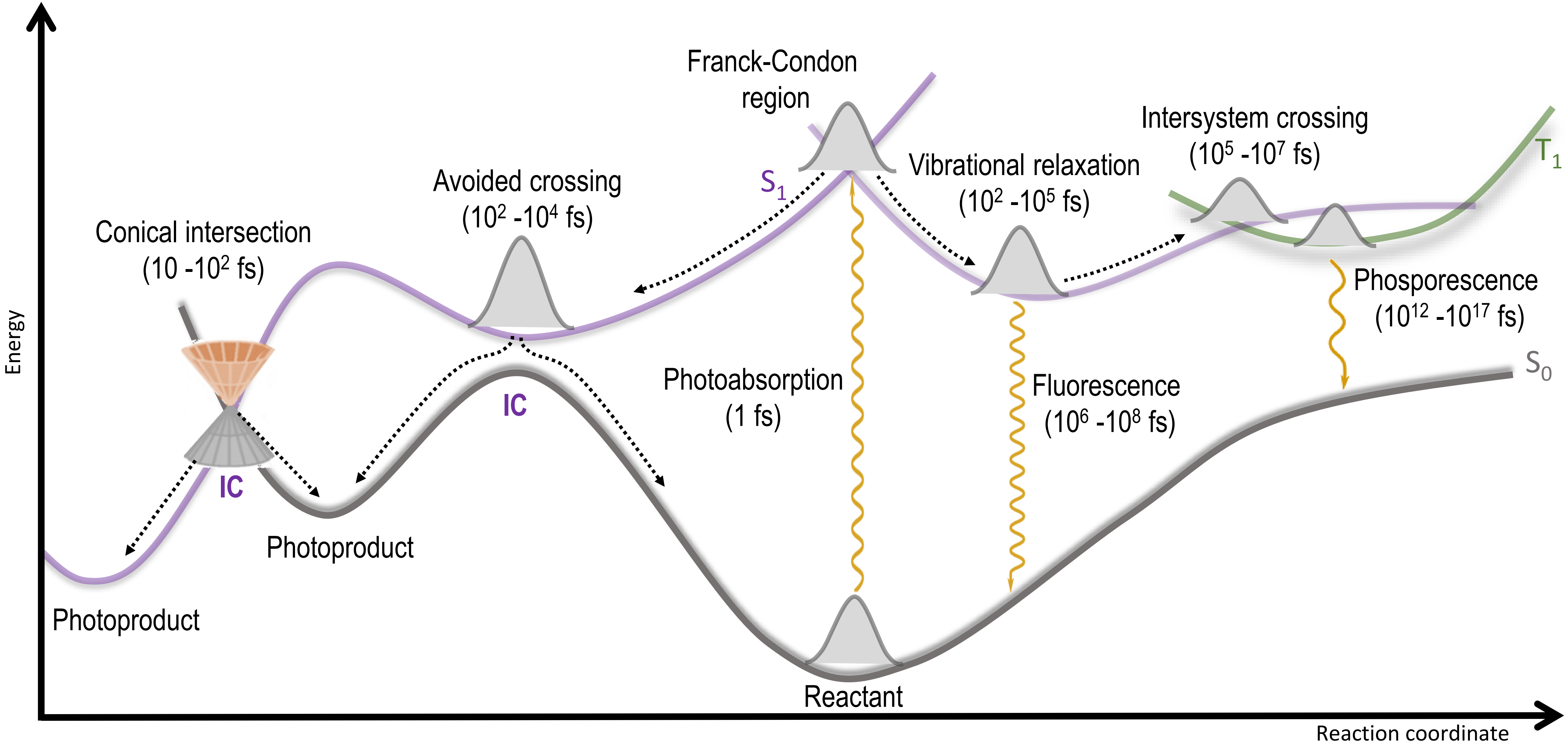


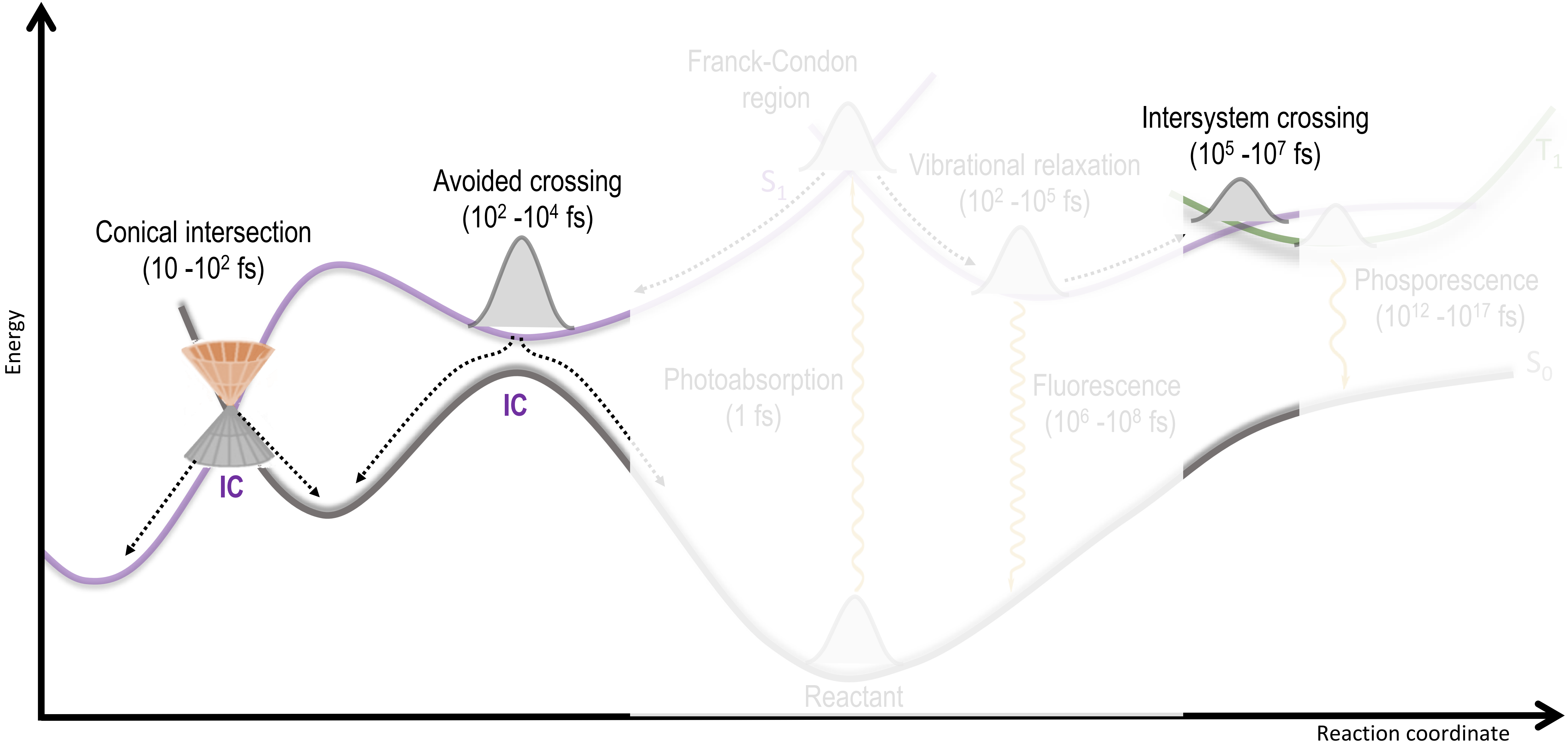
Potential Energy Surface (PES): the key concept

Photochemical and photophysical behavior is encoded in the excited-state potential energy surfaces.



Potential Energy Surface (PES): the key concept

Photochemical and photophysical behavior is encoded in the excited-state potential energy surfaces.

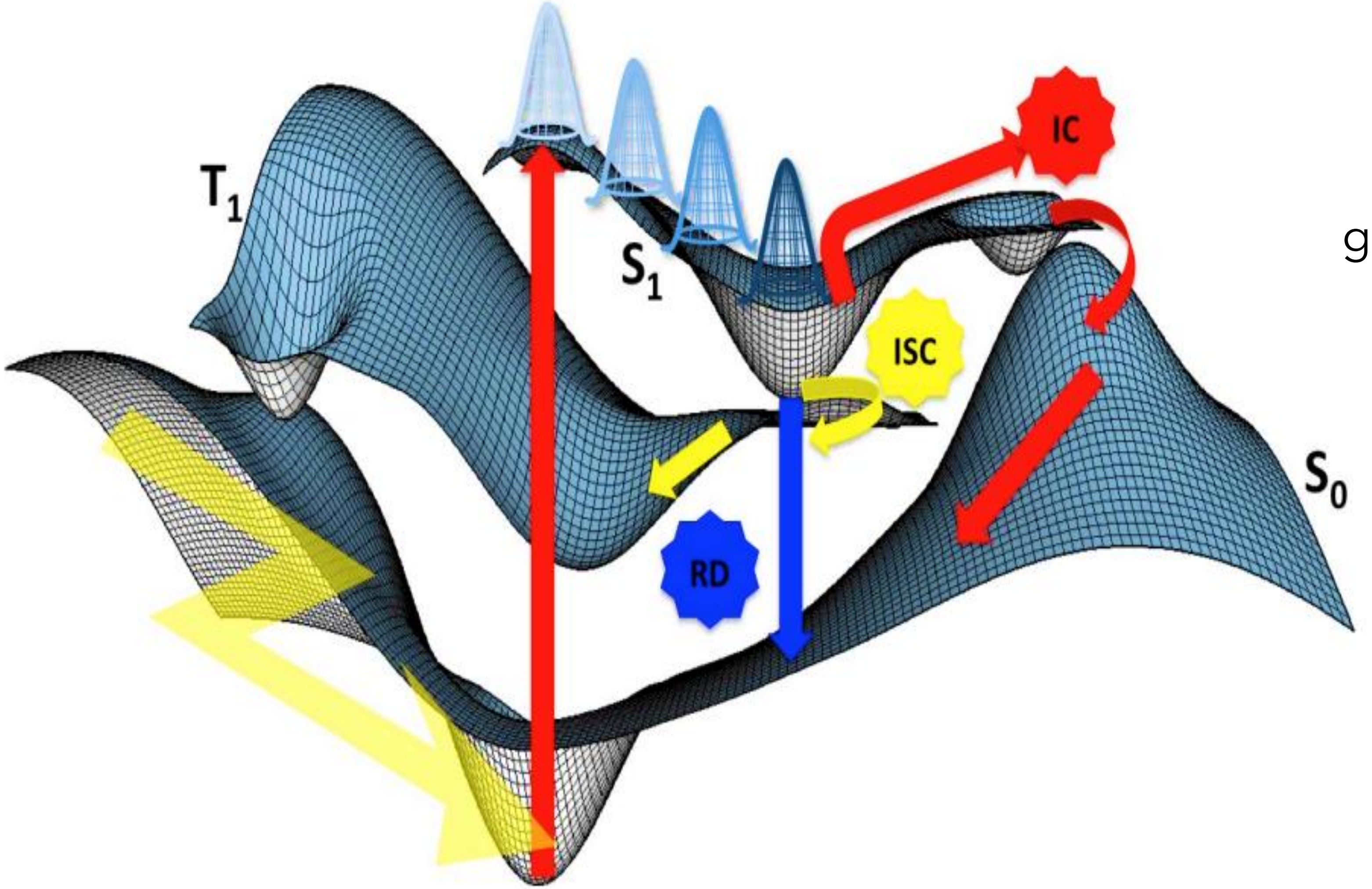


Outline

1. PES and the breakdown of Born-Oppenheimer approximation
2. Nonadiabatic couplings and internal conversion
3. Conical Intersections
4. Avoided crossings
5. Intersystem crossing and spin-orbit coupling
6. Summary and take-home messages

Potential Energy Surfaces are multidimensional

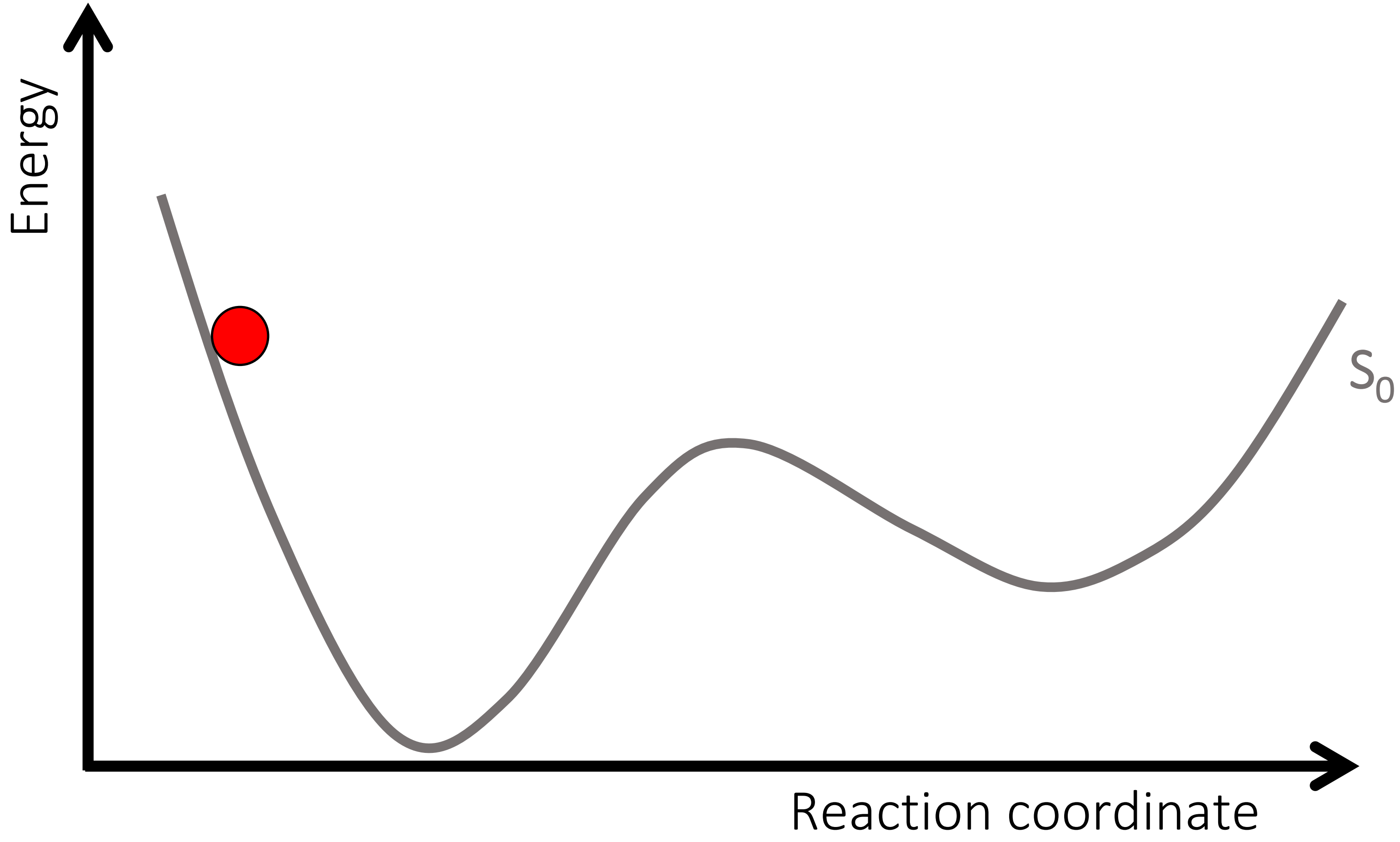
PES are generated by the solution of the electronic part of the Schrödinger Equation for every fixed position of the nuclei.



- One PES for each electronic state
- Energy plotted as a function of geometries : 3N – 6 dimensional surface.
- Born-Oppenheimer approximation: separation of nuclear and electronic degrees of freedom
- Near-degeneracies are common: coupling between the surfaces

Adiabatic *vs* nonadiabatic dynamics

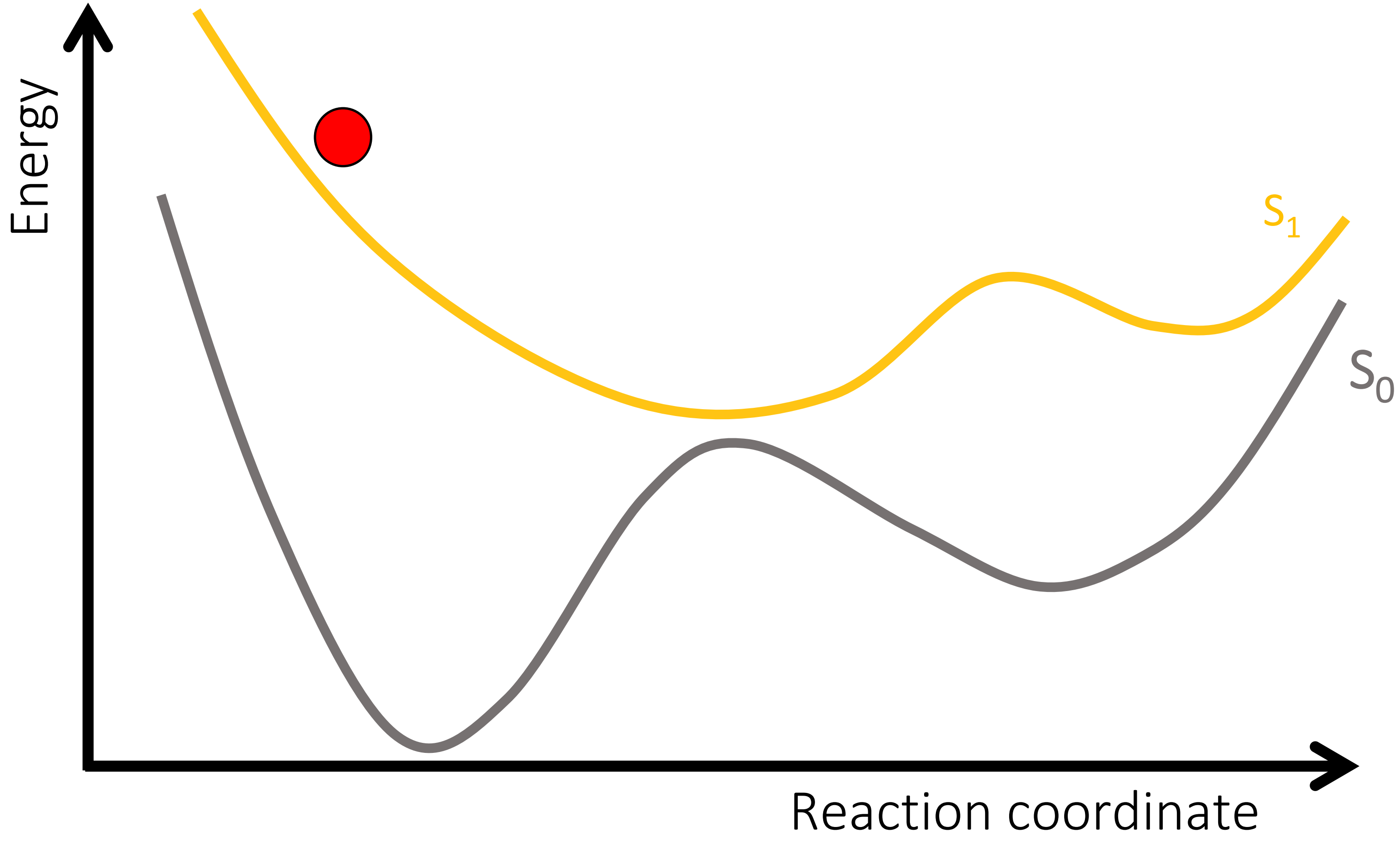
Adiabatic processes: Nuclei evolve in a single PES.
Coupling between electronic states and nuclear motions can be neglected.
Born-Oppenheimer approximation is valid!



Ex: Thermal reactions.

Adiabatic *vs* nonadiabatic dynamics

Nonadiabatic processes: more than one electronic state participates in a process.
Requires considering the coupling between electronic and nuclear motions.
Breakdown of BO approximation.



Photoinduced processes involves the time evolution of the nuclear wavepacket through a manifold of excited states.

The rate for nonadiabatic transitions depends on the energy gap.

Nuclear dynamics beyond BO: Nonadiabatic coupling terms

Assuming that the motion of electrons and nuclei can be separated to solve the SE, and writing the total expanded wavefunction as a product of electronic and nuclear wavefunctions for state I :

$$\Psi^T(\mathbf{r}, \mathbf{R}) = \sum_I \Psi_I(\mathbf{r}; \mathbf{R})\chi_I(\mathbf{R})$$

Electronic

$$H^e \Psi_I^e = E_I^e \Psi_I^e$$

Nuclear

$$\left(T^N + E_I^e\right)\chi_I = E^T \chi_I$$

In practical terms, when more than one electronic state are involved, we truncate this expansion (Born-Huang expansion). The total Schrödinger Equation becomes:

$$[T^n + E_I]\chi_I - \sum_J \sum_\alpha \frac{1}{2M_\alpha}(2f_{IJ}^\alpha \cdot \nabla_\alpha \chi_J + K_{IJ}^\alpha \chi_J) = E^T \chi_I$$

Coupling terms:

$$K_{IJ}(\mathbf{R}) = \sum \langle \Psi_I(\mathbf{r}; \mathbf{R}) | \nabla_\alpha^2 \Psi_J(\mathbf{r}; \mathbf{R}) \rangle$$

BO corrections (K_{II})

$$f_{IJ}^\alpha(\mathbf{R}) = \langle \Psi_I(\mathbf{r}; \mathbf{R}) | \nabla_\alpha \Psi_J(\mathbf{r}; \mathbf{R}) \rangle$$

Derivative couplings or nonadiabatic couplings

Matsika, *Chem. Rev*. **2021**, *121,* 9407−9449

Nonadiabatic coupling (derivative coupling)

$\mathbf{f}_{IJ}$ is a vector with dimensionality N, the dominant term which drives the nonadiabatic transitions.

It measures of the **variation of the character** of the electronic wavefunction with respect to the nuclear coordinates.

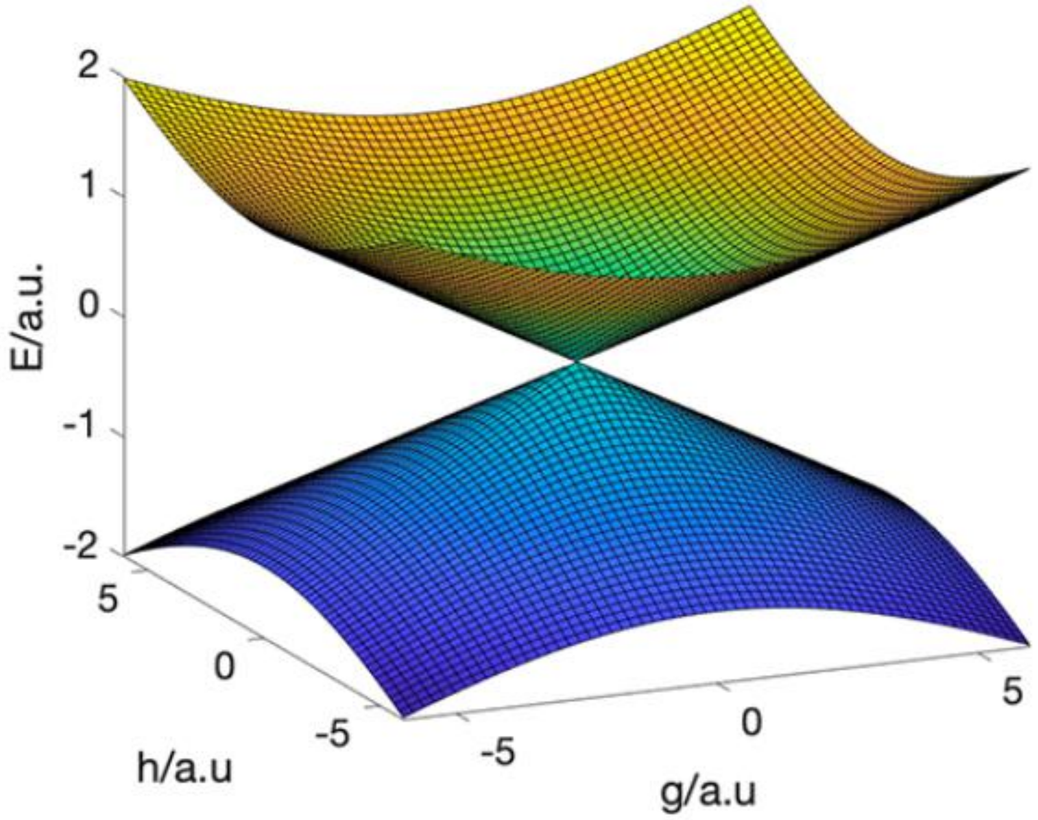
The derivative coupling is inversely proportional to the energy difference of the two electronic states:

$$\mathbf{f}_{IJ}(\mathbf{R}) = \frac{\langle \Psi_I | \nabla H | \Psi_J \rangle}{E_J - E_I}$$

The smaller the difference, the larger the coupling.

The **efficiency of a nonadiabatic** transition between two states depends on the nonadiabatic coupling! Consequently, the internal conversion rate.

Conical Intersections



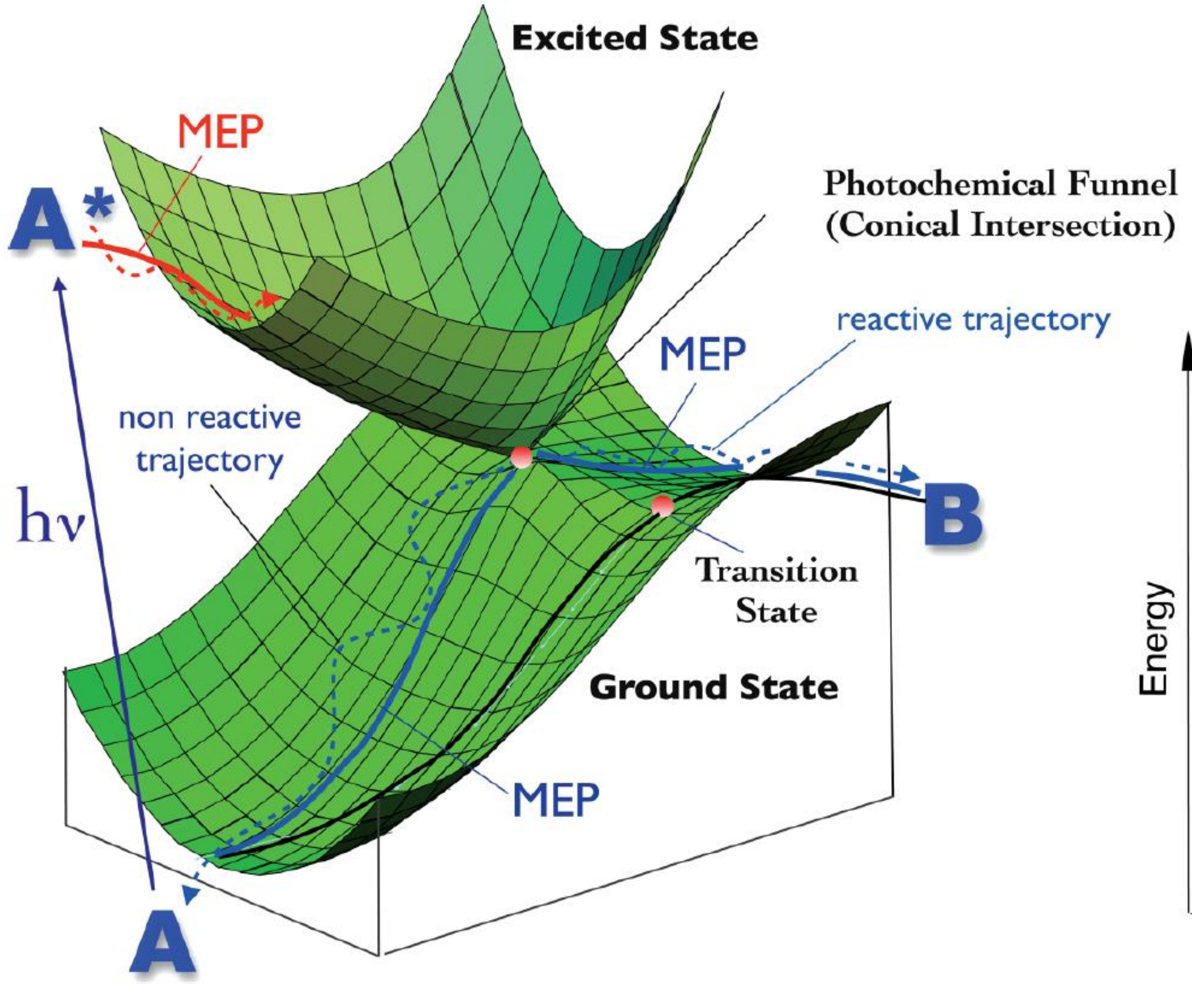
$$\mathbf{f}_{IJ}(\mathbf{R}) = \frac{\langle \Psi_I | \nabla H | \Psi_J \rangle}{E_J - E_I}$$

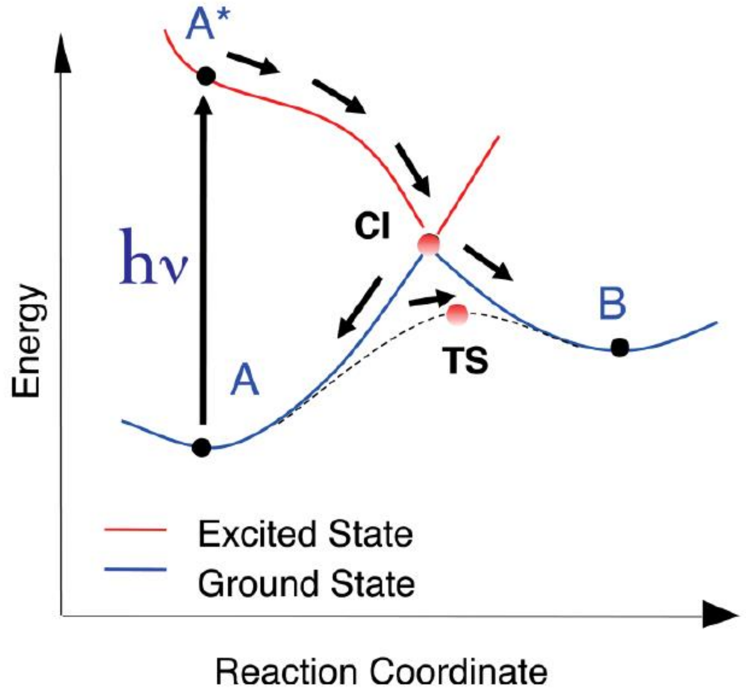
"Point of crossing between two electronic states of the same spin multiplicity (most commonly singlets or triplets)."

1929 by von Neumann and Wigner
1937 Teller

Domcke, Yarkony, Köppel, **2004**. *Conical Intersections: Electronic Structure, Dynamics and Spectroscopy.*

Conical Intersections as Photochemical Funnels





Schapiro, Photochem. Photobiol. Sci., **2011**, 10, 867–886

Dimensionality and conditions for degeneracy

Suppose a two-level molecule whose electronic Hamiltonian is H(R), where R is the internuclear coordinate.

The Hamiltonian for this two-level system

$$\mathbf{H} = \begin{pmatrix} H_{11}(\mathbf{R}) & H_{12}(\mathbf{R}) \\ H_{21}(\mathbf{R}) & H_{22}(\mathbf{R}) \end{pmatrix}$$

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle$$

The eigenvalues for this Hamiltonian are

$$E_{1,2} = \bar{H} \pm \sqrt{\Delta H^2 + H_{12}^2}$$

$$\Delta H = (H_{11} - H_{22})/2$$

$$\bar{H} = (H_{11} + H_{22})/2$$

Dimensionality and conditions for degeneracy

$$E_{1,2} = \bar{H} \pm \sqrt{\Delta H^2 + H_{12}^2}$$

$$\Delta H = (H_{11} - H_{22})/2 \qquad \bar{H} = (H_{11} + H_{22})/2$$

For the eigenvalues of this matrix to be degenerate two conditions must be satisfied:

$$\boxed{E_1 = E_2} \longrightarrow \begin{array}{ll} H_{11}(\mathbf{R}) - H_{22}(\mathbf{R}) = 0 & \text{(i)} \\ H_{12}(\mathbf{R}) = 0 & \text{(ii)} \end{array}$$

These conditions define the **dimensionality** of a conical intersection:

$$\mathrm{N}^{\mathrm{int}} - 2 \qquad \text{or} \qquad 3\mathrm{N} - 8$$

The Non-crossing rule and Avoided crossing

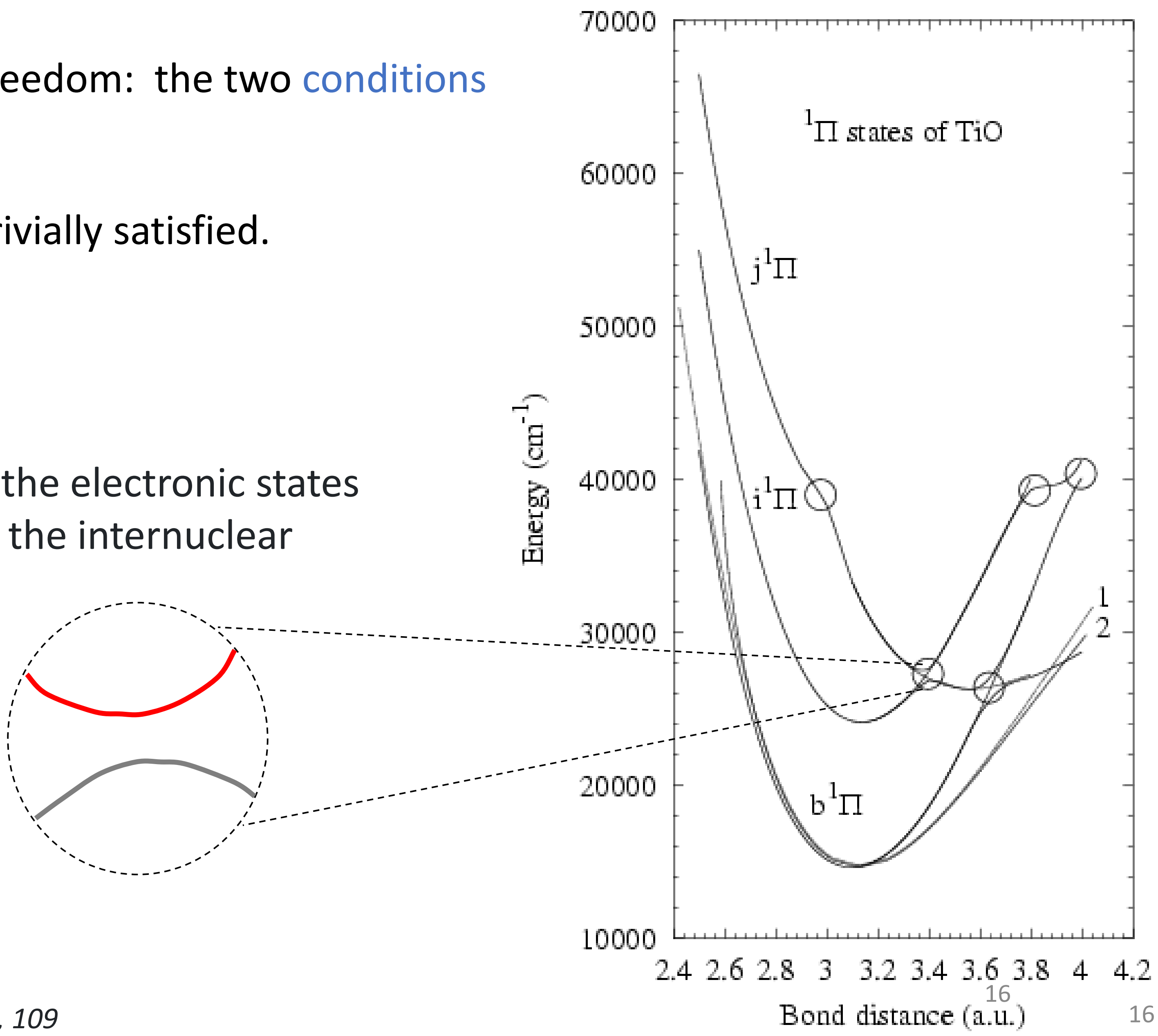
Diatomic molecules have only one degree of freedom: the two conditions can never be simultaneously satisfied.

If the states have different symmetries, (ii) is trivially satisfied.

The non crossing rule:

"For diatomics, the potential energy curves of the electronic states of the same symmetry species cannot cross as the internuclear distance is varied."

Avoided crossing



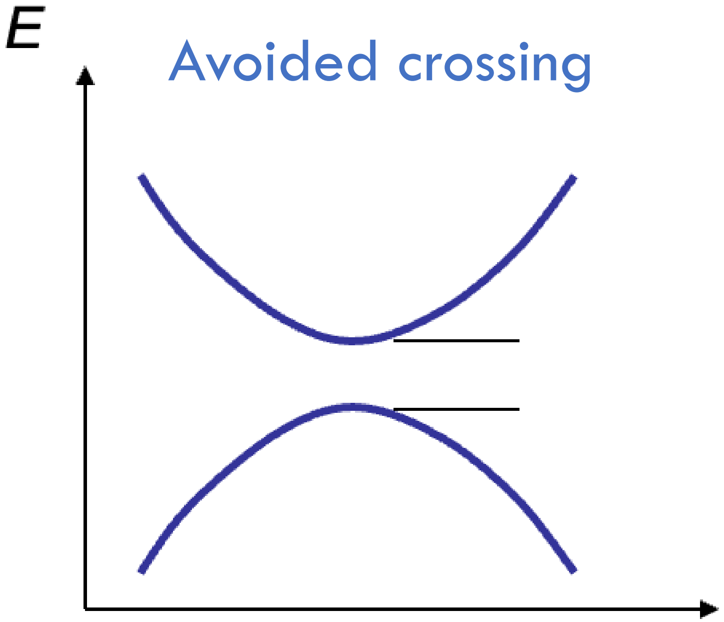
von Neumann and Wigner, *Z. Phyzik 1929,* 30, 467; Teller, *JCP, 1937, 41, 109*

Avoided crossing *vs* conical intersections

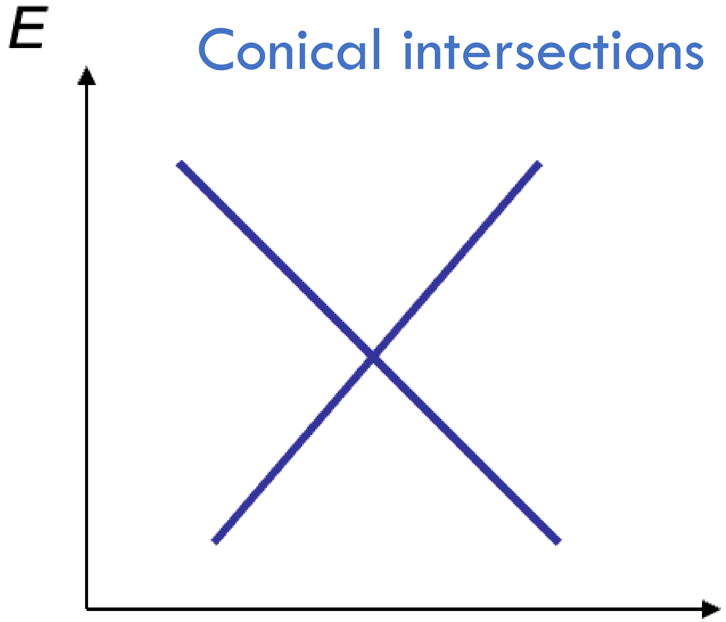
What happen if the molecule has more than one degree of freedom?

✓ $H_{11}(\mathbf{R}) - H_{22}(\mathbf{R}) = 0$

✓ $H_{12}(\mathbf{R}) = 0$



Diatomic molecules do not cross!



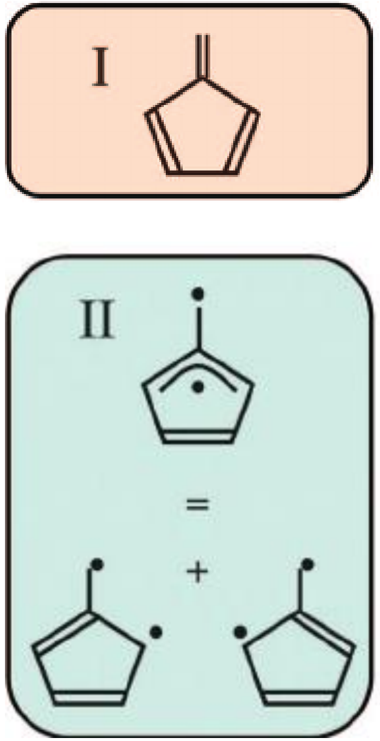
In polyatomics 3N-6 internal coordinates:
seam of intersections

"When one encounters a local minimum (along a path) of the gap between two potential energy surfaces, almost always it is the shoulder of a conical intersection. ***Conical intersections are not rare****; true avoided intersections are much less likely."*

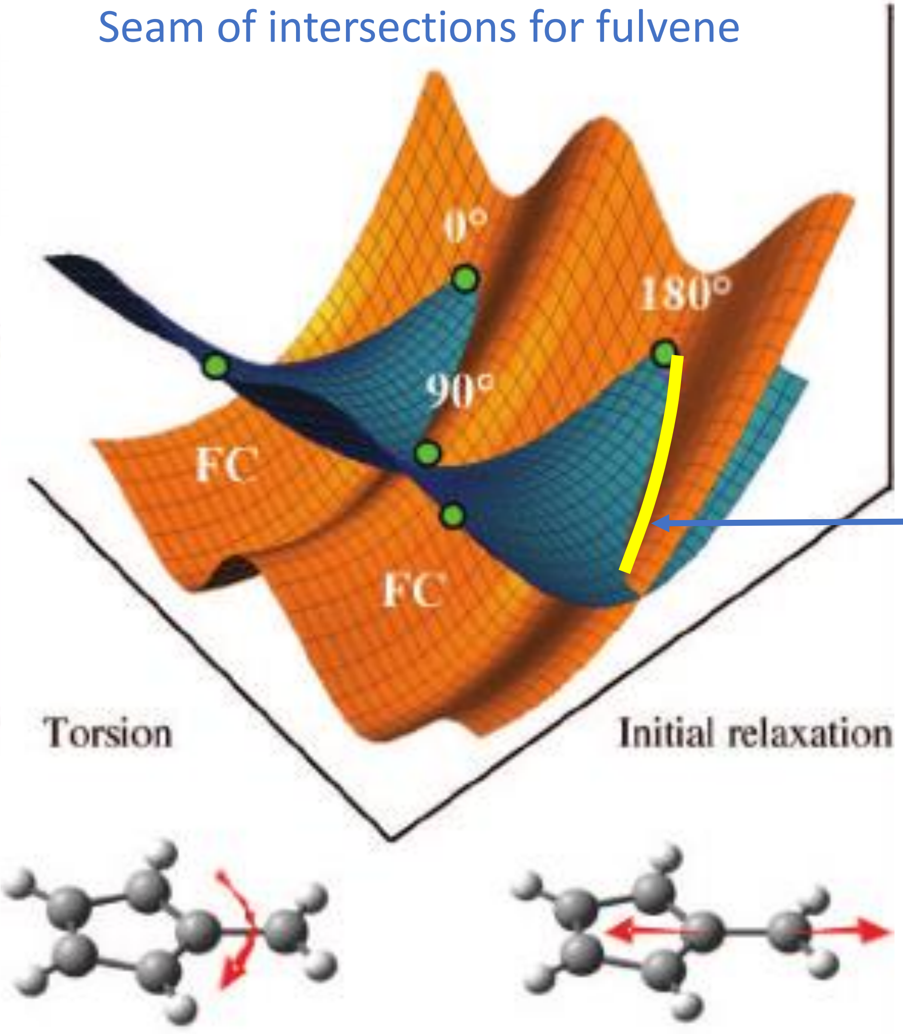
Truhlar, Mead, *Phys. Rev. A* 68, 2003, 032501.

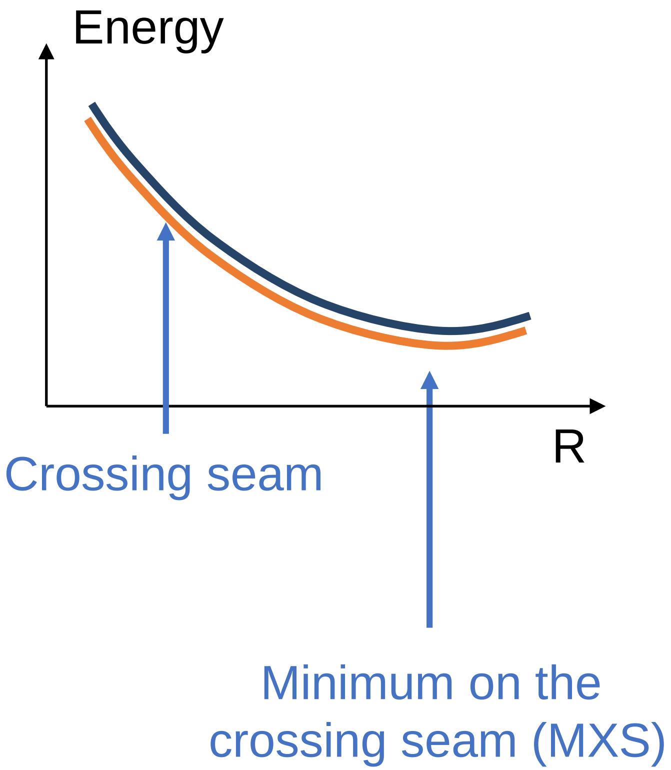
The intersection space or seam

The $N^{int} - 2$ subspace, where the states are degenerated, is called seam or intersection space.



Seam of intersections for fulvene





Crossing seam

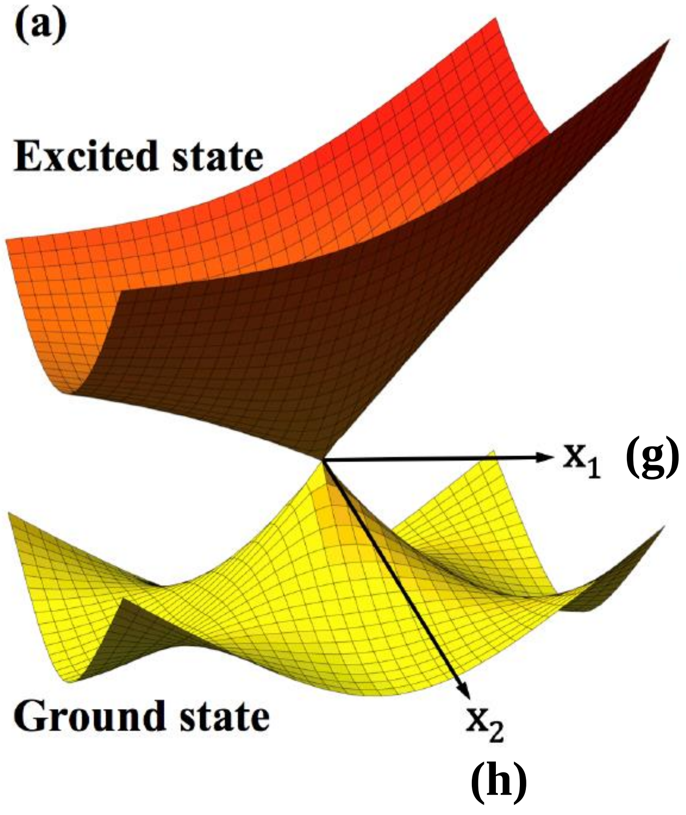
Minimum on the crossing seam (MXS)

Conical intersections are connected!

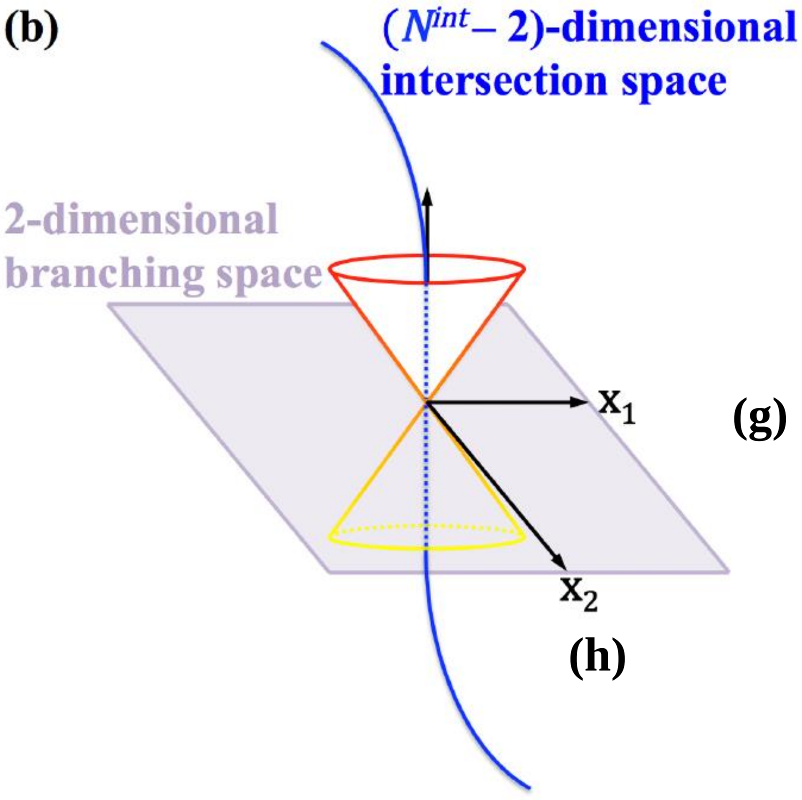
Mendive-Tapia et al, J. Chem. Phys. 2012, 137, 22A548

The branching space

The two-dimensional space orthogonal to the seam is called the branching space or g − h space.



Typical double cone topology for a conical intersection



Relation between the branching space (x_1, x_2) and the intersection space

The two independent coordinates fulfilling the degeneracy requirements are:

$$\mathbf{g} = \mathbf{x_1} = \frac{\partial(E_1 - E_2)}{\partial R}$$

Gradient difference

$$\mathbf{h} = \mathbf{x_2} = \left\langle \psi_1 \middle| \frac{\partial \hat{H}^{el}}{\partial R} \middle| \psi_2 \right\rangle$$

Coupling vector

Boggio-Pasqua. Computational mechanistic photochemistry: The central role of conical intersections. Universite Toulouse III, 2015.

The branching space

The energies of the double cone is set to zero are given by:

$$E_{1,2}(x,y) = s_1 x + s_2 y \pm \sqrt{(gx)^2 + (hy)^2}$$

- x, y : displacements along the **g** and **h** directions
- s_1, s_2: projections of $(g_I + g_J)/2$ onto the branching plane

- g, h : gives the slope of the conical intersection
- s_1, s_2: gives the tilt of the conical intersection

The topography of the PES in the vicinity of the CIs plays a significant role to promote a nonadiabatic transition.

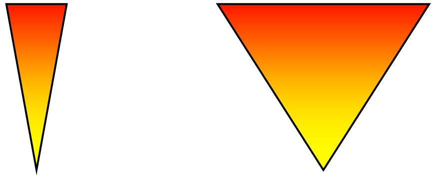
Characteristics of the branching space

It can be rewritten as a general cone equation:

$$E_{1,2} \approx d_{gh}\left[\sigma_x x + \sigma_y y \pm \left(\frac{1}{2}\left(x^2 + y^2\right) + \frac{\Delta_{gh}}{2}\left(x^2 - y^2\right)\right)^{1/2}\right]$$

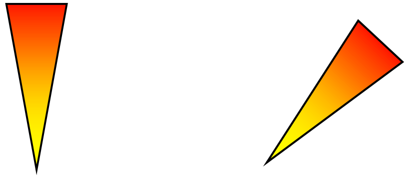
$$d_{gh} = \left(|\mathbf{g}|^2 + |\mathbf{h}|^2\right)^{1/2}$$

pitch parameter



$$\left.\begin{aligned}\sigma_x &= \frac{\mathbf{s}}{d_{gh}} \cdot \frac{\mathbf{g}}{|\mathbf{g}|} \\ \sigma_y &= \frac{\mathbf{s}}{d_{gh}} \cdot \frac{\mathbf{h}}{|\mathbf{h}|}\end{aligned}\right\}$$

tilt parameters
(degree of slope)



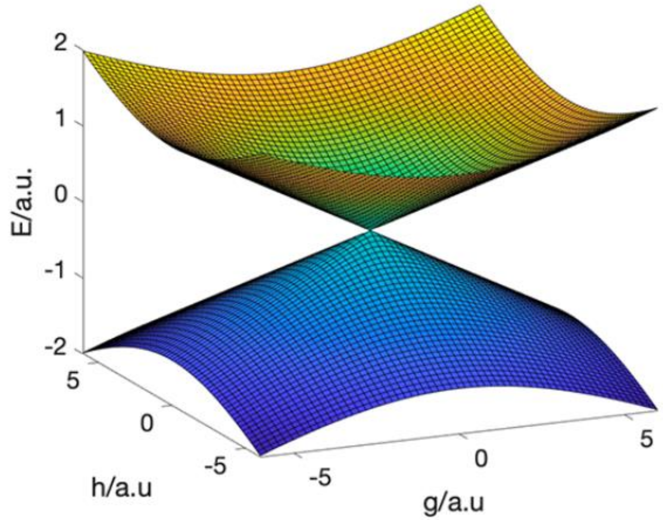
$$\Delta_{gh} = \frac{\left(|\mathbf{g}|^2 - |\mathbf{h}|^2\right)}{d_{gh}^2}$$

asymmetry parameter

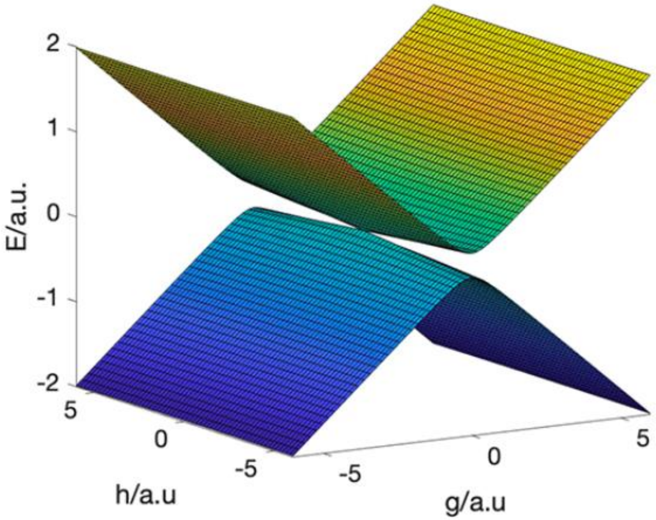
Yarkony, JCP, 2001, 114, 2601

Topography of conical Intersections

Vertical symmetric



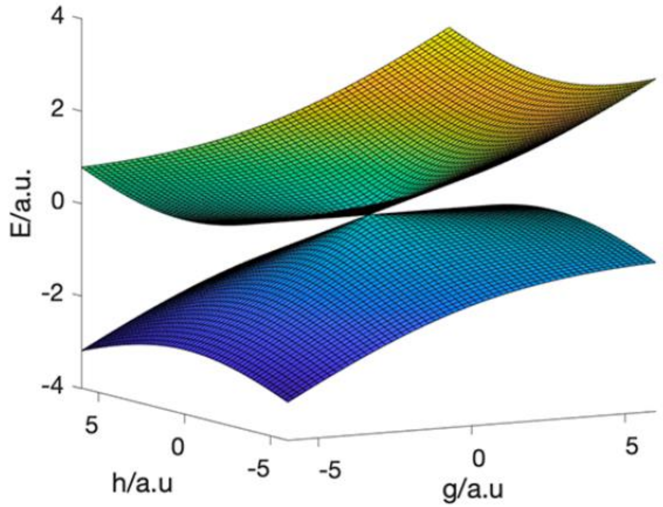
(a)



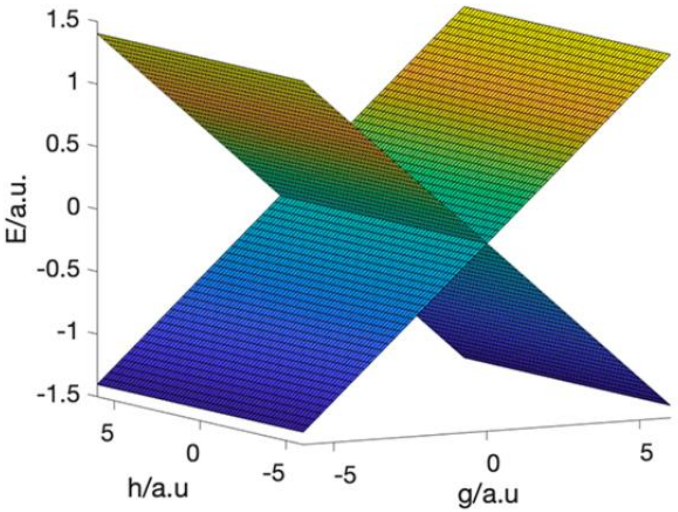
(b)

Vertical asymmetric

Tilted cone



(c)

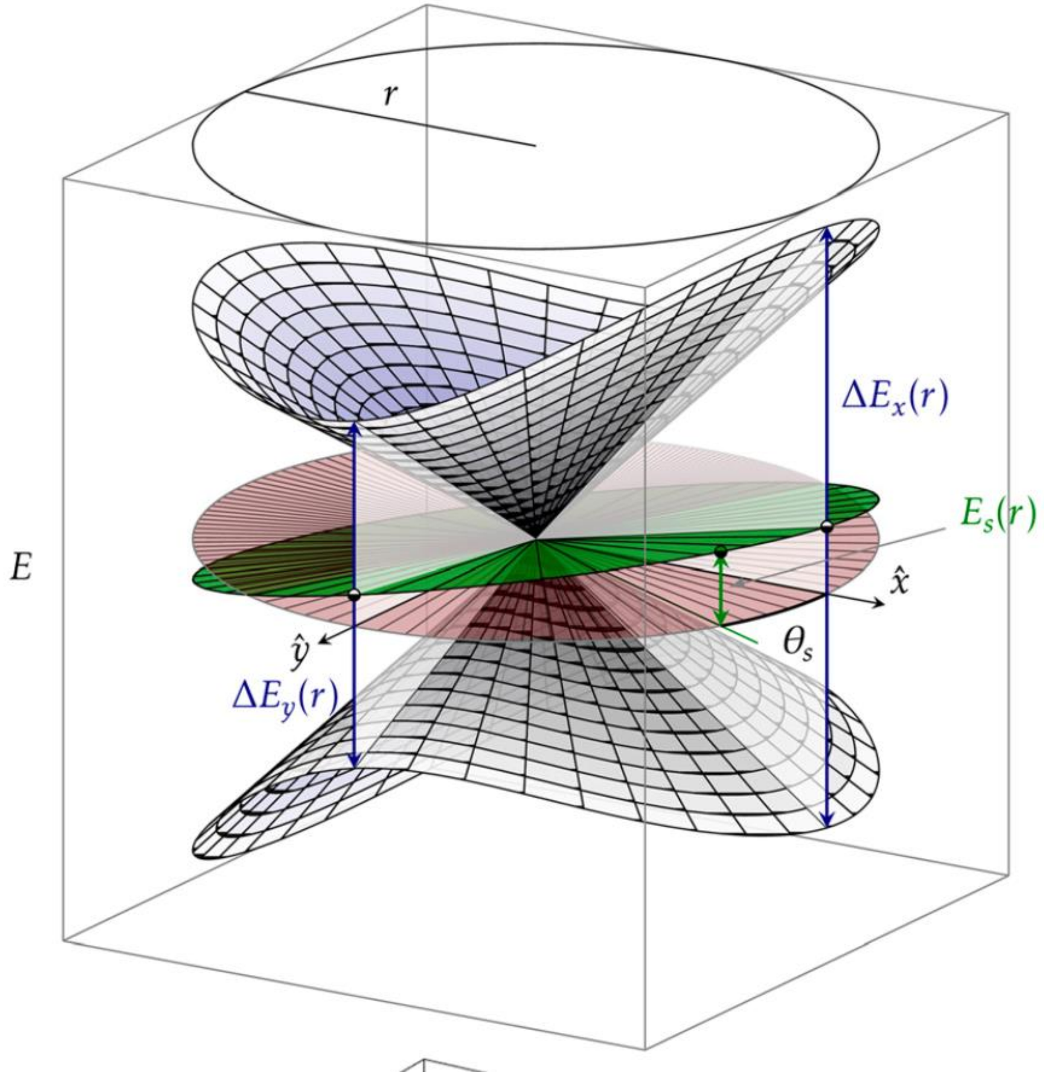


(d)

One branching
coordinate
and one seam

Matsika, *Chem. Rev*. **2021**, *121,* 9407–9449

Topographys of CIs in polar coordinates : *P* and *B* parameters



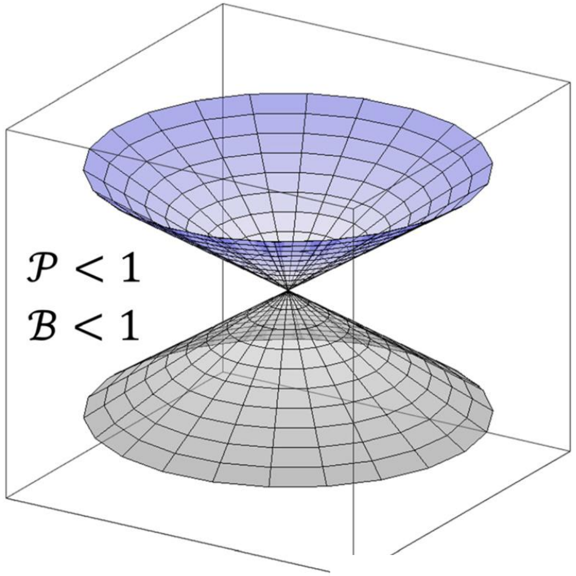
$$\mathcal{P} = \frac{\sigma^2}{1-\mathit{\Delta}^2}\left(1-\mathit{\Delta}\cdot\cos(2\theta_\mathrm{s})\right)\begin{cases} < 1 \text{ peaked} \\ > 1 \text{ sloped} \end{cases}$$

$$\mathcal{B} = \sqrt[3]{\frac{\sigma^2}{4\mathit{\Delta}^2}}\left(\sqrt[3]{(1+\mathit{\Delta})\cos^2(\theta_\mathrm{s})} + \sqrt[3]{(1-\mathit{\Delta})\sin^2(\theta_\mathrm{s})}\right)\begin{cases} < 1 & \text{bifurcating} \\ > 1 & \text{single-path} \end{cases}$$

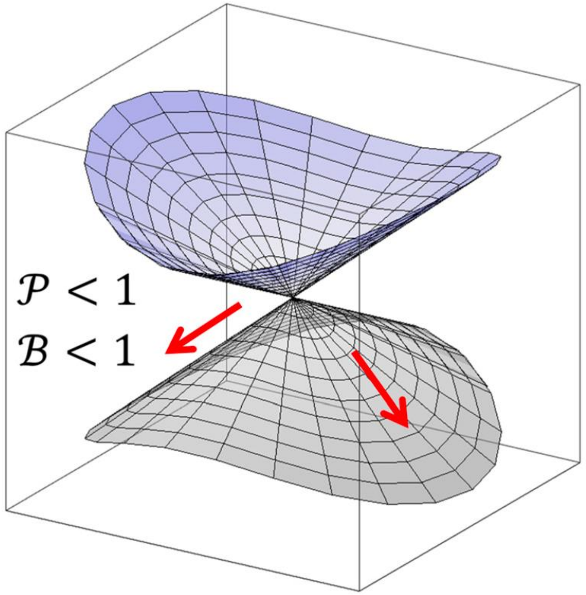
Fdez Galvan et al, J. Chem. Theory Comput. 2016, 12, 3636−3653

Topographys of CIs in polar coordinates : *P* and *B* parameters

b



c



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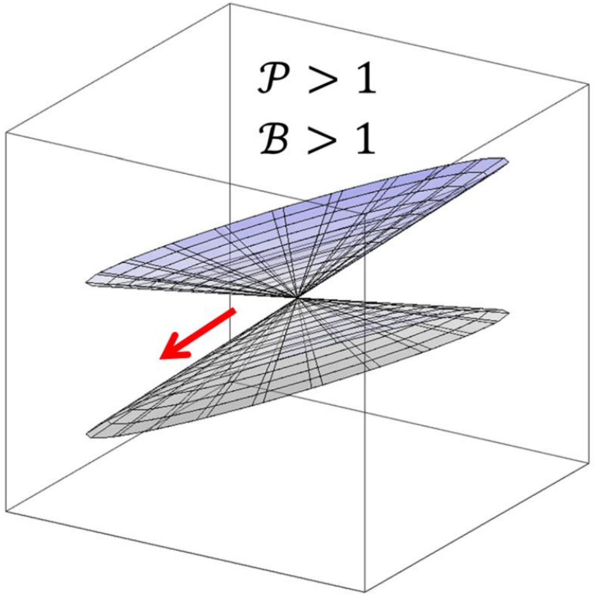

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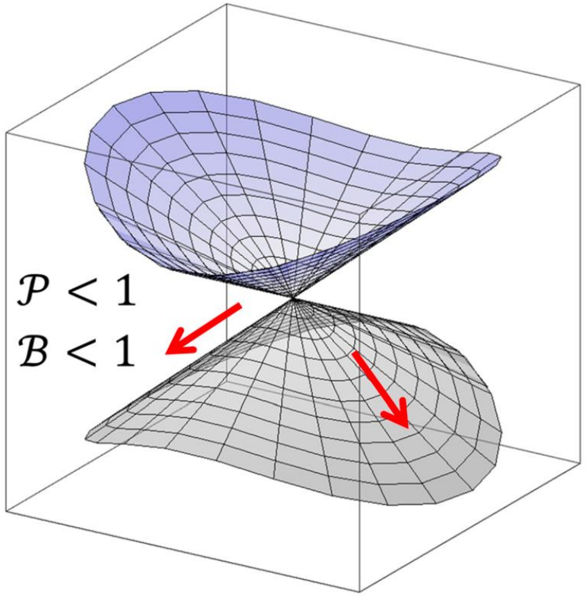

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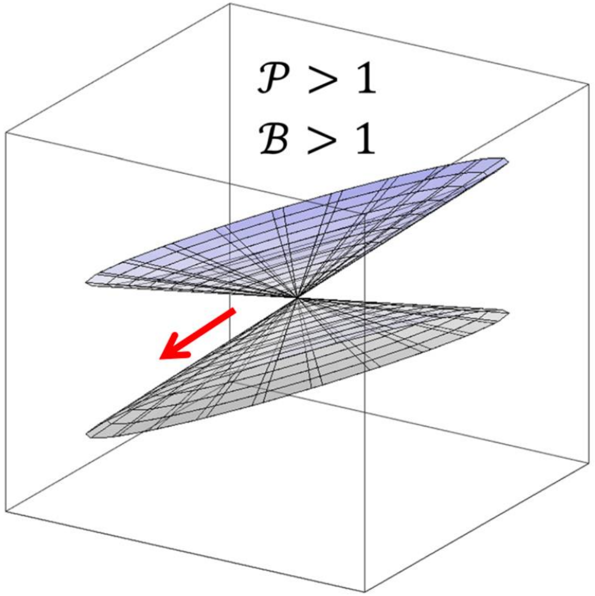
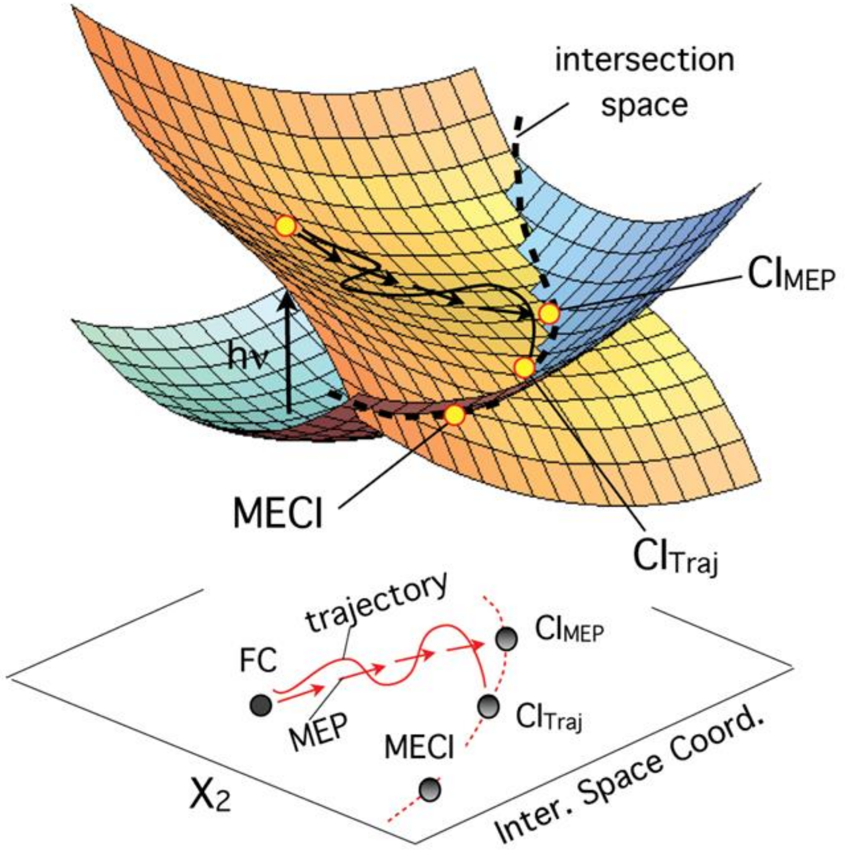


Fdez Galvan et al, J. Chem. Theory Comput. 2016, 12, 3636−3653

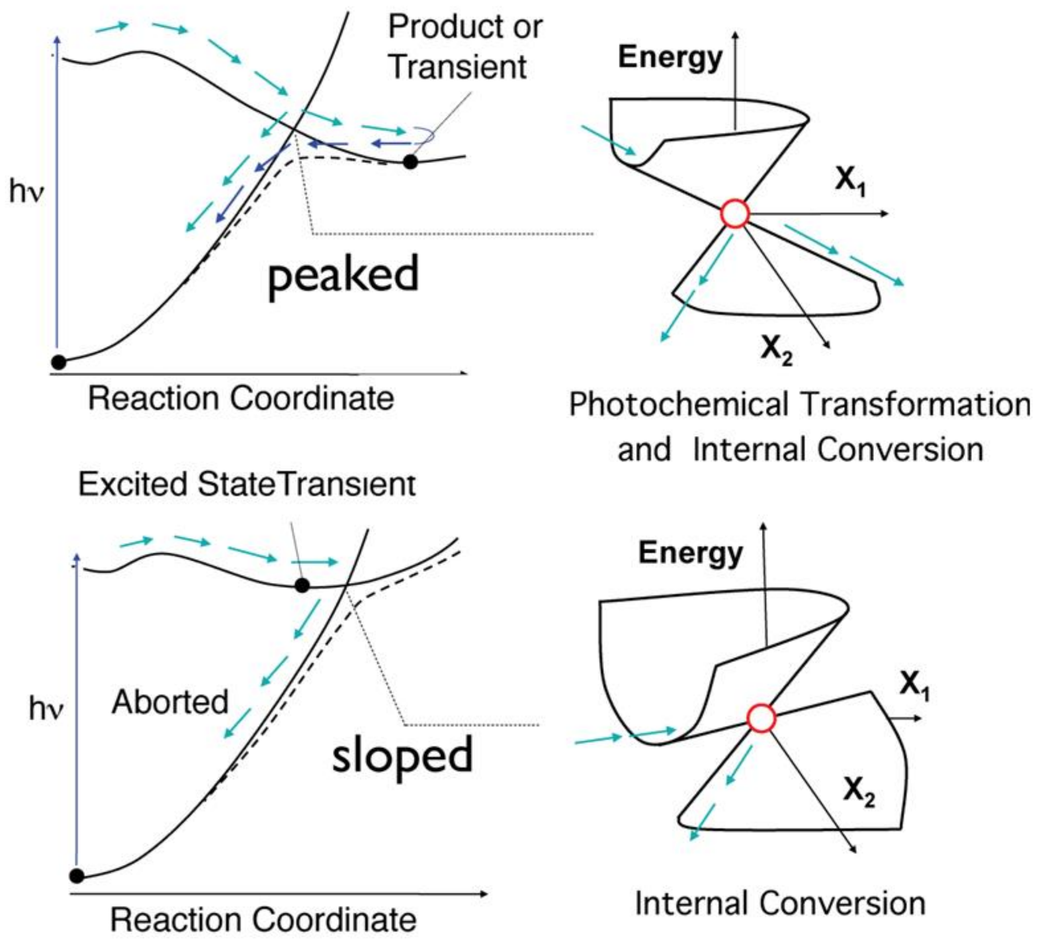
Implications of topography of CIs on photochemistry



CI_{MEP} = intercepted by the MEP

MECI = minimum energy CI

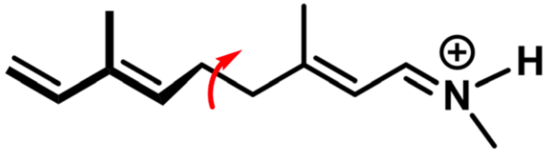
CI_{Traj} = intercepted by a classical trajectory



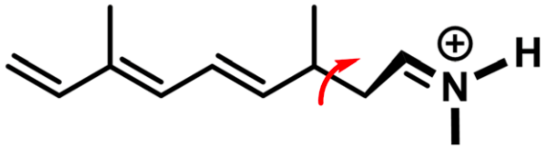
Schapiro, Photochem. Photobiol. Sci., 2011, 10, 867

Topography of CIs determines selectivity

The topography around the CIs determines the selectivity of retinal protonated Shiff Base.

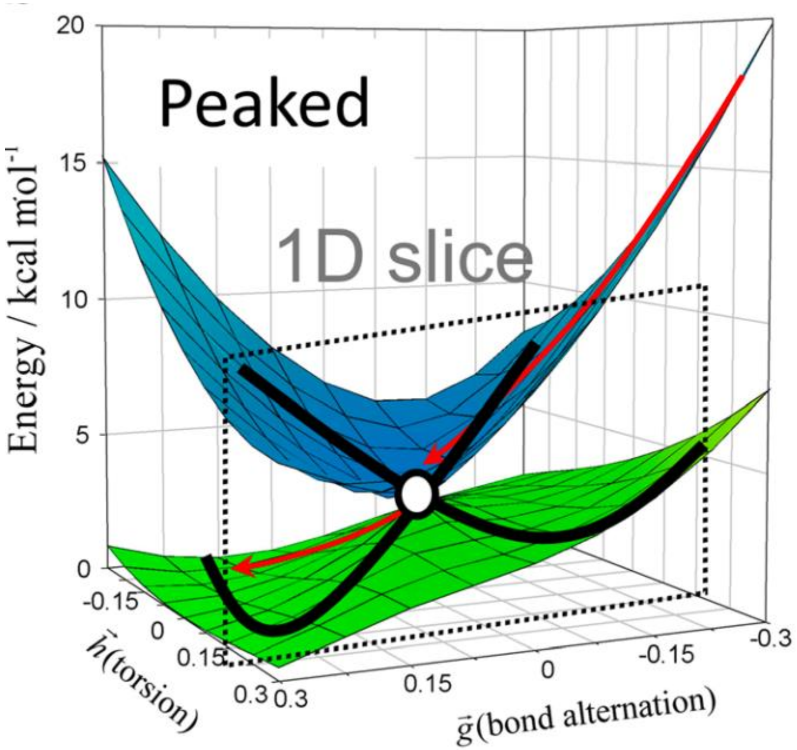


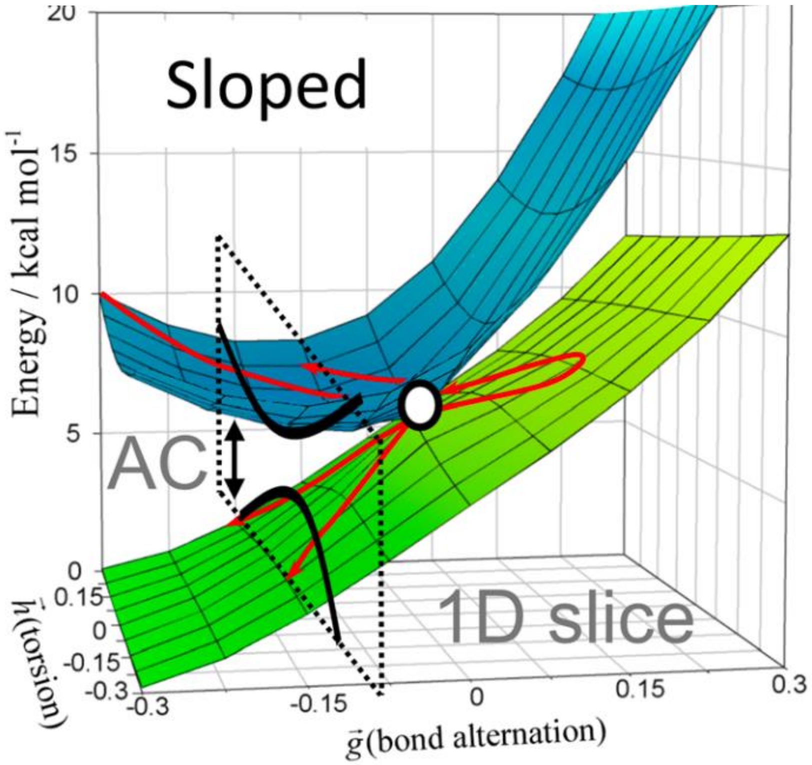
C_{11}=C_{12} twist
Peaked CoIn



C_{13}=C_{14} twist
Sloped CoIn

Only *cis* product





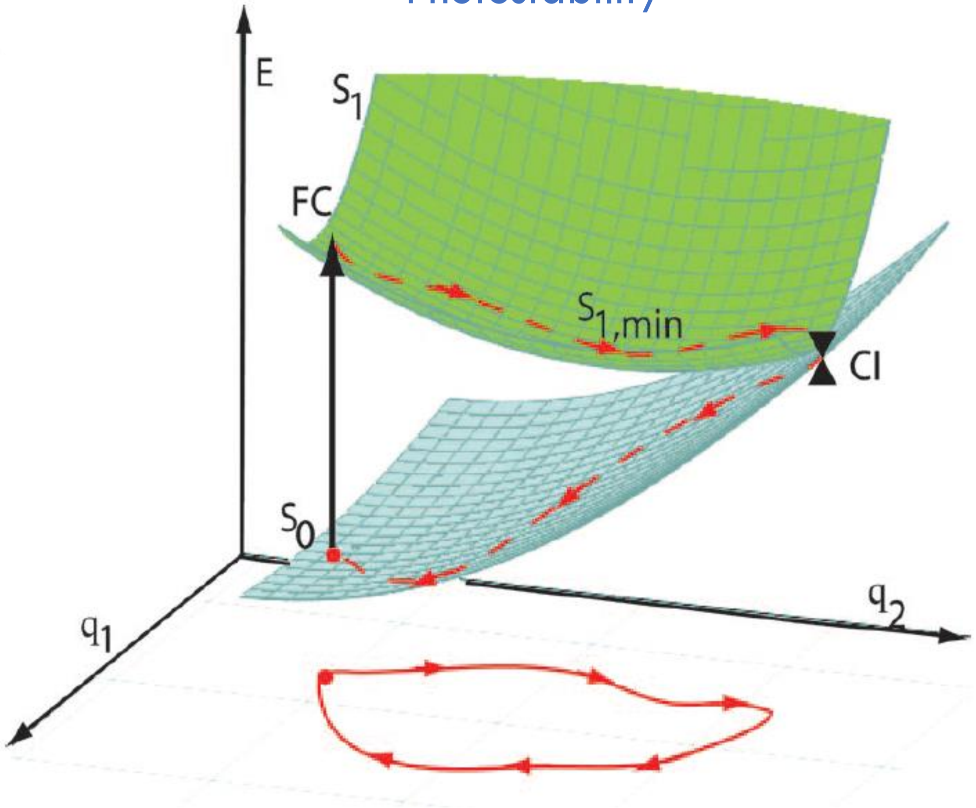
Statistical distribution of products

Ben-Nun, Martínez et al T. J. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 1769.

Photostability of nucleobases

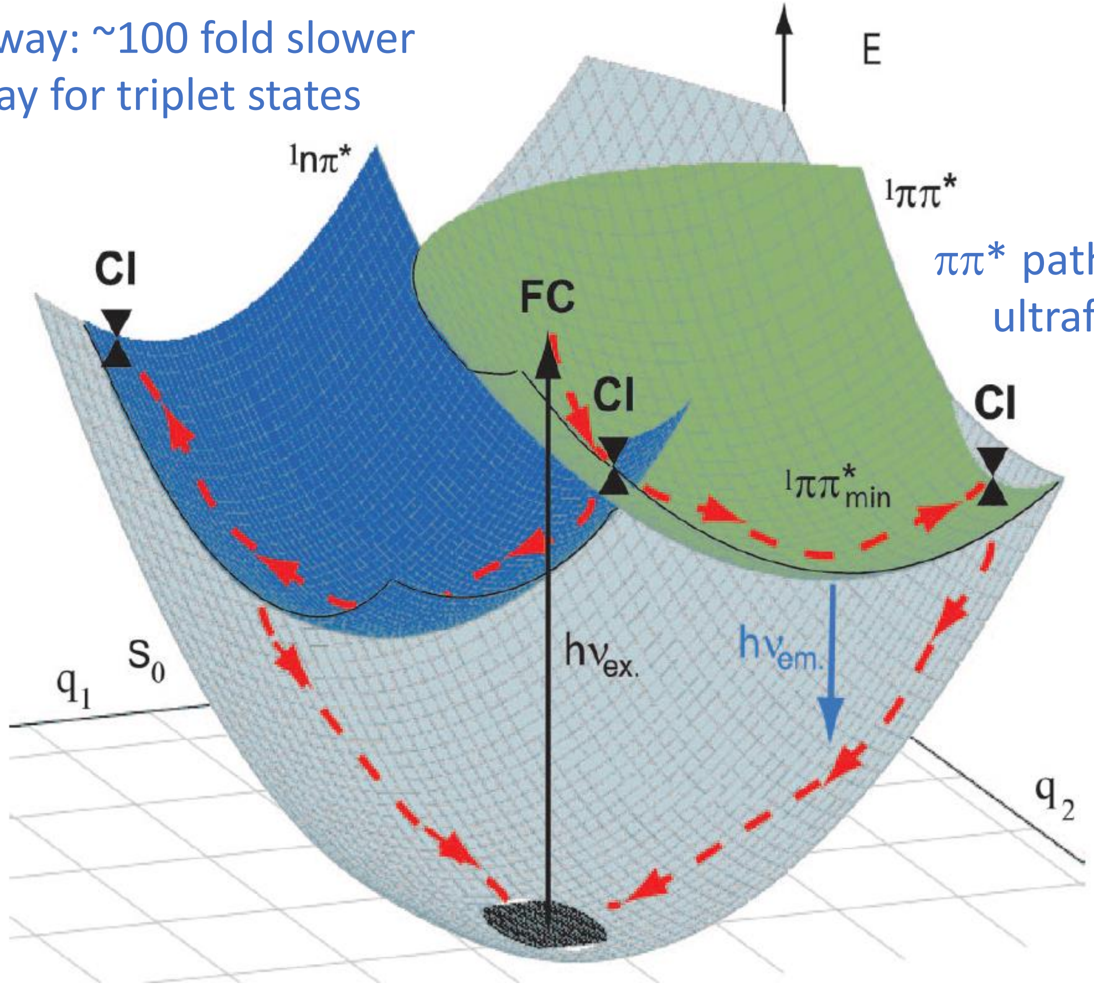
Internal conversion to the electronic ground state occurs via two distinct pathways for pyrimidine bases in aqueous solution.

Photostability



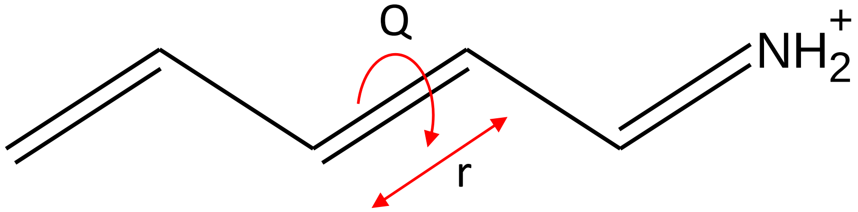
nπ* pathway: ~100 fold slower
Gateway for triplet states

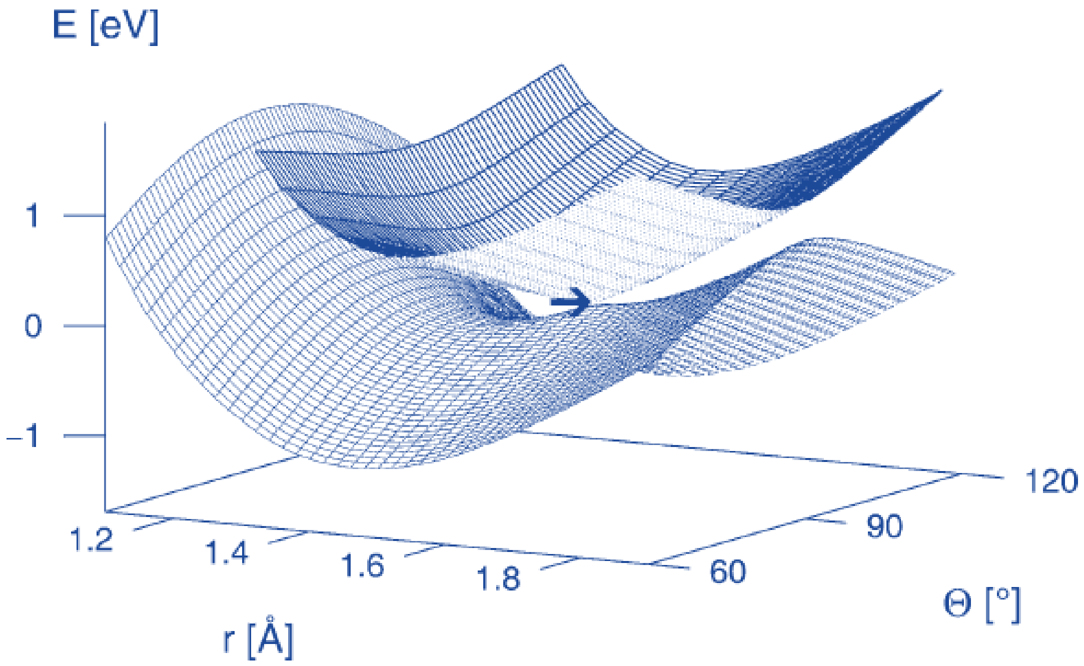
ππ* pathway:
ultrafast



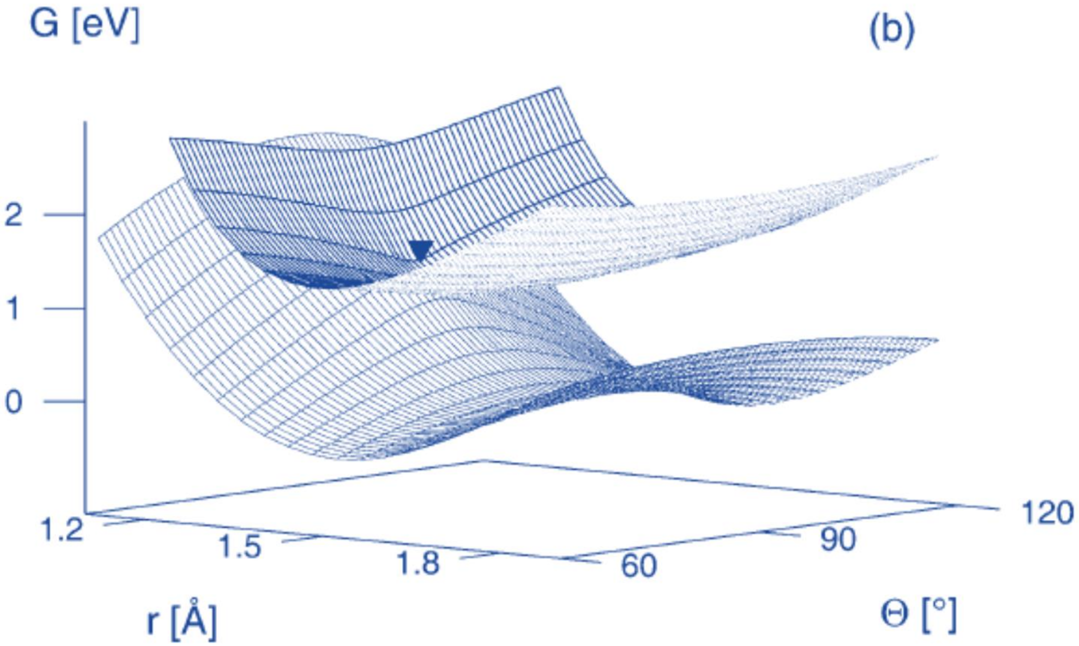
Hare, Crespo-Hernandez, Kohler, B. *PNAS,* 2007, **104**, 435–440

Solvent can changes the PES



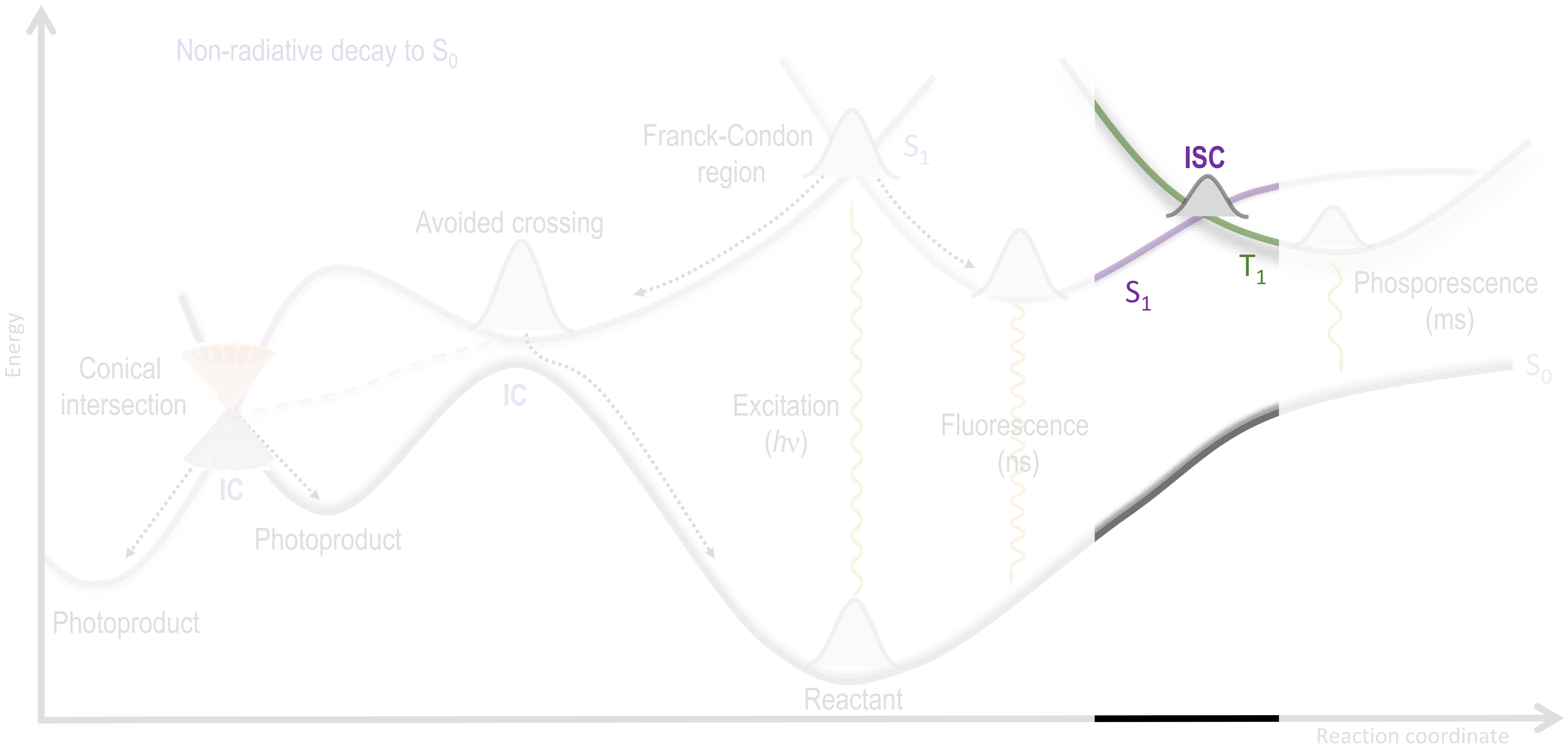


In gas phase



In water

Burghardt, Cederbaum, and Hynes, Faraday. Discuss. 127, 395 (2004)


Energy
Non-radiative decay to S_0
Franck-Condon region
S_1
ISC
S_1
T_1
Avoided crossing
Conical intersection
IC
IC
Photoproduct
Photoproduct
Excitation ($h\nu$)
Fluorescence (ns)
Phosporescence (ms)
S_0
Reactant
Reaction coordinate

Selection rules for ISC and the importance of SOC

ISC is a radiationless transition between two electronic states of different spin multiplicity.

1. Spin selection rule

- Pure spin transitions are formally forbidden.
- ISC becomes allowed due to **spin–orbit coupling**, which mixes singlet and triplet wavefunctions.
- The stronger the SOC, the higher the ISC rate.

2. El-Sayed rules

- ISC is most efficient when the transition involves a change in orbital type: SOC operator couples spin and orbital angular momentum; changes in orbital character enhance this coupling.

4. Heavy-atom effect

- Presence of heavy atoms strongly increases SOC.
- Leads to much faster ISC, sometimes overriding El-Sayed preferences.

Selection rules for ISC

5. Vibronic coupling

- Nuclear motion can mix electronic states.
- Vibrational modes that break symmetry can relax selection rules and enhance ISC.

6. Energy gap rule

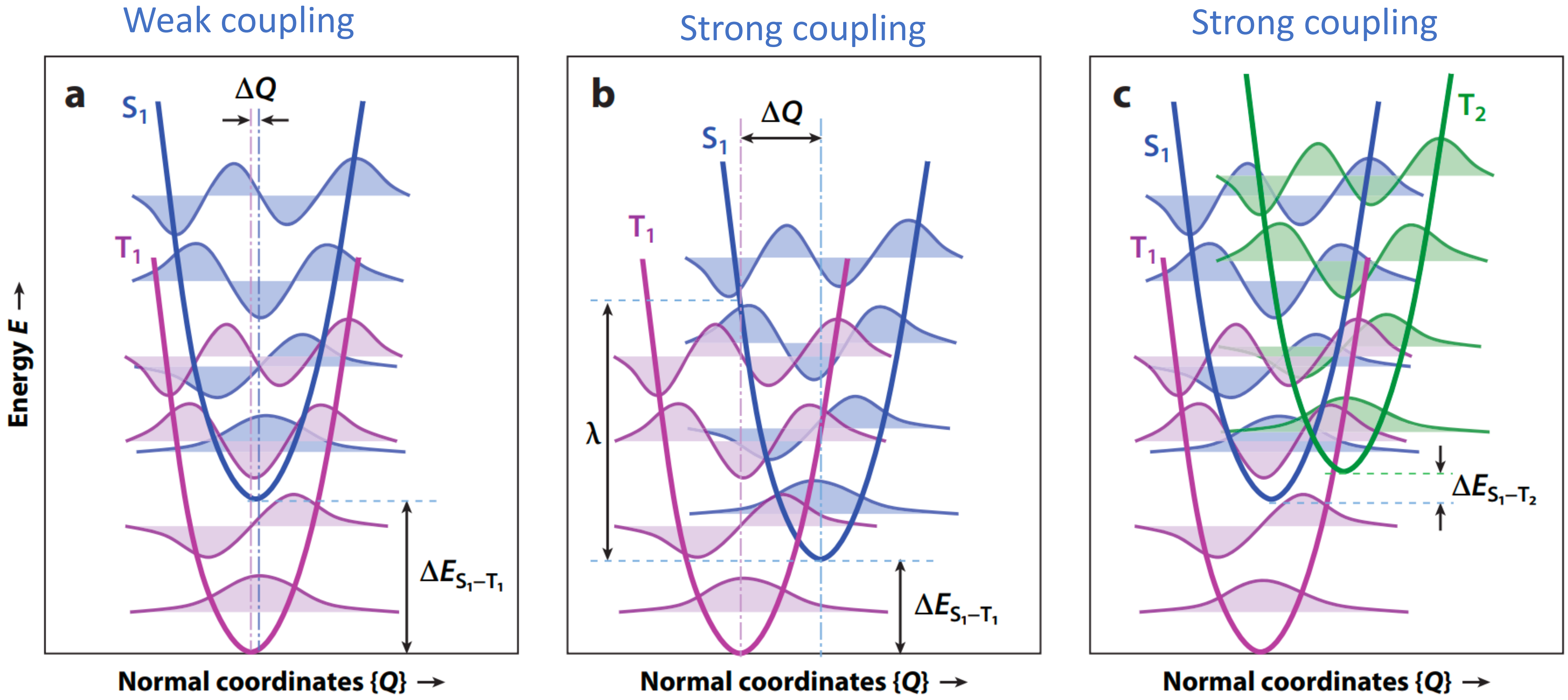
- Englman & Jortner : strong and week coupling
- SC rate increases as the energy gap between singlet and triplet states decreases.
- Near-degenerate states exhibit especially fast ISC.

7. Symmetry considerations

- ISC is more efficient when the two states belong to compatible molecular symmetries.
- Symmetry breaking (vibrations, solvent effects) can activate otherwise forbidden ISC pathways.

Intersystem crossing (ISC)

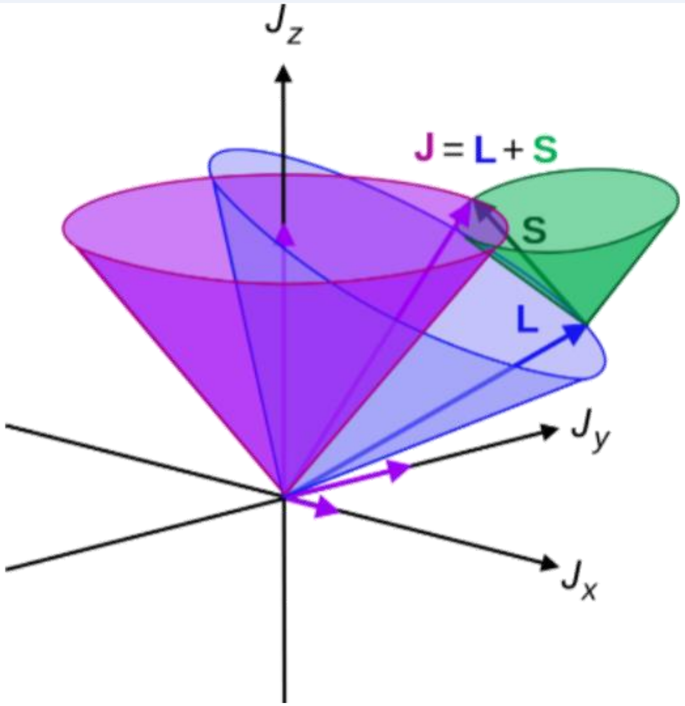
ISC is spin multiplicity mediated by the spin orbit coupling (SOC).



Marian, Annu. Rev. Phys. Chem. 2021. 72:617–40

Marian, C. M. *WIREs Comput. Mol. Sci.* **2012**, *2* (2), 187–203.

Spin-orbit coupling



- SOC describes the interaction between an electron's intrinsic spin magnetic moment and the magnetic field generated by its orbital motion around a nucleus

- SOC has relativistic root

- It provides the necessary coupling between singlet and triplet states, enabling the system to cross between PES of different spin.

- Several variants of spin-orbit coupling operators: based on effective potential and mean-field approaches:
  - Breit–Pauli Spin–Orbit Hamiltonian
  - Douglas–Kroll Transformed Spin–Orbit Coupling Operators
  - Mean-Field Spin–Orbit Coupling Operators (SOMF)
  - Atomic Mean-Field Integrals (AIMF) Approach
  - Spin–Orbit Coupling Operators with Effective Nuclear Charge

Marian, C. M. *WIREs Comput. Mol. Sci.* **2012**, *2* (2), 187–203.

Summary and take-home messages

- Couplings between PES are central to describe photochemistry and nonadiabatic events
- Surface topography (barrier separating FC and CI) controls competition between radiative and non-radiative processes
- Noncrossing rule: diatomics.
  Polyatomics: conical intersections and crossing seams
- Conical intersections topography has a key role in molecular dynamics
- CI topography (peaked vs. sloped) controls photophysical vs. photochemical outcome
- SOC controls ISC. Several different operators for SOC

Acknowledgements

Thank you for your attention!

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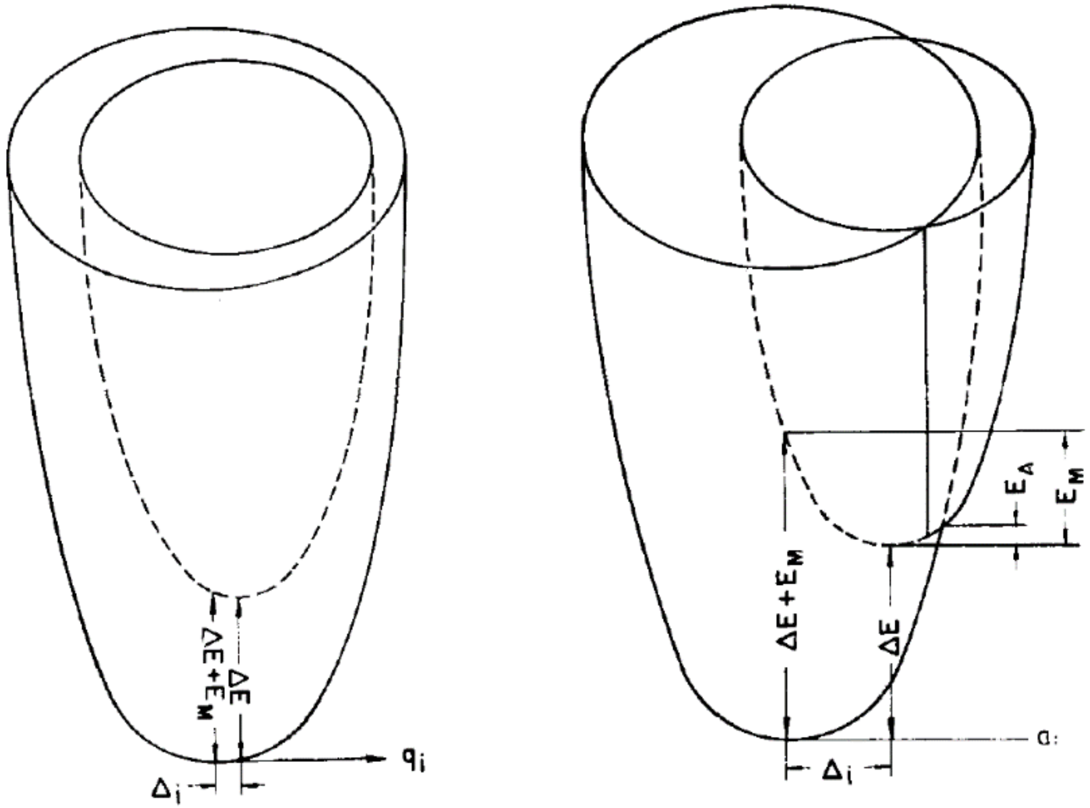
Université Claude Bernard Lyon 1

Energy gap rule

Weak coupling

Strong coupling



(a)

(b)

$$E_M = \frac{1}{2}\sum_j \hbar\omega_j \Delta_j^2,$$

$$E_M \gg \hbar\langle\omega\rangle \tanh\left(\frac{\hbar\langle\omega\rangle}{2k_BT}\right)$$

For estimating nonradiative decay rates between electronic states in internal conversion and intersystem crossing processes

Weak coupling regime: the transition is through vibrational coupling, without involving an intersection.

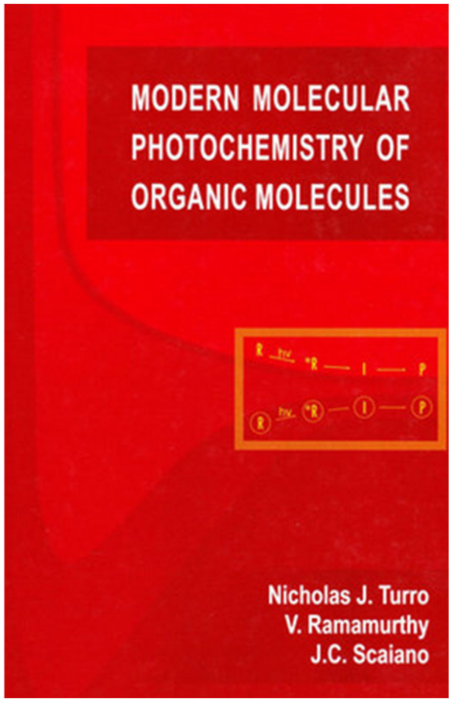
This regime happens when S_0 and S_1 minima are close.

Strong coupling regime: coupling between surfaces

Englman, R.; Jortner, J. The Energy Gap Law for Radiationless Transitions in Large Molecules. *Mol. Phys.* **1970,** *18*, 145-164.

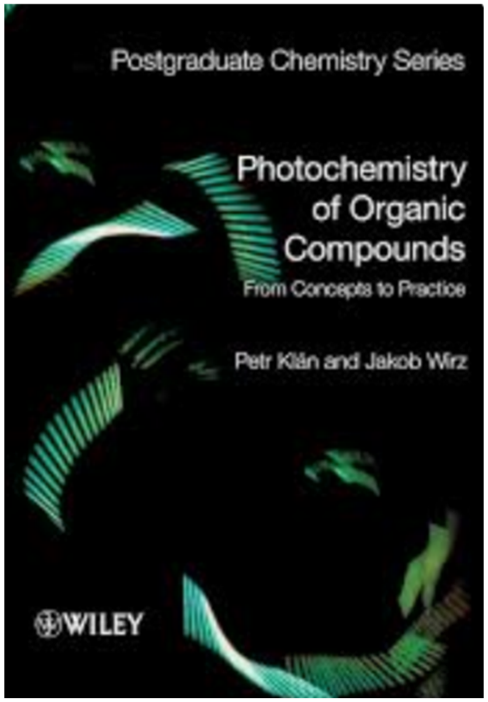
(Brief Comments on)

Organic Photochemistry



MODERN MOLECULAR PHOTOCHEMISTRY OF ORGANIC MOLECULES

Nicholas J. Turro
V. Ramamurthy
J.C. Scaiano



Postgraduate Chemistry Series

Photochemistry of Organic Compounds
From Concepts to Practice

Petr Klán and Jakob Wirz

WILEY

Igor Alabugin,
Florida State University

January 8, 2026

Why Photochemistry Matters

Light opens reaction pathways that are inaccessible thermally.

- What does light *do* to molecules?
    - Excitation instead of heating – precise delivery of energy into a molecule!
    - Access to **excited electronic states** with exceptional properties

- Why photochemistry is unique:
    - Reactions proceed **against ground state intuition**
    - Allows bond formations and cleavages otherwise forbidden

Take-home message:
Photochemistry is not “hot chemistry with light”.
It is chemistry on a different potential energy surfaces!

What is an “excited state” of a molecule?

$$A \xrightarrow{h\nu} A^*$$

Do we have the same number of electrons?
Do we have the same number of atoms?
Are they connected in the same way?

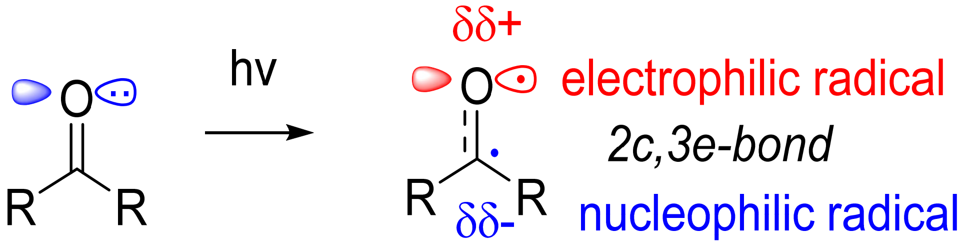
Excited states are “electronic isomers” (“electronomers”) of ground states

Excited states are electronomers

“Electronomers" are isomers that have the same chemical formula but differ in the way their electrons are distributed among the atoms and chemical bonds.

Different faces of familiar functionalities: changes in polarization, delocalization and chemical properties!

Examples: Umpolung with light in ketones



n/π* excited state

Aromatic compounds changing to antiaromatic species

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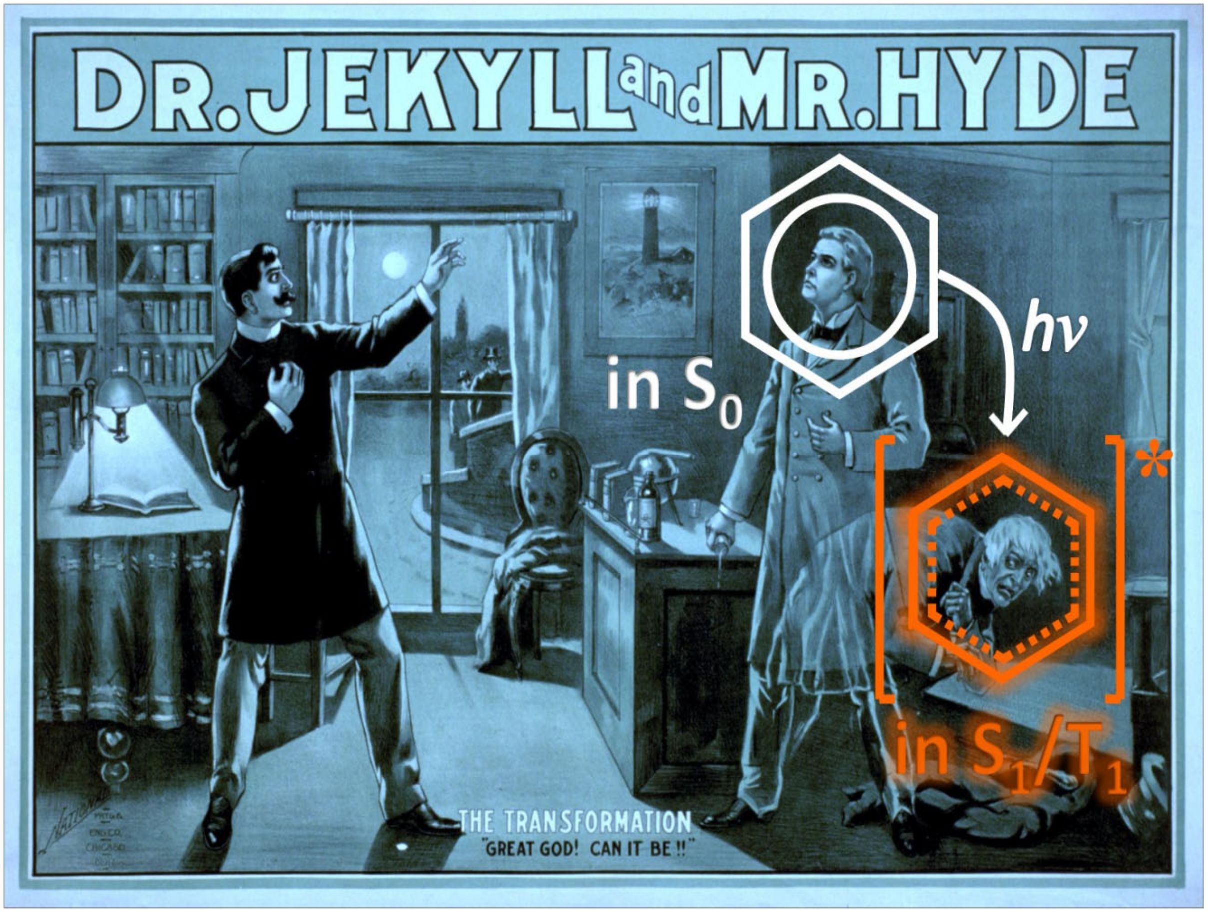
Excites states: “the evil twins of ground states?”

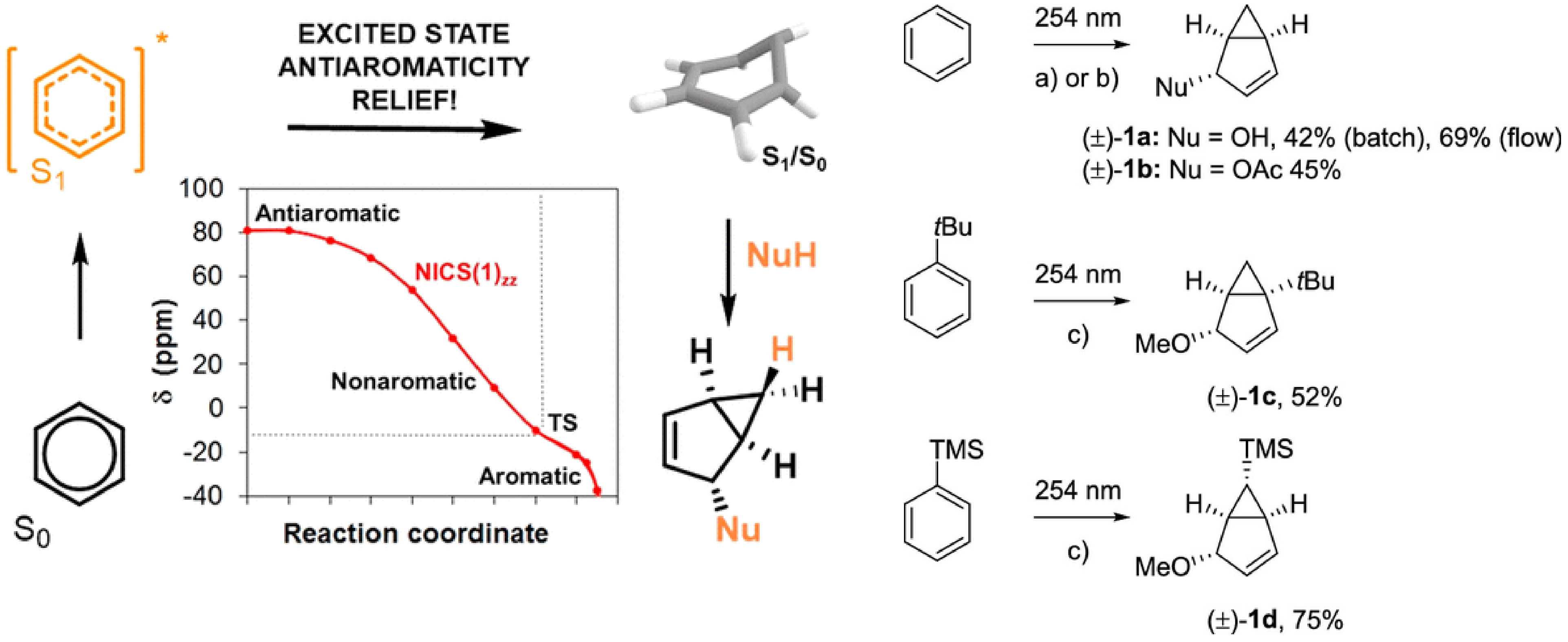


Ottosson and coworkers:
”Benzene in the S_0 state is a well-behaved molecular ”Dr. Jekyll” while in its T_1 and S_1 states it is an evil and ugly molecular ”Mr. Hyde” that initiates photorearrangements and other photoreactions.”

Papadakis & Ottosson *Chem. Soc. Rev.* 2015 DOI: 10.1039/C5CS00057B.

Application in reaction design: The Missing C1−C5 Cycloaromatization Reaction: Triplet State Antiaromaticity Relief and Self-Terminating Photorelease of Formaldehyde for Synthesis of Fulvenes from Enynes. Mohamed, R. K.; Mondal, S.; Jorner, K.; Faria Delgado, T.; Ottosson, H.; Alabugin, I. V. *J. Am. Chem. Soc.*, **2015**, *137,* 15441–15450. http://pubs.acs.org/doi/abs/10.1021/jacs.5b07448.
Also: *J. Am. Chem. Soc*. **2020**, *142*, 10942–10954, https://pubs.acs.org/doi/full/10.1021/jacs.9b13769.

“Antiaromatic benzene” is not an oxymoron!
The world of photochemistry is full of suprises

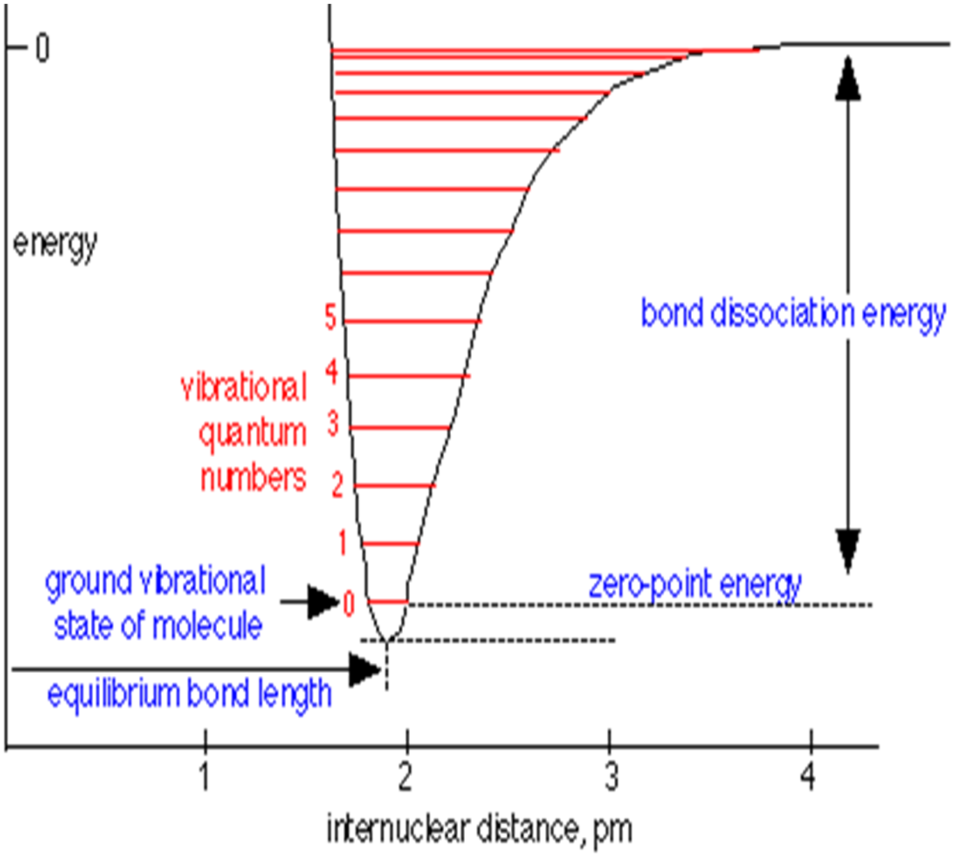


Benzene can do crazy things to escape antiaromaticity

Slanina, T.; Ayub, R.; Toldo, J.; Sundell, J.; Rabten, W.; Nicaso, M.; Alabugin, I.; Fdez. Galván, I.; Gupta, A. K.; Lindh, R.; Orthaber, A.; Lewis, R. J.; Grönberg, G.; Bergman, J.; Ottosson, H. Impact of Excited-State Antiaromaticity Relief in a Fundamental Benzene Photoreaction Leading to Substituted Bicyclo[3.1.0]hexenes. *J. Am. Chem. Soc.* **2020**, *142* (25), 10942–10954. https://doi.org/10.1021/jacs.9b13769

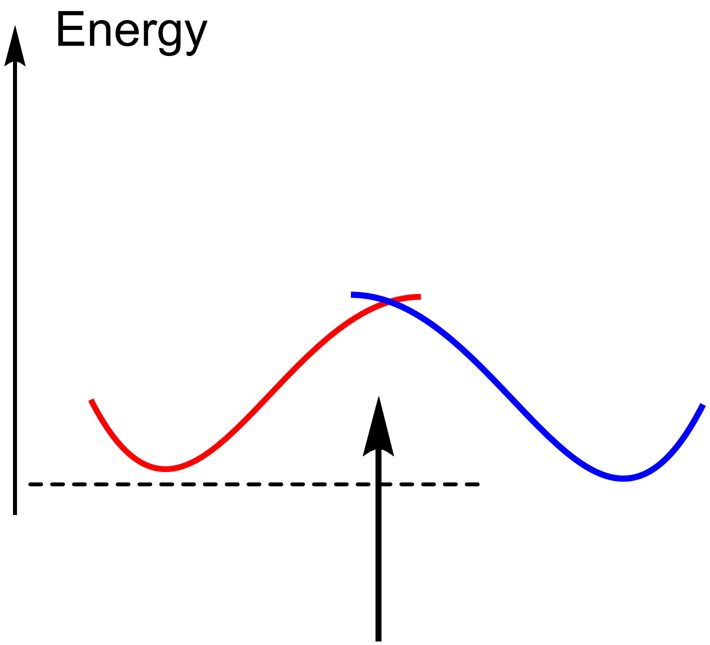
Many chemical bonds are hard to break

Energy goes up when chemical reactions break a bond



Energy is needed to get out of the potential energy well

Why there is a barrier in chemical reactions?



Energy goes up because we break a bond

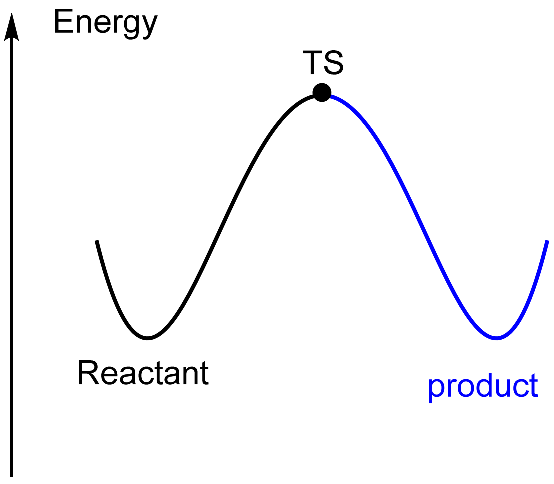
Energy goes down because we make a bond

Transition state

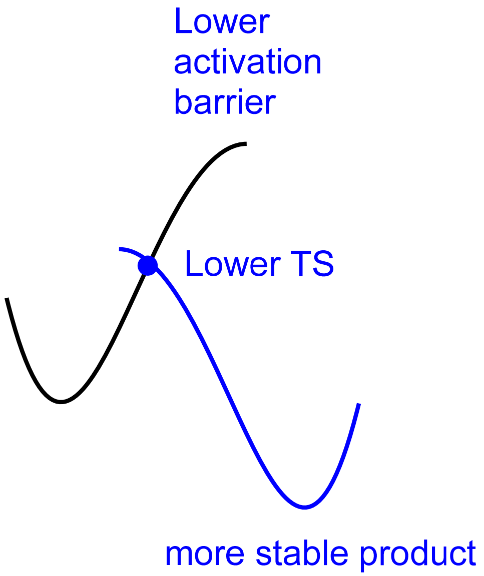
Crossing of two potential energy surfaces (PES): reactant and product

This model allows us to understand the key connections between kinetics and thermodynamics

How to lower the activation barrier?

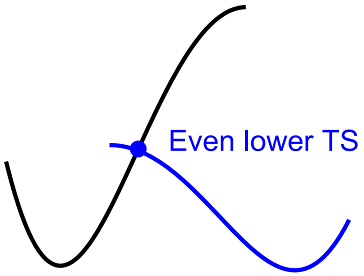


strong bond into
a strong bond



strong bond into a strong bond in an exothermic reaction

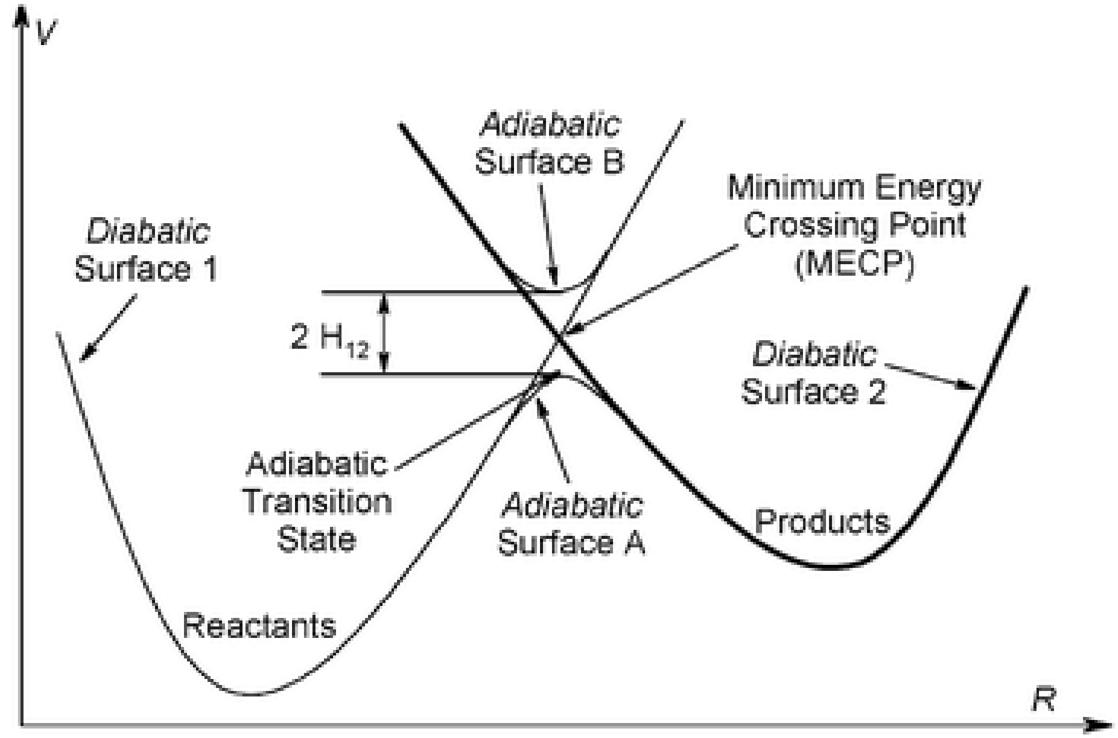
Make a weak bond!



converting a strong bond into a weak bond and make the potential energy curve shallow (change the “intrinsic barrier”)

But where is the excited state in this model?

A more advanced crossing model



Crossing of two electronic states: reactant and product creates TWO potential energy surfaces.

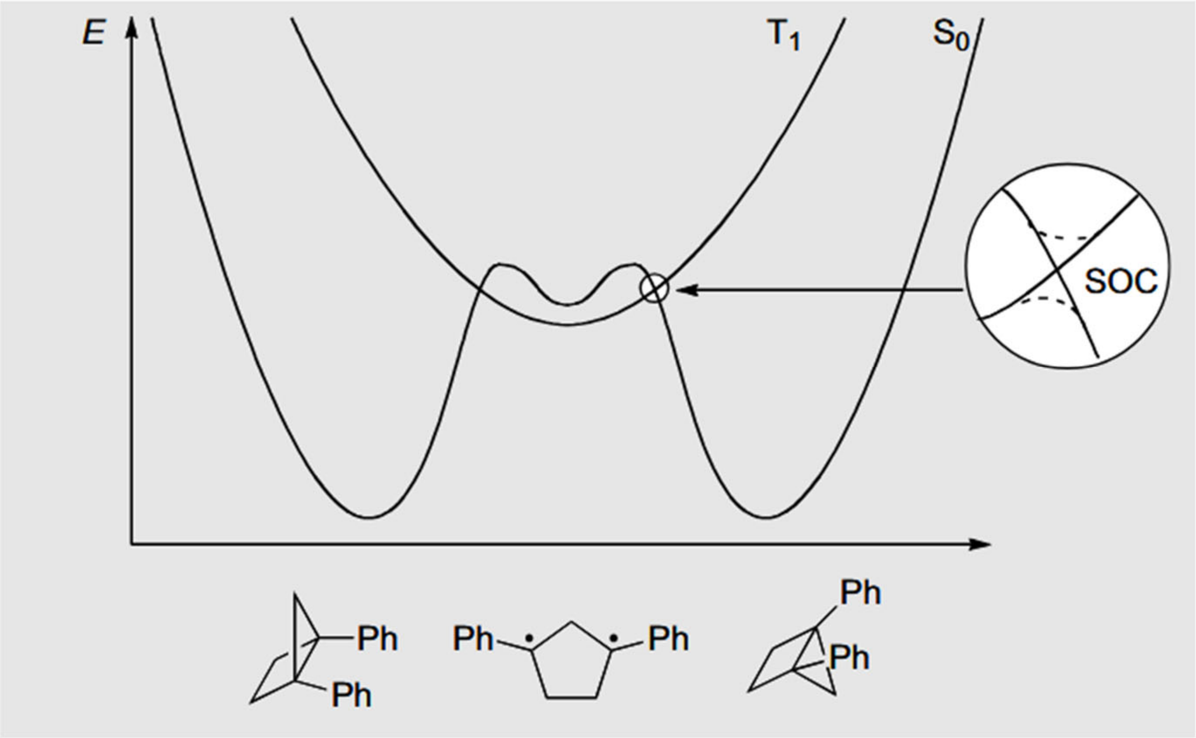
Do you see TS at the top surface?

What happens if we move along the same reaction coordinate but on the excited state surface?

The best way to lower the barrier is to remove it completely!

Which is what one can do with photochemistry!

Let’s look at a model bond breaking reaction



How does the excited state of a transition state look like?

What happened to the barrier for the diradical formation in the excited state?

1,3-Diphenylclopentane-1,3-diyl can be generated by thermal homolysis of the central bond of 1,4-diphenylbicyclo[2.1.0]pentane (housane).

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Unique electronic properties?

Sounds great!

Atom-economic formation of reactive species?

Fantastic!

But what is the catch?

Electronic Excitation: What Actually Happens?

Core message: Understanding excited states is essential.

- Ground vs excited states
  - $S_0 \rightarrow S_1$ (singlet)
  - Intersystem crossing to T_1 (triplet)
- Lifetimes (short!):
  - Singlets: ns
  - Triplets: μs–ms (longer lived but still reactive!)

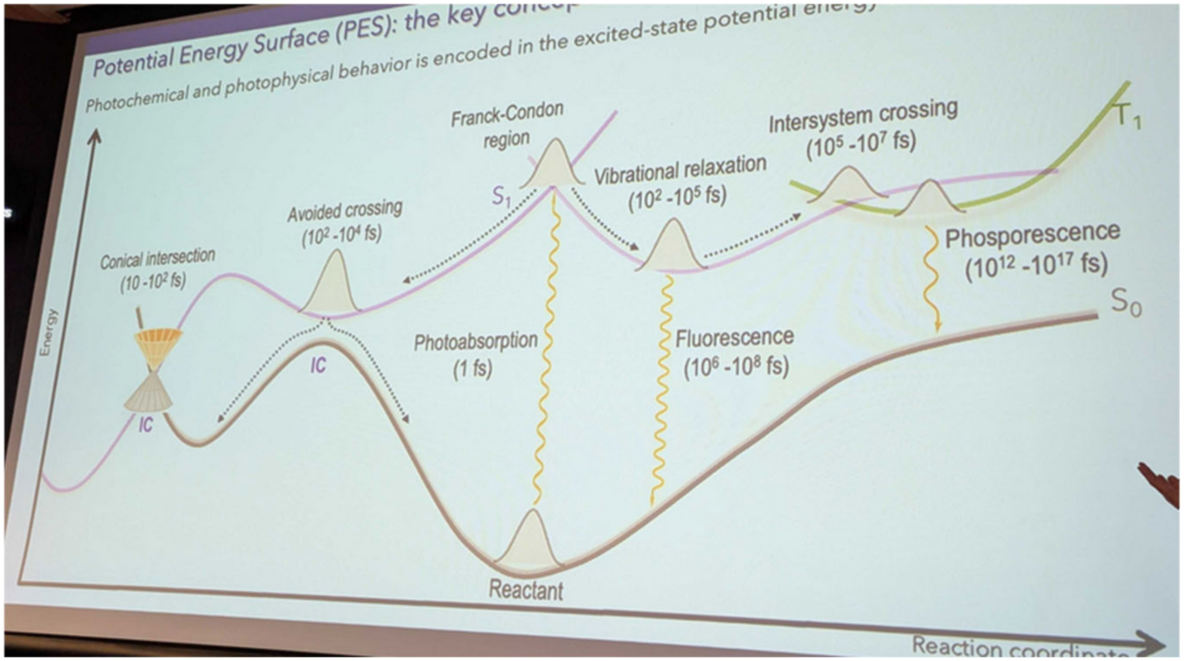
Key conceptual diagram: Jablonski diagram

Take-home message:
Excited states are real chemical species with their own reactivity.

Why Time Scales Matter in Photochemistry

- reactivity is a race against time

Limited time window!



Potential Energy Surface (PES): the key conc

Photochemical and photophysical behavior is encoded in the excited-state potential energ

Kinetics is very important. Excited states are transient.

All photochemistry completes with going back to the ground state.

Slide from Prof. J. Toldo

Photochemical Reactivity vs Thermal Reactivity

Core message: Rules change in excited states.
- Orbital symmetry rules are inverted or bypassed
  - Woodward–Hoffmann vs photochemical allowedness
- Reactivity patterns:
  - Bond homolysis
  - Pericyclic reactions that are forbidden thermally

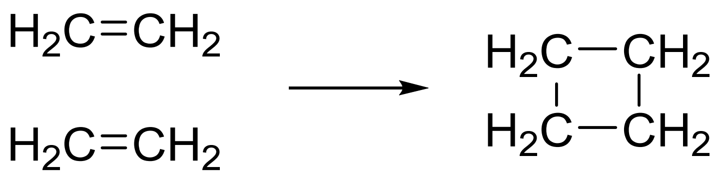
- Why photochemistry often favors radicals and diradicals

Classic examples:
- [2+2] cycloadditions
- Electrocyclic ring openings/closures

Take-home idea:
Photochemistry rewrites the “allowed vs forbidden” rulebook.

[2+2] Cycloaddition of Alkenes

A simple thermodynamically favorable reaction:

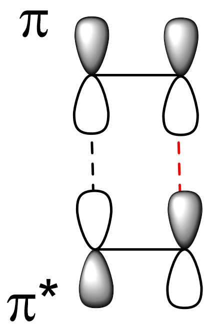

$H_2C{=}CH_2 + H_2C{=}CH_2 \longrightarrow$ cyclo-$(CH_2)_4$

ΔH_{rxn} = -18.2 kcal/mol

Why is it “forbidden”?

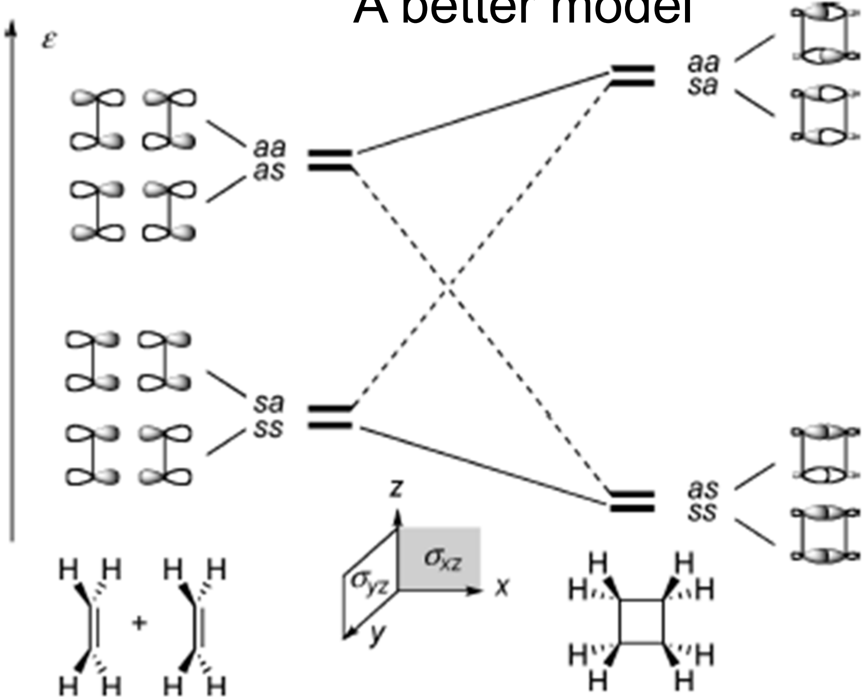
[2+2]

Unfavorable Frontier MO symmetry



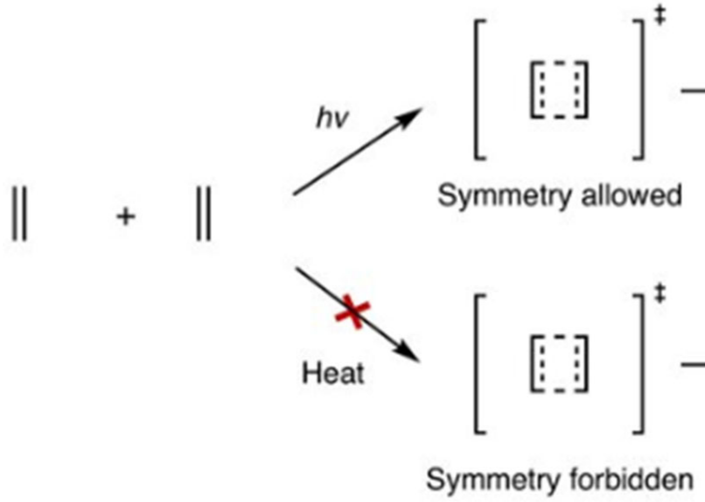
The simplest explanation

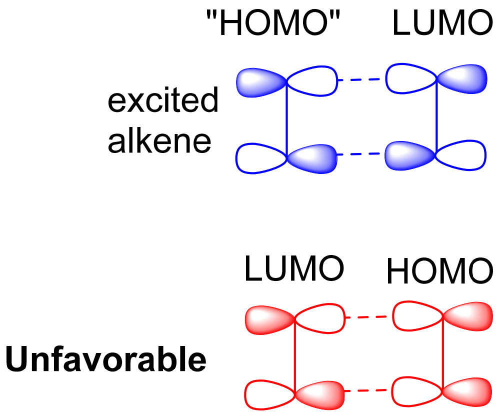
A better model



Photochemistry of Organic Compounds: …P. Klán, J. Wirz

Photochemical [2+2] Cycloaddition of Alkenes





- **Thermally: π2s + π2s is forbidden**
- Photochemically:
  - Once one alkene is excited, symmetry now allows overlap
- Result: a reaction that **cannot happen in the dark** proceeds photochemically

Why this is essential

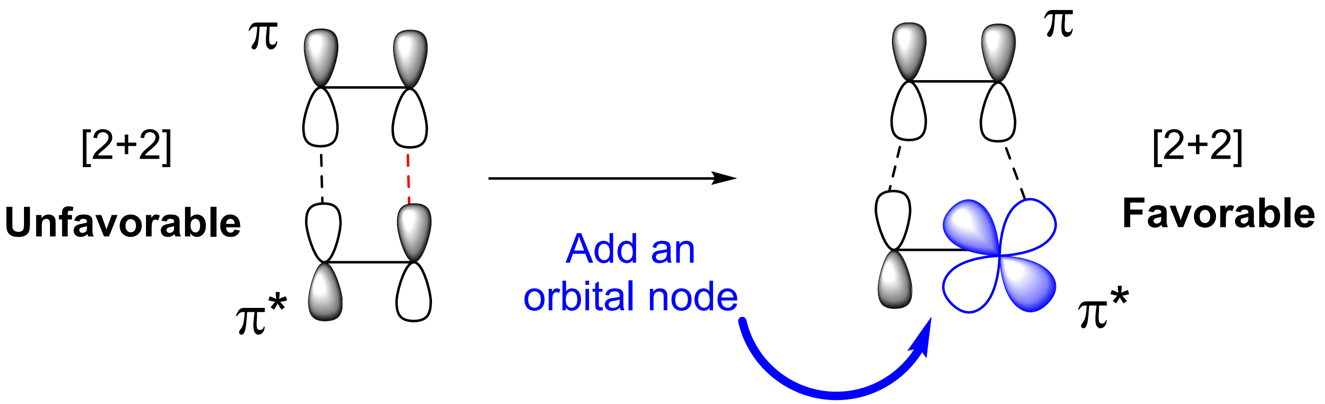
- A clean **illustration** that:
  - Thermal rules ≠ photochemical rules
  - Light changes *orbital interaction symmetry*
- We immediately see that photochemistry is **qualitatively different**

One-line takeaway:

Light turns a forbidden reaction into an allowed one.

We can apply lessons from photochemical reactions in design of ground state reactions!

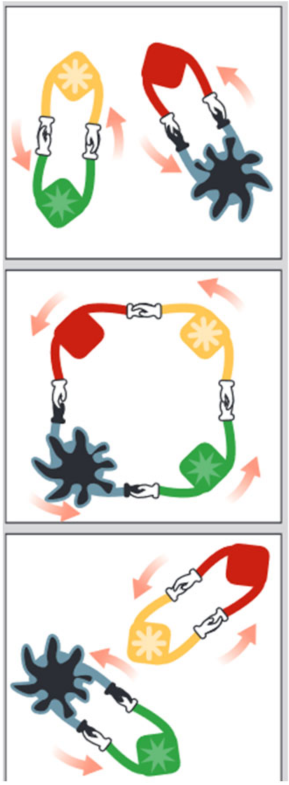
The striking effect of orbital symmetry on [2+2] cycloadditions



[2+2]
Unfavorable

Add an
orbital node

[2+2]
Favorable

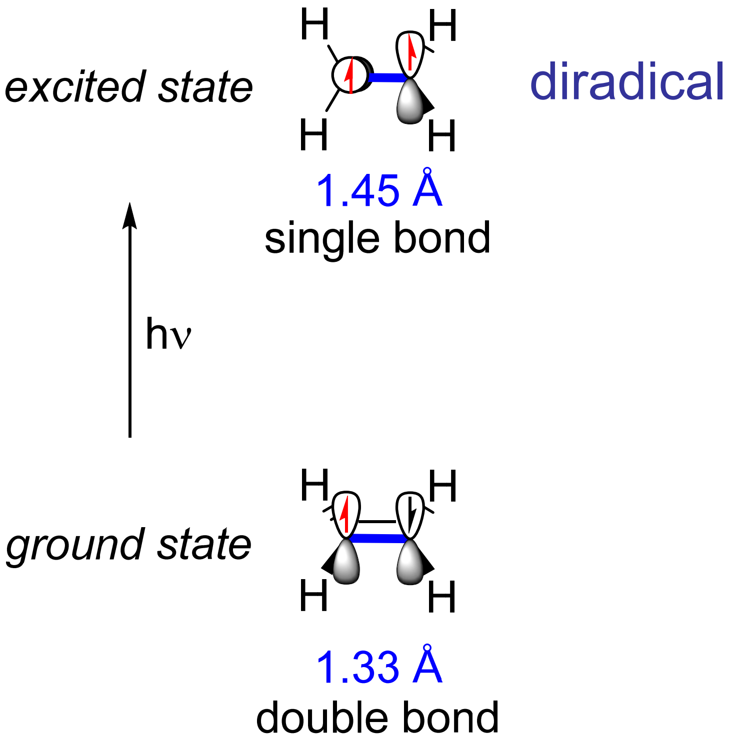


An extra orbital node is the difference between a failed reaction and a Nobel Prize!

From Alabugin, “Stereoelectronic effects”

Excited states are chameleonic

Excited state of ethylene (π, π*): can be a diradical or a zwitter-ion



excited state

diradical

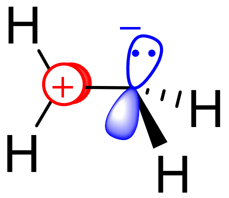
1.45 Å
single bond

ground state

1.33 Å
double bond

Want to make a
zwitter-ion instead?

Pyramidalize at one carbon



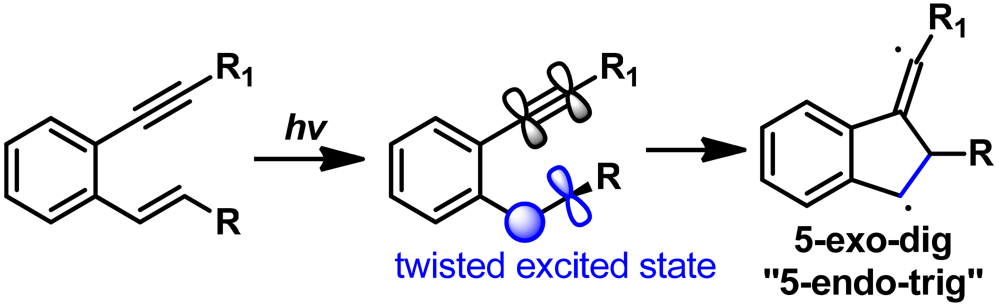
"spontaneous
polarization"
- singlet

Triplet States, Spin, and Radical Pathways

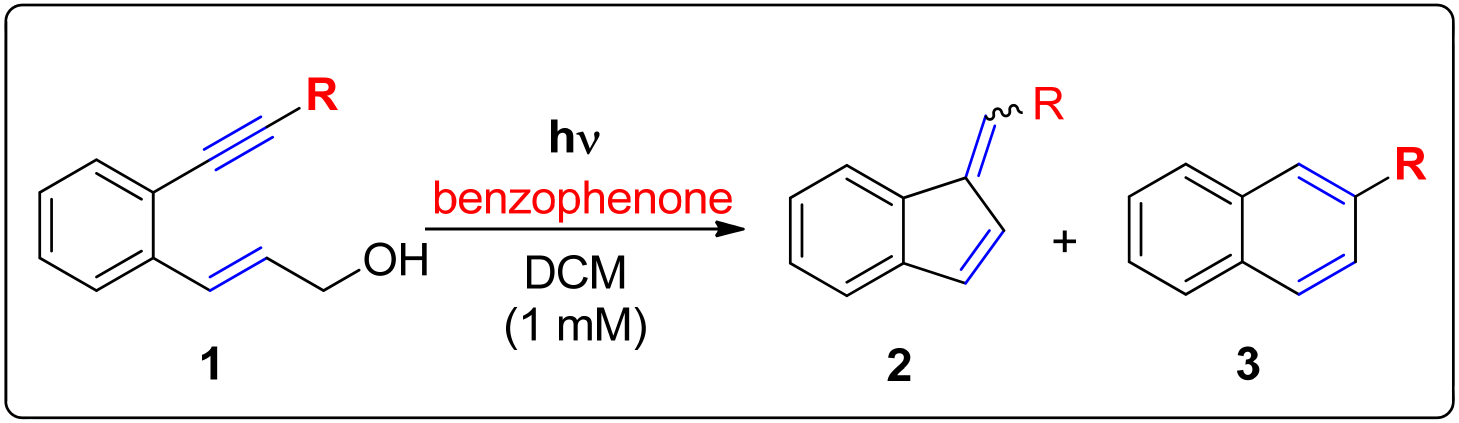
Core message: Connection between photochemistry and radical chemistry.

- Why triplets are different from singlet states:
    - Long lifetimes
    - Radical character
- Spin conservation and reactivity
- Oxygen as a photochemical quencher (and participant!)

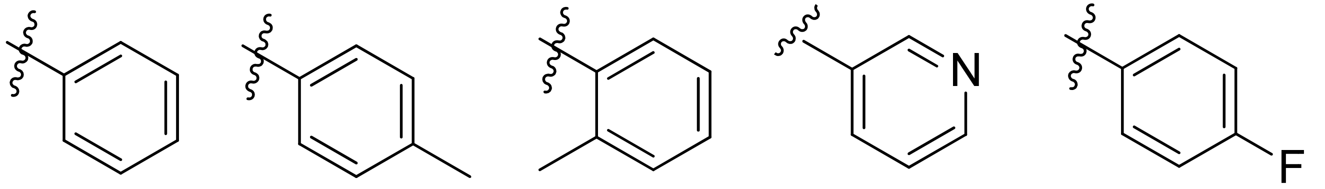
Take-home idea:
Triplet states turn molecules into controlled radical generators.



Triplet sensitization yields fulvene as the only product



R =

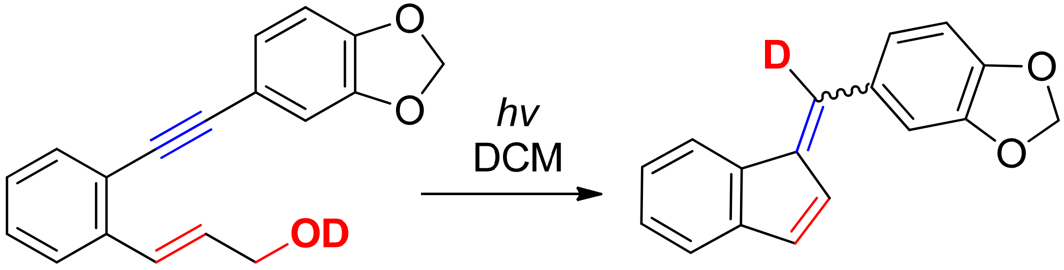


yield (%)	2b, 24% 3b, 69%	2c, 29% 3c, 58%	2d, 30% 3d, 60%	2e,24% 3e,47%	2f,30% 3f,60%
yield (%) T1	2b, 84%	2c, 89%	2d, 90%	2e, 74%	2f, 88%

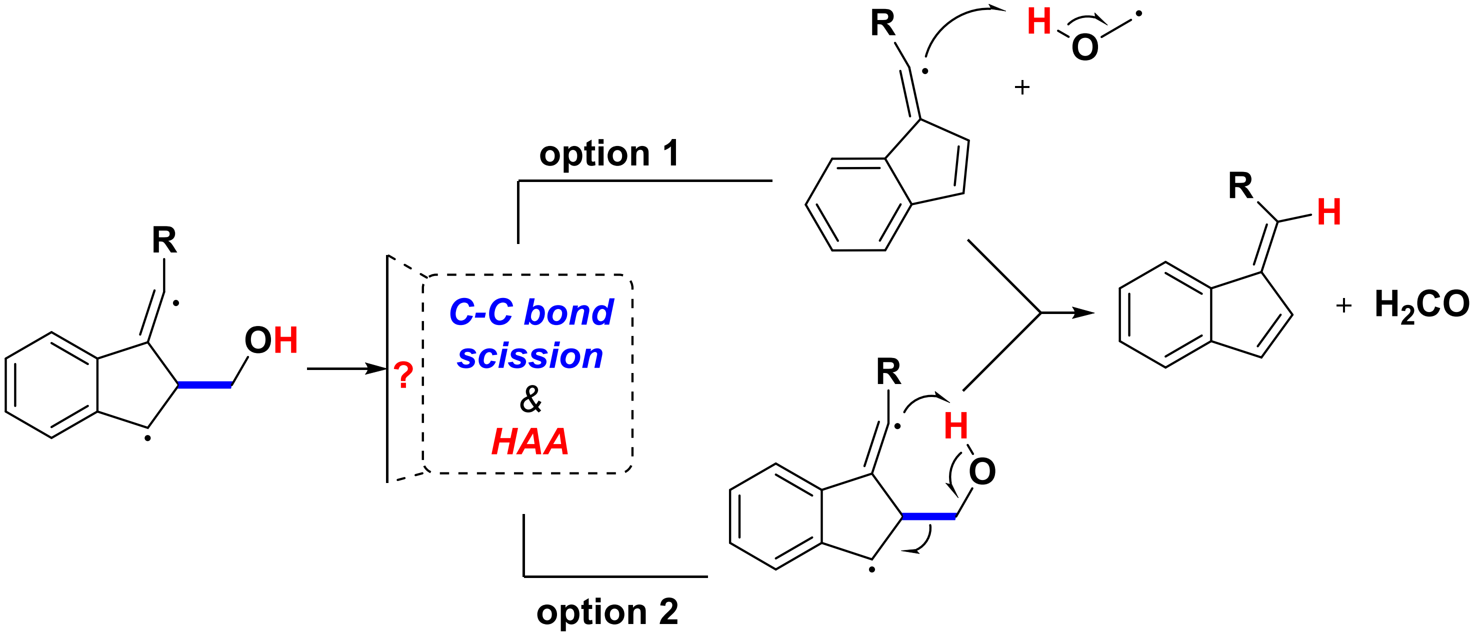
+ benzo-phenone

Mohamed, R. K.; Mondal, S.; Jorner, K.; Faria Delgado, T.; Ottosson, H. *J. Am. Chem. Soc.*, **2015**, *137,* 15441

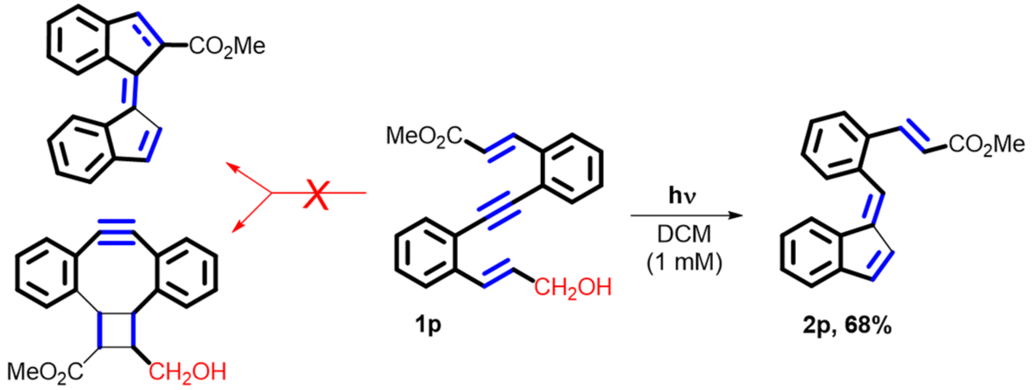
Self-quenching radical scission forms formaldehyde



Intramolecular H-transfer

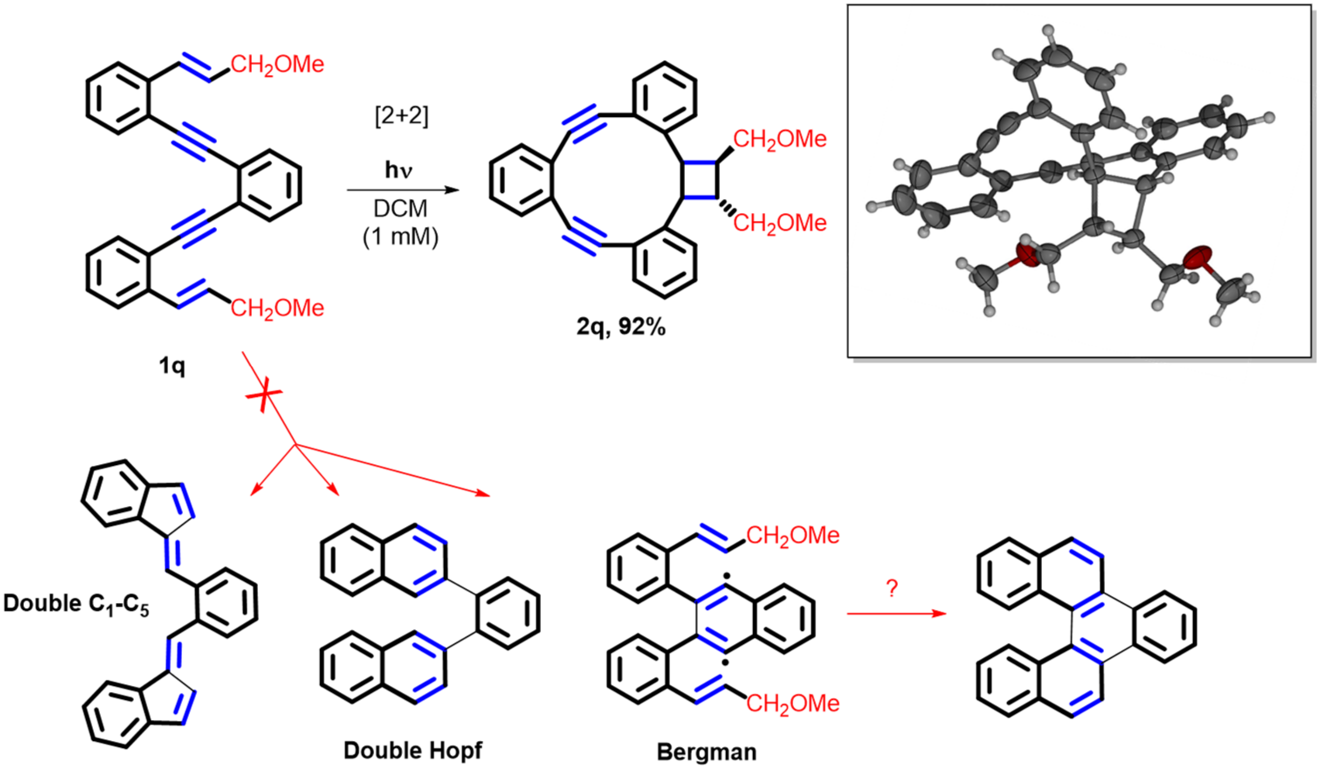


Competition with other photochemical reactions



1p

2p, 68%



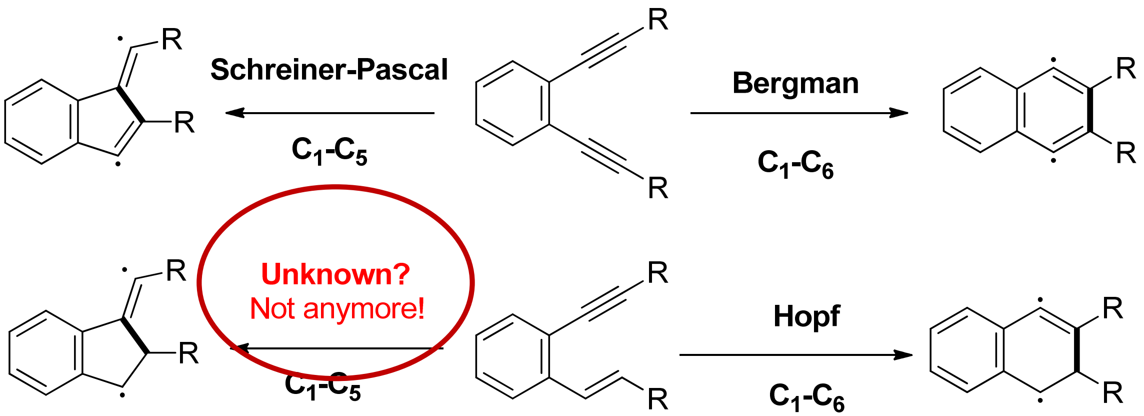
1q

2q, 92%

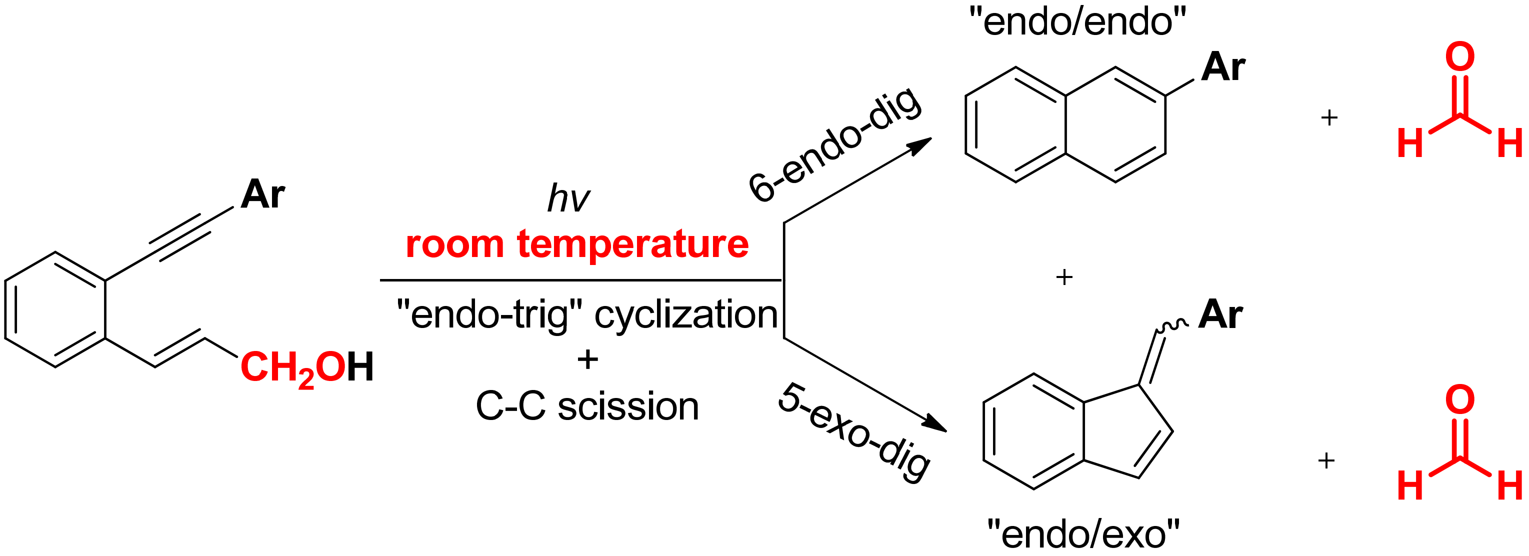
Double Hopf

Bergman

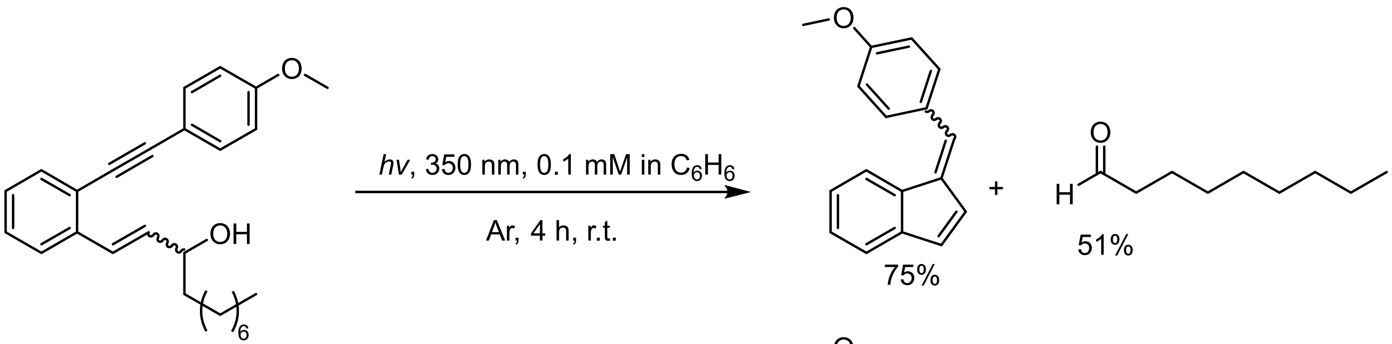
The last of the four archetypal cycloaromatization reactions of diynes and enynes is made possible by escape from ESAA!

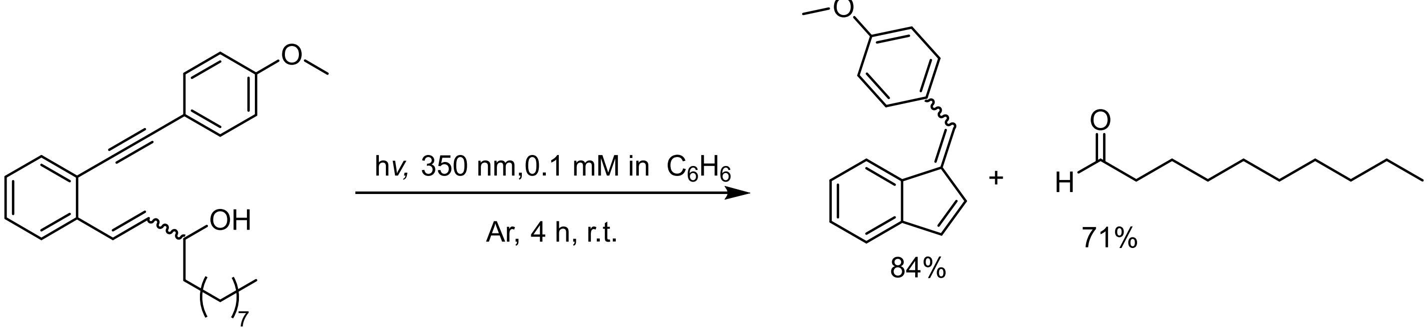


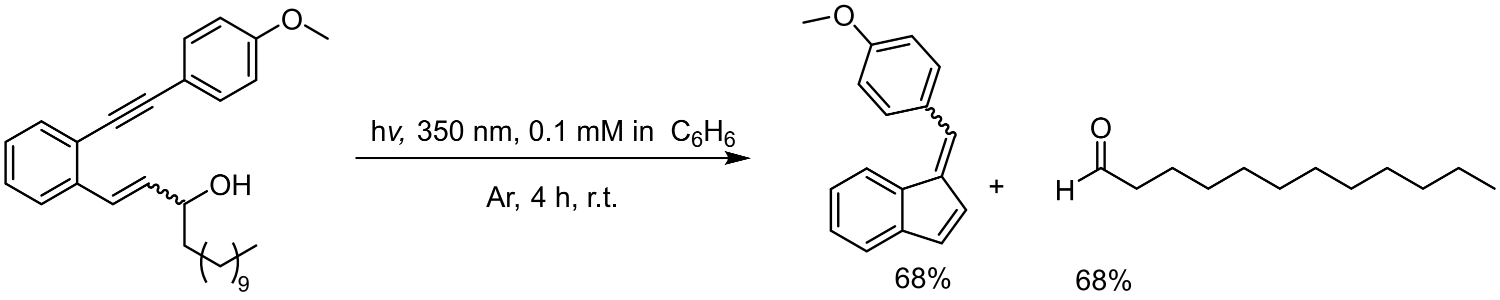
A photochemical approach to making aldehydes?



Photorelease of fragrance aldehydes

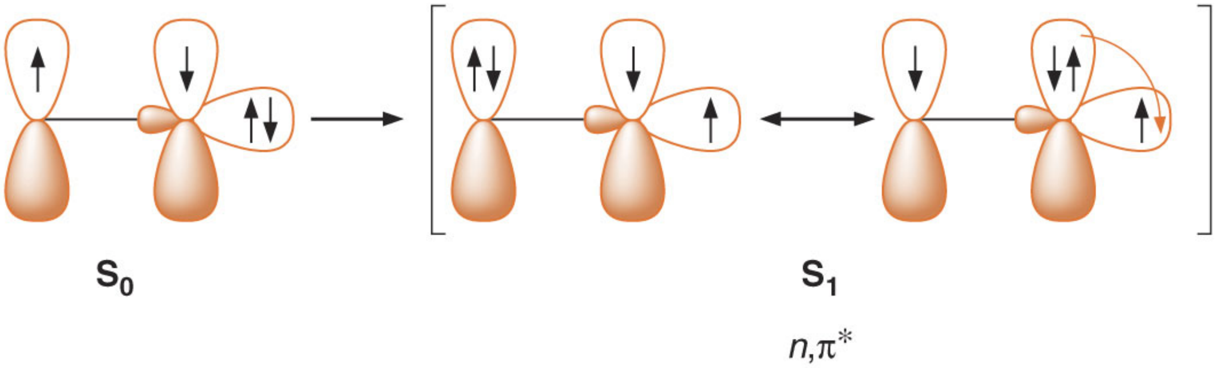






A. Campbell, N. R. Dos Santos, I. V. Alabugin, *Molecules,* **2023**, *28,* 10.3390/molecules28155704 (special issue for V. Ramamurthy)

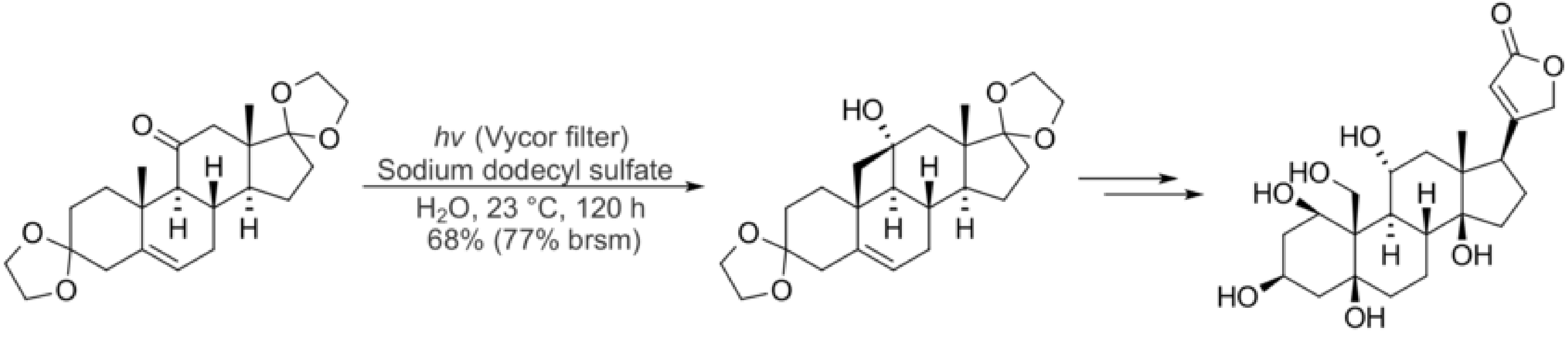
n,π* Excited state of carbonyl compounds – another entry into controlled radical chemistry



How does polarization of carbonyl moiety change upon n,π*-excitation?

n,π*-excited states of carbonyls: Umpolung by light

How does this reaction occur?



hν (Vycor filter)
Sodium dodecyl sulfate
H_2O, 23 °C, 120 h
68% (77% brsm)

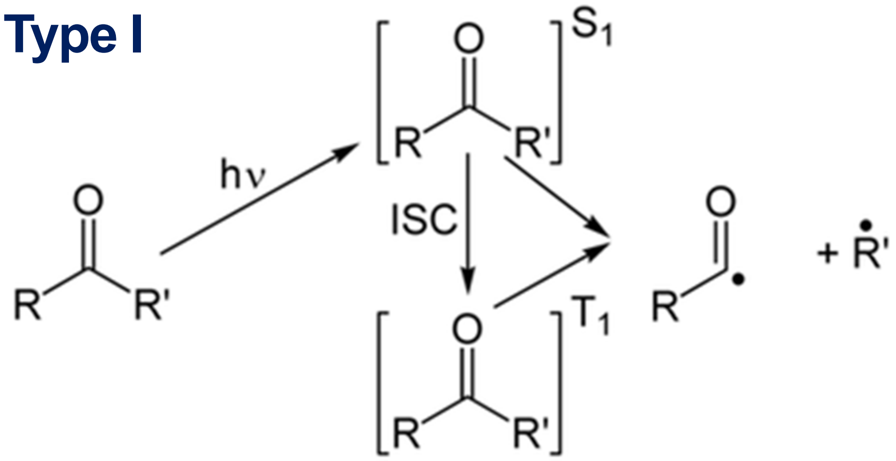
Ouabagenin

Let’s start thinking about excites states mechanistically!

Renata, H.; Zhou, Q.; Baran, P. S. Science. **2013,** 339, 59–63

Norrish Type I / Type II Photochemistry

Type I

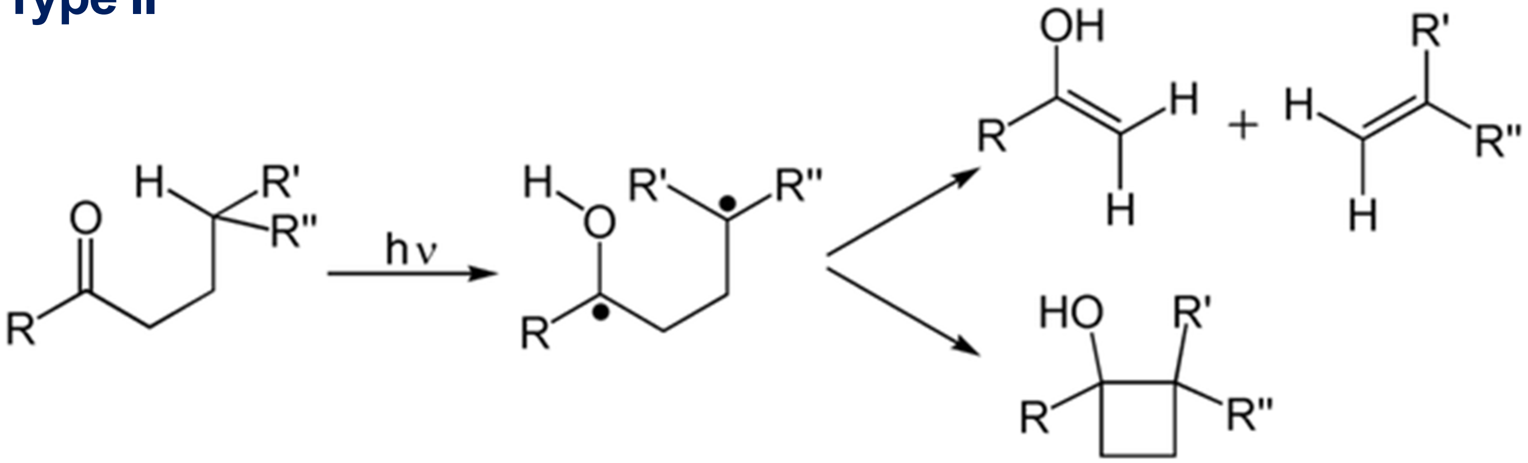


- Connects photochemistry to **radical reactivity**

$n \rightarrow \pi^*$ excitation weakens adjacent σ bonds

- Bond cleavage becomes fast and selective

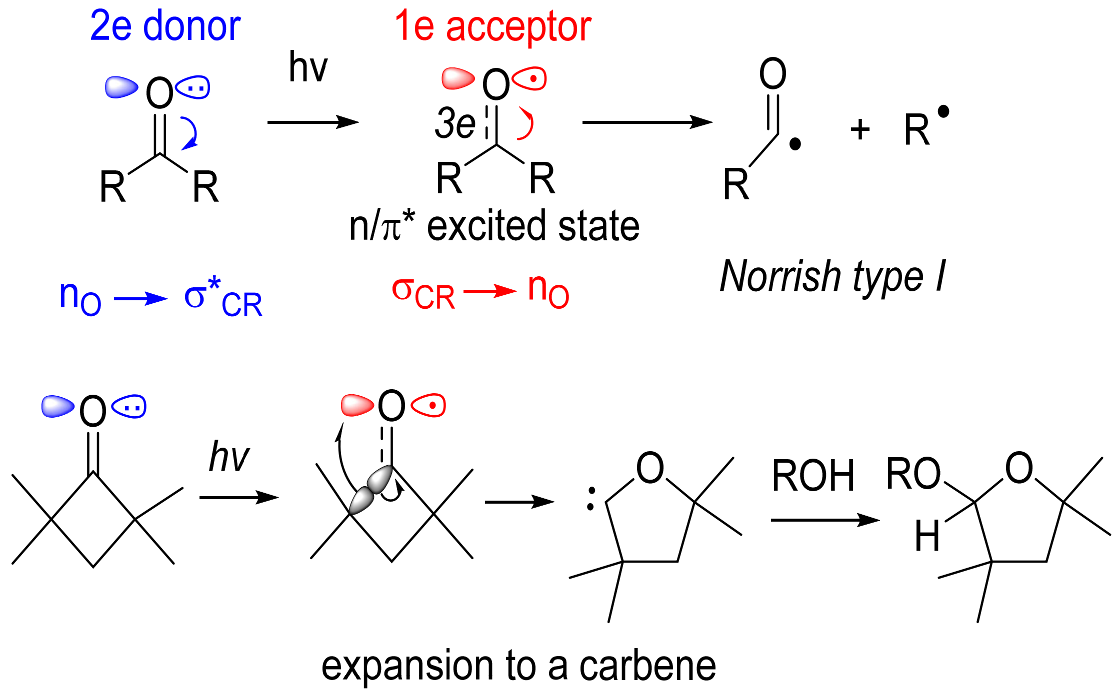
Type II



Umpolung of anomeric effect in excited states

Oxygen switches its stereoelectronic personality from a p-donor (oxygen lone pair) or a p-acceptor (O-centered radical)

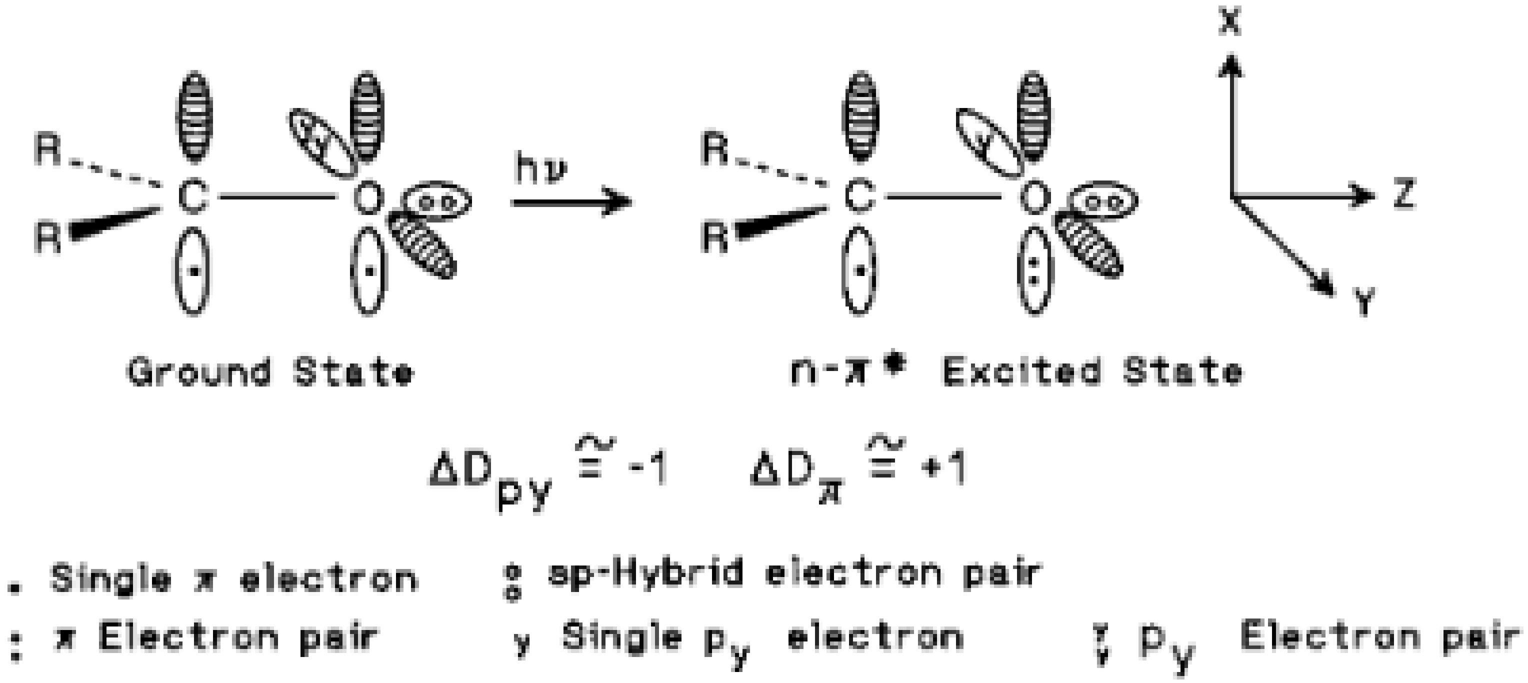
Umpolung of anomeric effect by light: fragmentations/rearrangements



Umpolung of anomeric effect by light leads to typical photochemical reactions of ketones

Stereoelectronic Power of Oxygen in Control of Chemical Reactivity: the Anomeric Effect is not Alone. I. V. Alabugin, L. Kuhn, M. G. Medvedev, N. V. Krivoshchapov, V. A. Vil', I. A. Yaremenko, P. Mehaffy, M. Yarie, A. O. Terent'ev, M.A. Zolfigol. *Chem. Soc. Rev.* **2021**, *50*, 10253-10345, https://pubs.rsc.org/en/content/articlelanding/2021/cs/d1cs00386k

n, π*-excited states of carbonyls: Umpolung by light

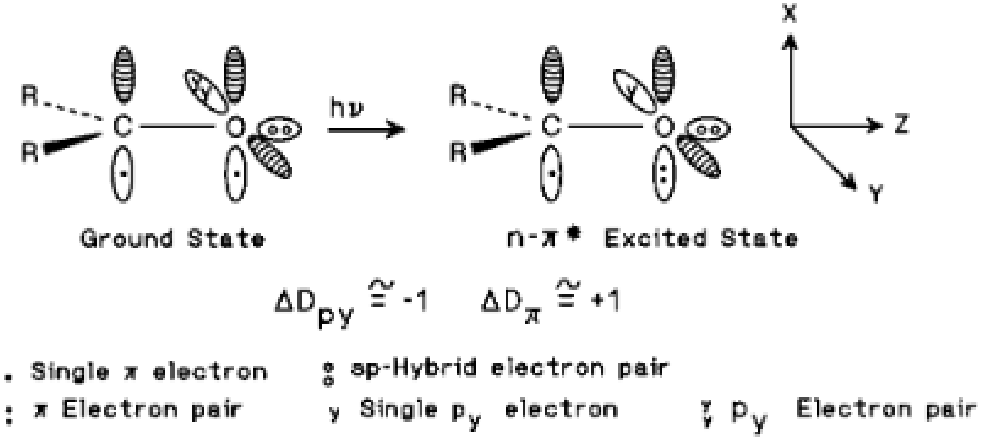


Howard
Zimmerman

How to predict photochemical reactivity from this simple picture?

H. E. Zimmerman, I. V. Alabugin *J. Am. Chem. Soc.* **2000**, 122, 952-953

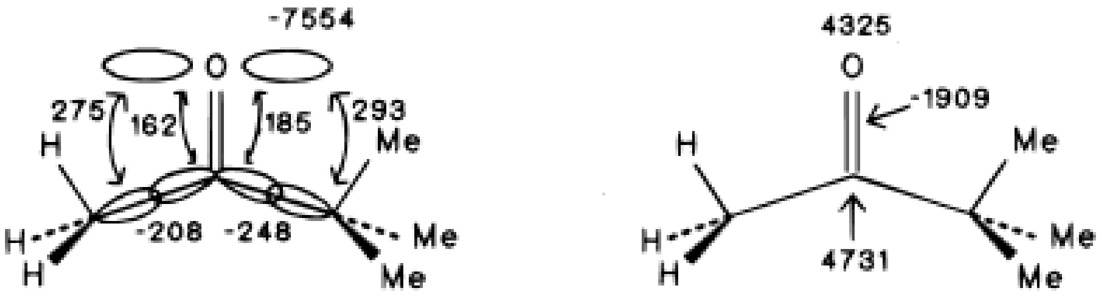
n, π*-excited states of carbonyls: Umpolung by light



Changes in bond orders and electron densities can be quantified

A “ΔD Matrix” gives the change in electron densities and bond orders at different molecular sites as a result of electronic excitation

$$\Delta D_{rt} = D^*_{rt} S^*_{rt} - D^o_{rt} S^o_{rt}$$



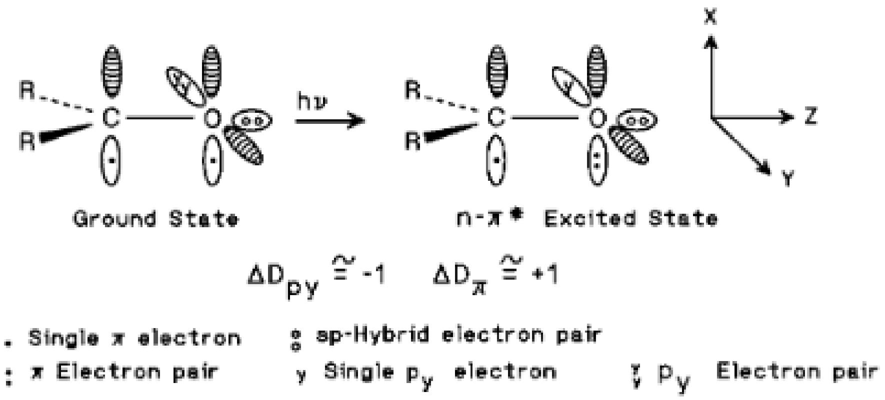
In-Plane Orbitals

Out-of-Plane Orbitals

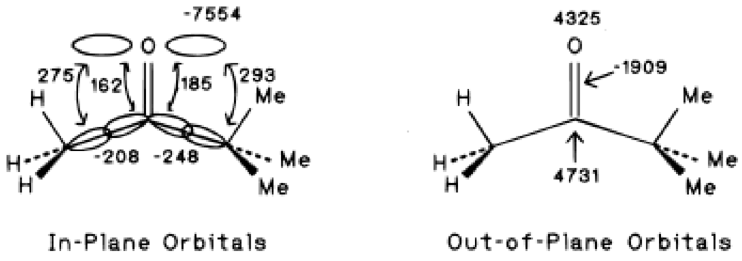
ΔD Matrix values for orbital pairs in methyl tert-butyl ketone. Values are expanded by 10 000

H. E. Zimmerman, I. V. Alabugin *J. Am. Chem. Soc.* **2000**, 122, 952-953

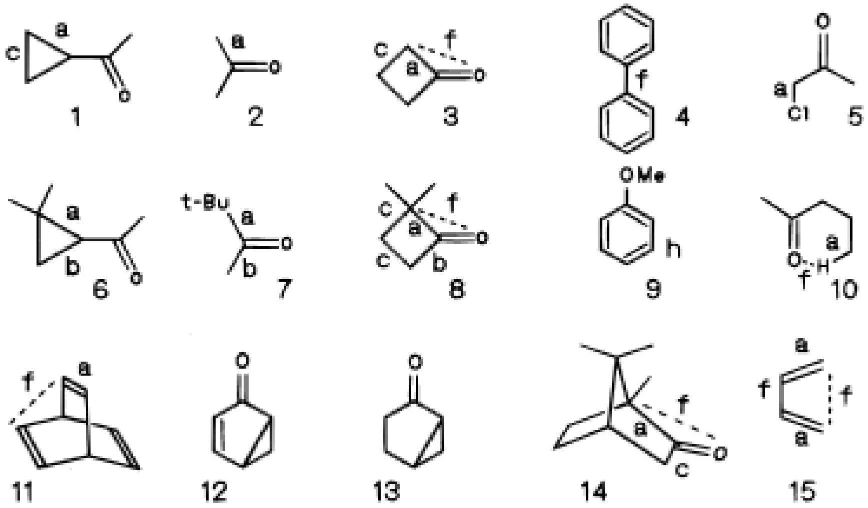
n,π*-excited states of carbonyls: Umpolung by light



How to predict photochemical reactivity?



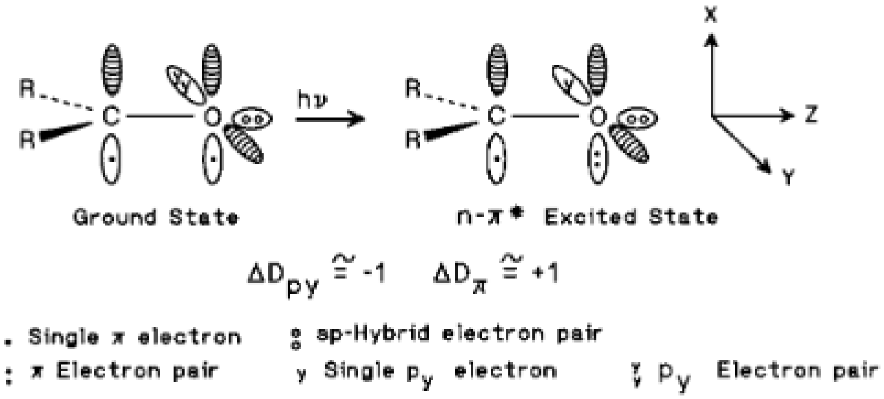
The bonds becoming most antibonding, as indicated by possessing most negative ΔD elements and having the most concentrated excitation energy, are indeed the ones breaking experimentally in the primary photochemical process

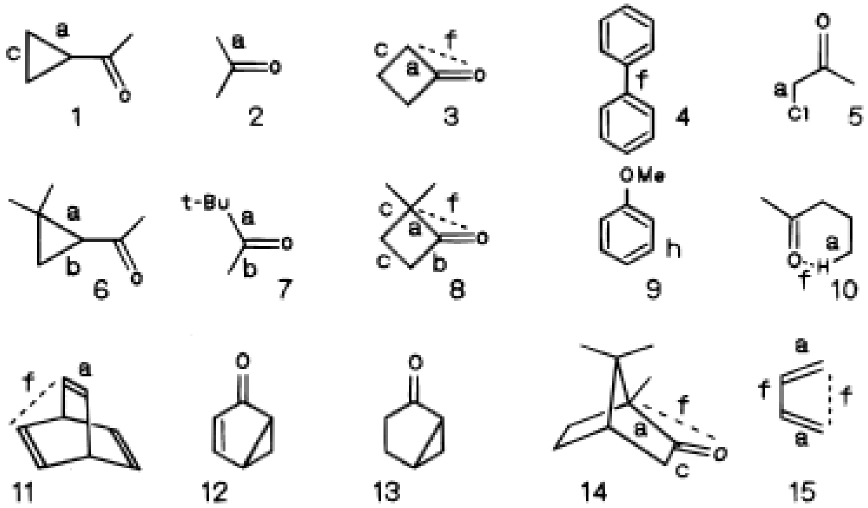


[a] Key: (a) largest negative ΔD; (b) lesser negative ΔD; (c) very small ΔD, nonbreaking bond; (f) large positive ΔD, bond forming; (h) increased one-center ΔD.

H. E. Zimmerman, I. V. Alabugin *J. Am. Chem. Soc.* **2000**, 122, 952-953

n,π*-excited states of carbonyls: Umpolung by light





Let’s predict five intramolecular photochemical reactions of ketones

Driven by electron deficient oxygen

Migration:

Norrish type I Fragmentation:

H-atoms transfer (two pathways via γ C-H):

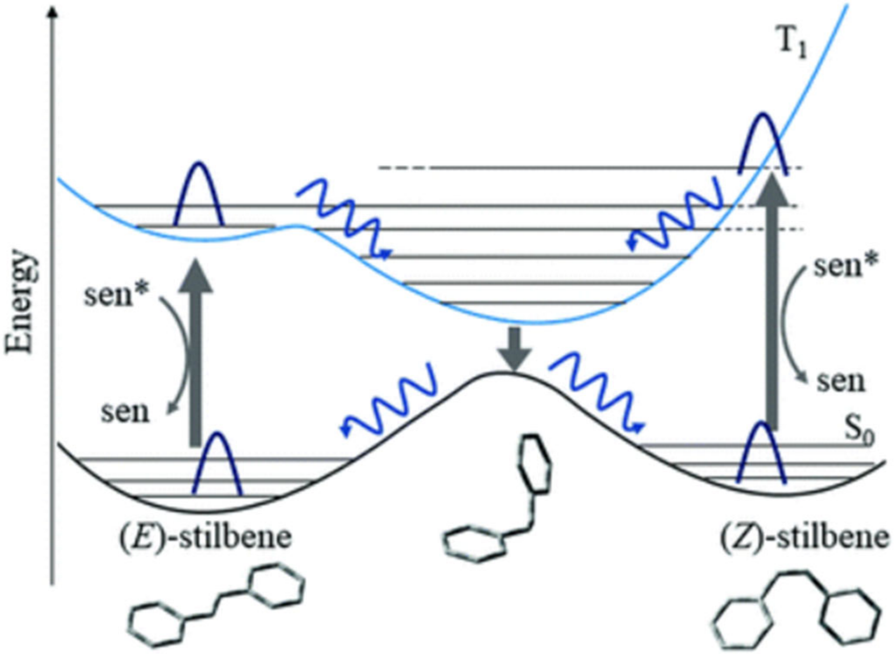
a) Fragmentation (Norrish II)
b) Cyclization (Norrish-Yang)

Driven by electron-rich carbon:

α-expulsion

H. E. Zimmerman, I. V. Alabugin *J. Am. Chem. Soc.* **2000**, 122, 952-953

Cis–Trans Isomerization of Alkenes



Triplet sensitized (denoted as sen) isomerization of stilbene

https://pubs.rsc.org/en/content/articlehtml/2022/cp/d1cp04672a

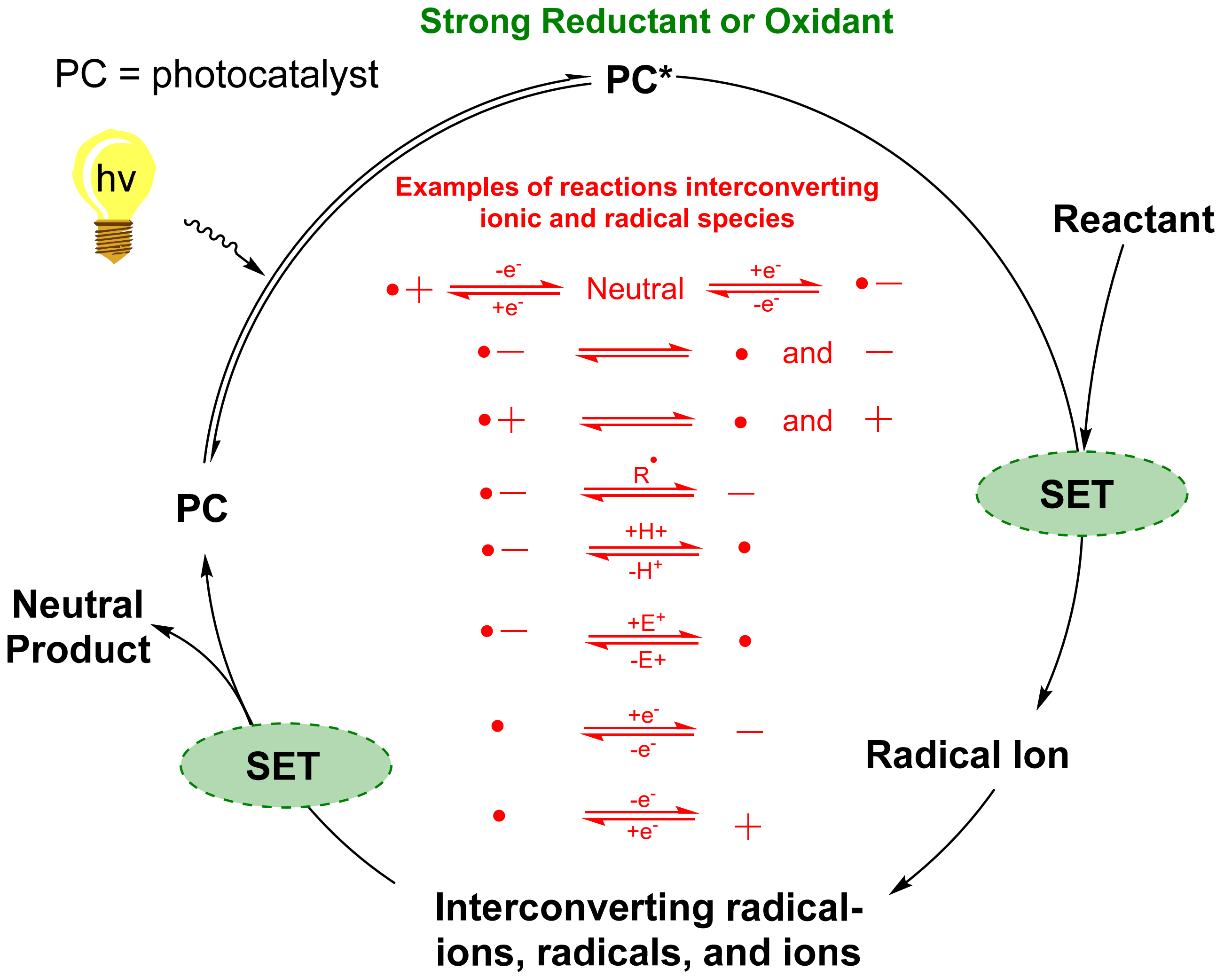
- Excited states **flatten (or even remove) energy barriers**
- Rotations forbidden thermally become allowed
- Biologically relevant (retinal)

The excited state:

- π bond order drops
- Rotation becomes easy
- Relaxation locks in a new geometry

Photoredox and SET

- Visible-light catalyst → radical ion chemistry



Strong Reductant or Oxidant

PC = photocatalyst

hv

PC*

Examples of reactions interconverting ionic and radical species

$\bullet + \;\underset{+e^-}{\overset{-e^-}{\rightleftharpoons}}\; \text{Neutral} \;\underset{-e^-}{\overset{+e^-}{\rightleftharpoons}}\; \bullet -$

$\bullet - \;\rightleftharpoons\; \bullet \text{ and } -$

$\bullet + \;\rightleftharpoons\; \bullet \text{ and } +$

$\bullet - \;\overset{R^\bullet}{\rightleftharpoons}\; -$

$\bullet - \;\underset{-H^+}{\overset{+H+}{\rightleftharpoons}}\; \bullet$

$\bullet - \;\underset{-E+}{\overset{+E^+}{\rightleftharpoons}}\; \bullet$

$\bullet \;\underset{-e^-}{\overset{+e^-}{\rightleftharpoons}}\; -$

$\bullet \;\underset{+e^-}{\overset{-e^-}{\rightleftharpoons}}\; +$

Reactant

SET

Radical Ion

Interconverting radical-ions, radicals, and ions

SET

Neutral Product

PC

Light can move electrons, not just “excite bonds”

Why This Matters Today

Core message: Photochemistry is central to modern synthesis and materials.

- Applications:
    - Drug synthesis
    - Polymer chemistry
    - Green chemistry (mild conditions)
    - Biological labeling and imaging
- Connection to:
    - Photoredox catalysis
    - Solar energy conversion
    - Molecular machines

Photochemistry is where physical chemistry, organic synthesis, and biology intersect

LIMITATIONS,

COMPLICATIONS,

AND PITFALLS

OF THE ESA & ESAA CONCEPTS

LIMITATIONS:

- TO WHICH ELECTRONICALLY EXCITED STATES CAN THE CONCEPTS WE APPLIED?
- AT WHAT RING SIZE ARE THE CONCEPTS NOT APPLICABLE ANYMORE?

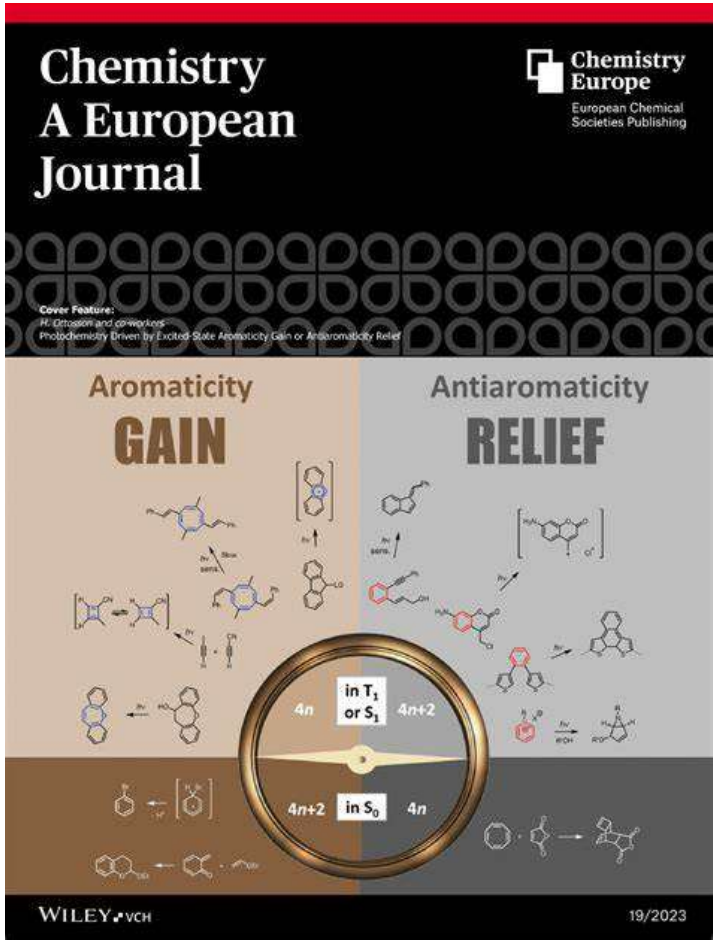
COMPLICATIONS:

- COMPUTATIONAL METHOD VARIATIONS (*e.g.*, FUNCTIONALS) …
- AS WELL AS VARIATIONS BETWEEN AROMATICITY DESCRIPTORS

PITFALLS:

- COMPUTATIONAL: AROMATICITY INDICATORS FALSELY INDICATING AROMATICITY
- CONCEPTUAL: EXCITED STATE HÜCKEL-AROMATICITY INSTEAD OF BAIRD-AROMATICITY

FLOWCHART FOR INVESTIGATIONS OF TENTATIVE EXCITED STATE (ANTI)AROMATICITY EFFECTS



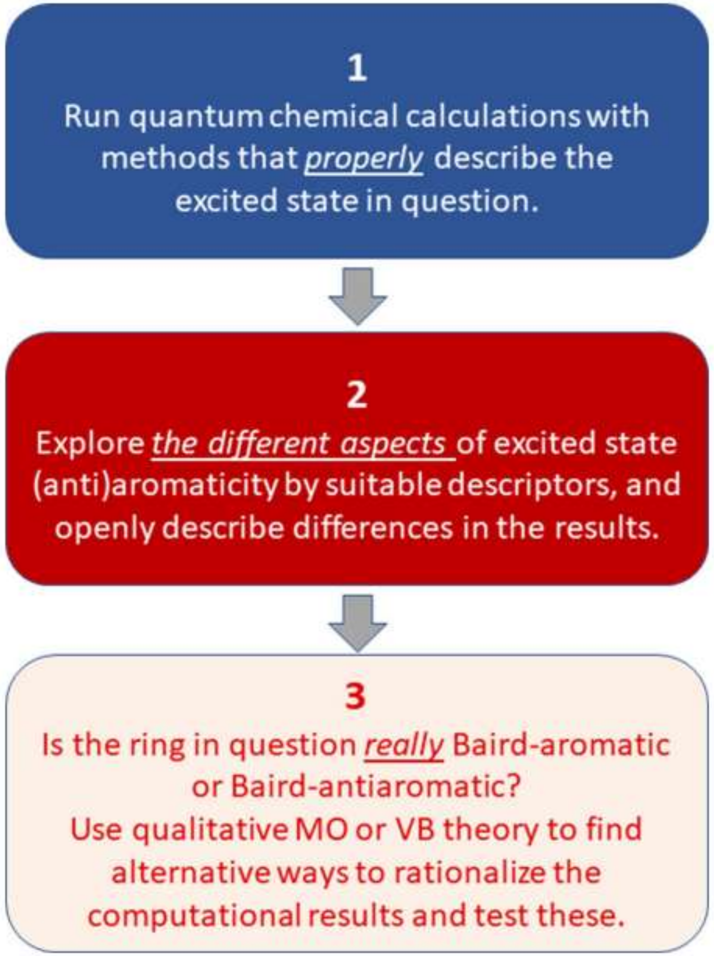
Chemistry
A European
Journal

Chemistry
Europe
European Chemical
Societies Publishing

Cover Feature:
H. Ottosson and co-workers
Photochemistry Driven by Excited-State Aromaticity Gain or Antiaromaticity Relief

WILEY-VCH

19/2023



1
Run quantum chemical calculations with methods that *properly* describe the excited state in question.

2
Explore *the different aspects* of excited state (anti)aromaticity by suitable descriptors, and openly describe differences in the results.

3
Is the ring in question *really* Baird-aromatic or Baird-antiaromatic?
Use qualitative MO or VB theory to find alternative ways to rationalize the computational results and test these.

Reflection & outlook:

With a critical stance we learn something new, and expand the ESA & ESAA concepts beyond Baird-type (anti)aromaticity.

Yan, Slanina, Bergman & Ottosson, *Chem. Eur. J.* **2023**, *29*, e202203748

OTHER FORMS OF ESA & ESAA, AND SOME PITFALLS

- **Excited state Hückel-aromaticity**
  - **The trivial case, and**
  - **The non-trivial case**
- **Hückel-Baird hybrid aromaticity**
- **…**
- **False indications of excited state aromaticity or antiaromaticity**
- **Tug-of-war between ESA and ESAA in nπ* states**

LIMITATIONS:

- TO WHICH ELECTRONIC STATES CAN THE CONCEPTS WE APPLIED?
- AT WHAT RING SIZE ARE THE CONCEPTS NOT APPLICABLE ANYMORE?

COMPLICATIONS:

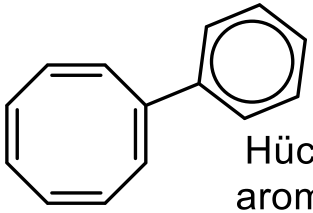
- COMPUTATIONAL METHOD VARIATIONS (*e.g.*, FUNCTIONALS) …
- AS WELL AS VARIATIONS BETWEEN AROMATICITY DESCRIPTORS

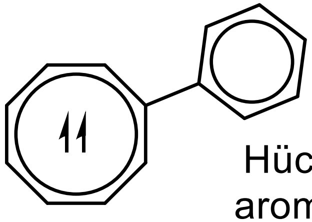
PITFALLS:

- COMPUTATIONAL: AROMATICITY INDICATORS FALSELY INDICATING AROMATICITY
- CONCEPTUAL: EXCITED STATE HÜCKEL-AROMATICITY INSTEAD OF BAIRD-AROMATICITY

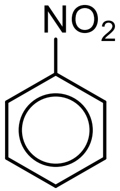
EXCITED STATE HÜCKEL-AROMATICITY: TRIVIAL CASES

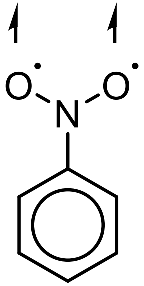
- **Phenylcyclooctatetraene in the T_1 state:** The Ph group is aromatic in both S_0 and T_1. However, it just remains regular Hückel-aromatic as the triplet excitation is fully localized to the COT ring.





- **Nitrobenzene:** A similar situation occurs in nitrobenzene which is computed to be aromatic in both S_0 and T_1. However, the triplet excitation is localized to the nitro substituent.





Can nitrobenzene in the T_1 state have any influence of Baird-aromaticity? No, this would require a dicationic or dianionic benzene ring with 4 or 8 π-electrons.

EXCITED STATE HÜCKEL-AROMATICITY: NONTRIVIAL CASES

Can be found in:

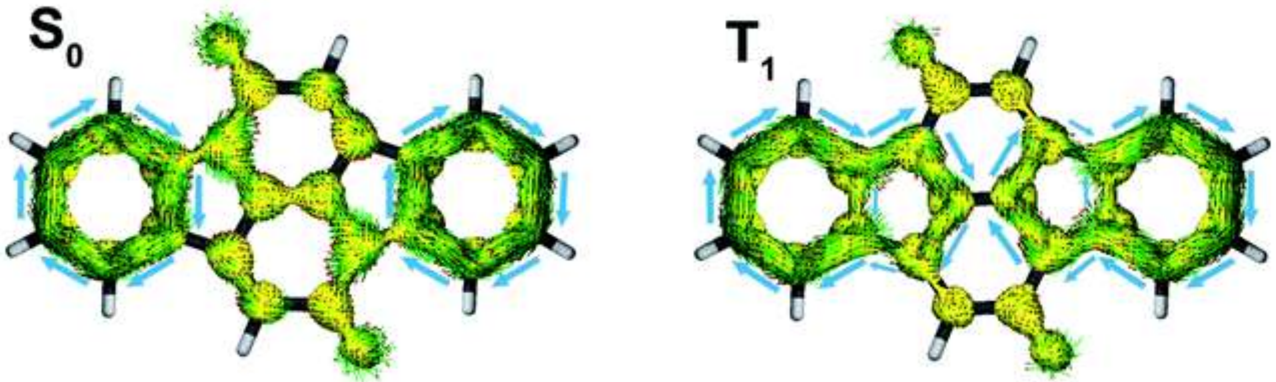
- **Polycyclic molecules with functional groups, e.g., carbonyl groups**

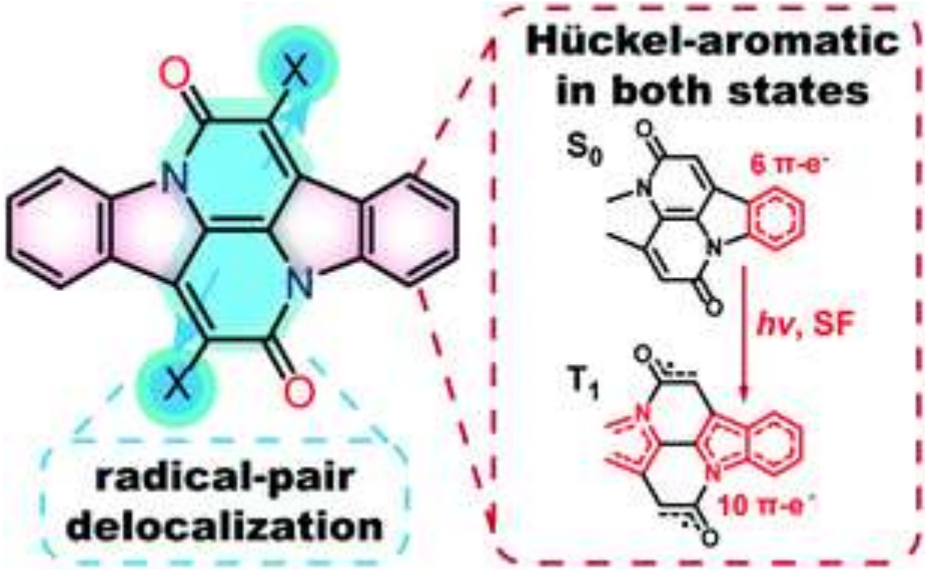
- **Monocyclic molecules where substituents facilitate the access of charge transfer states stabilized by Hückel-aromaticity.**

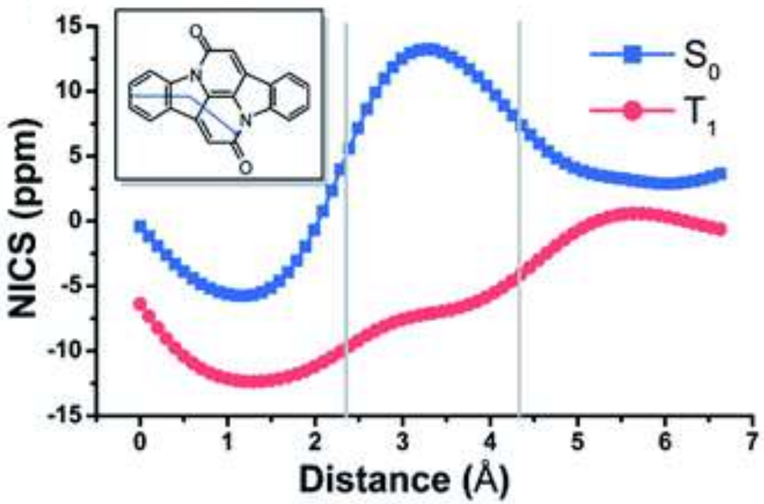
- **… and cases yet not identified.**

EXCITED STATE HÜCKEL-AROMATICITY: CIBALACKROTS AS EXAMPLES

- **Molecules can be Hückel-aromatic in excited states.**
- **In polycyclics, the Hückel-aromaticity can shift from monocyclic to bicyclic.**



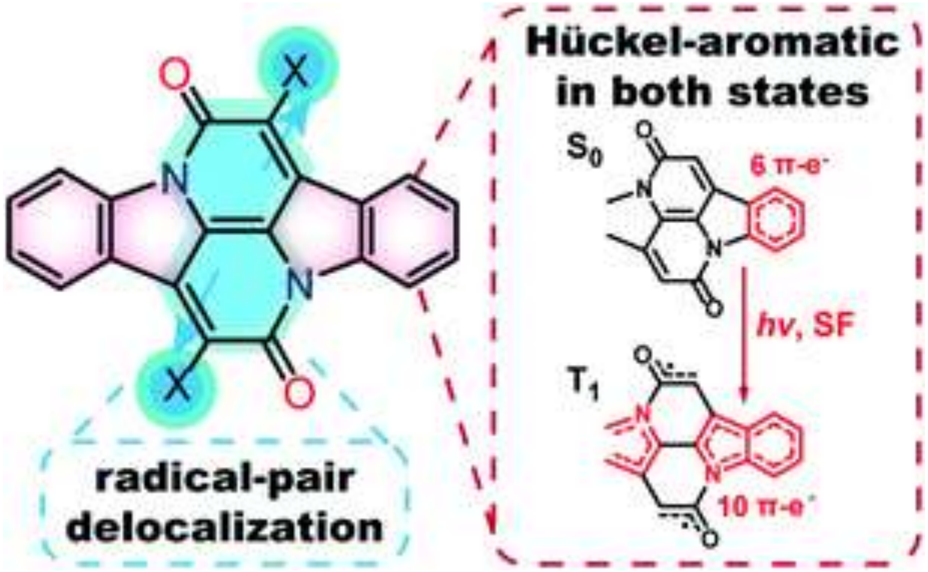


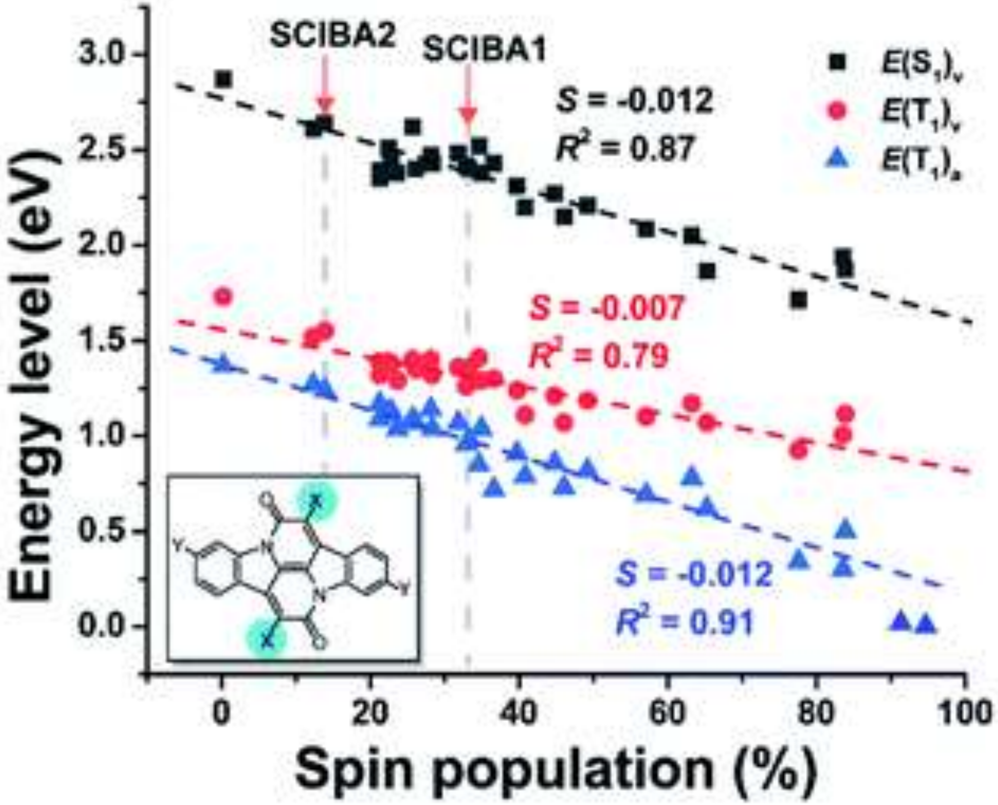


Zeng, El Bakouri, Szczepanik, Bronstein & Ottosson *Chem. Sci*, **2021**, *12*, 6159.

EXCITED STATE HÜCKEL-AROMATICITY: CIBALACKROTS AS EXAMPLES

- **Knowledge on aromaticity-type allows for improved molecular design.**
- **In Cibalackrots, radical stabilizing groups X at C_α position lower $E(T_1)$ and $E(S_1)$.**

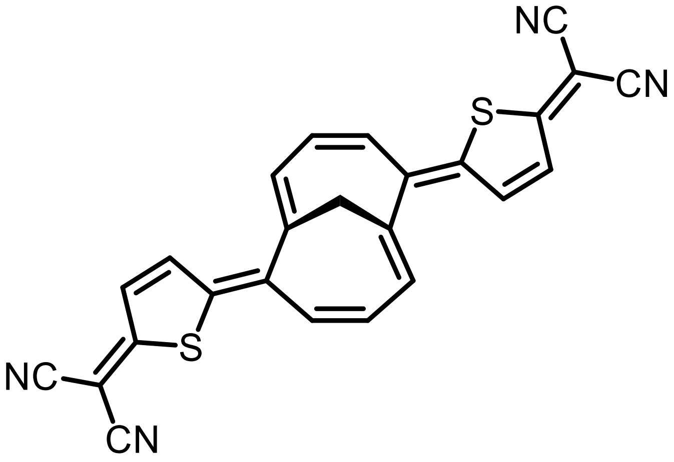


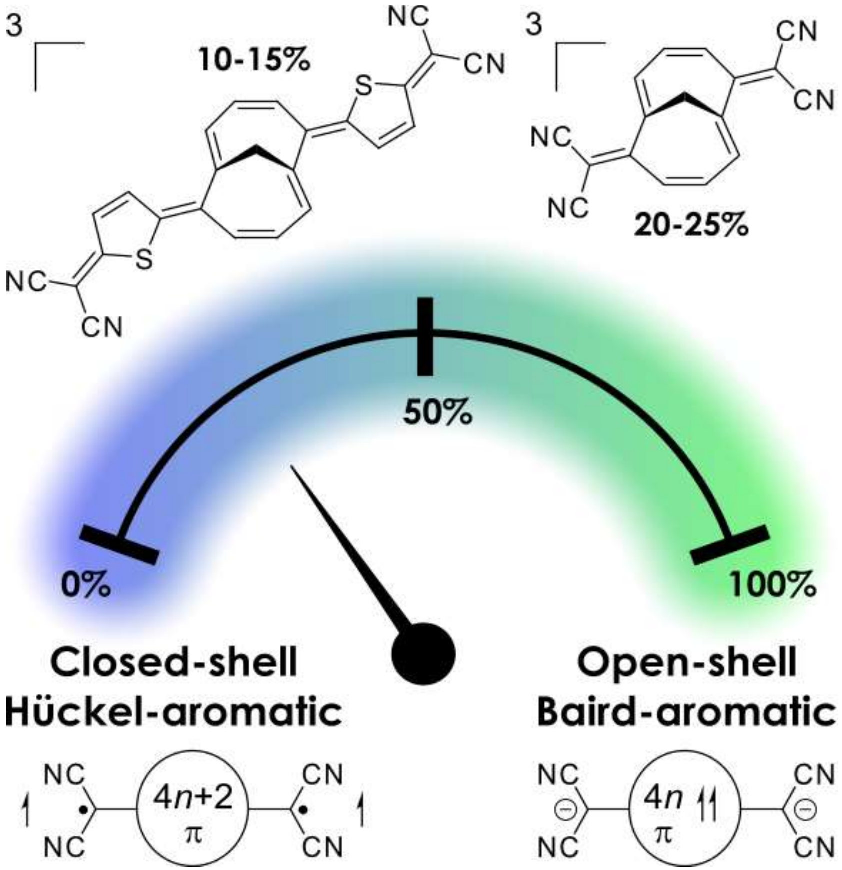


Zeng, El Bakouri, Szczepanik, Bronstein & Ottosson *Chem. Sci*, **2021**, *12*, 6159.

HÜCKEL-BAIRD HYBRID AROMATICITY

- **TMTQ** synthesized and characterized by the groups of Tovar and Casado in 2015
- A S_0-T_1 energy gap of merely 4.9 kcal/mol was attributed to Baird-aromatic stabilization of the T_1 state
- However, it this hypothesis well-founded?





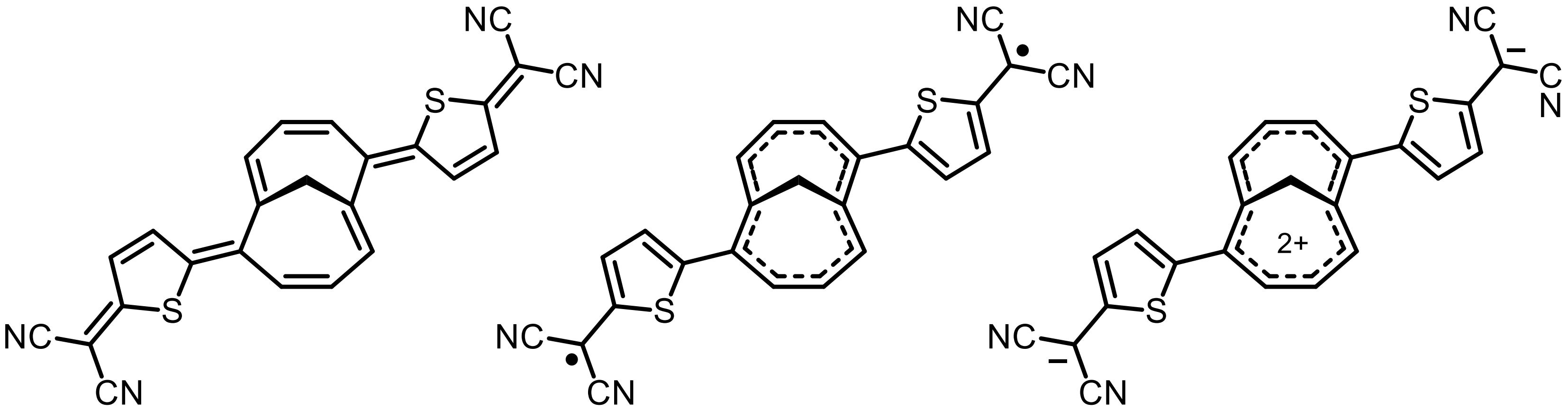
Angew. Chem., Int. Ed. 2015, *54*, 5888.

Jorner, Feixas, Ayub, Lindh, Solà, Ottosson. *Chem. - Eur. J.* 2016, *22*, 2793

HÜCKEL-BAIRD HYBRID AROMATICITY

Resonance structures for the S_0 and T_1 states:

- Tovar & Casado: The T_1 state is best described by the Baird-aromatic structure **TMTQ-c**
- But what favors **TMTQ-c** over Hückel-aromatic **TMTQ-b** as a normal pro-aromatic?



TMTQ-a
Quinoidal

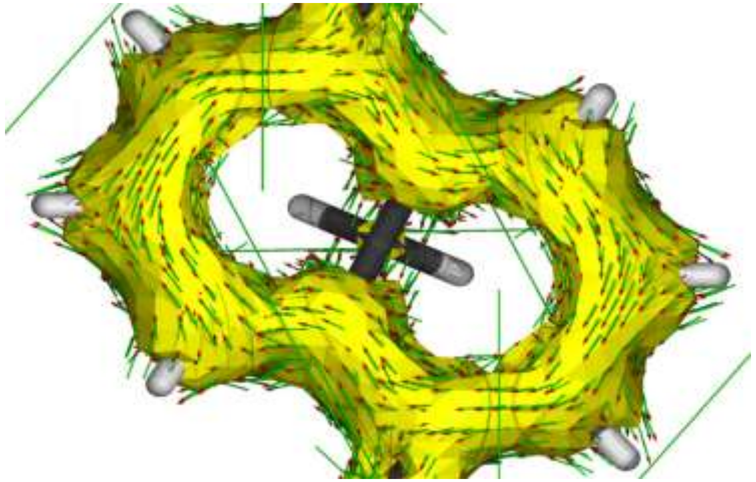
TMTQ-b
Hückel-aromatic

TMTQ-c
Baird-aromatic

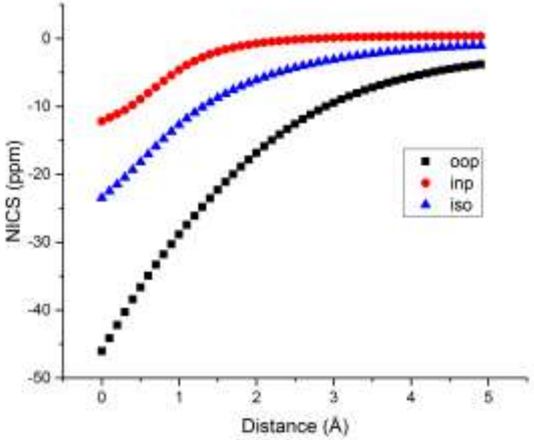
- DFT study with B3LYP, M06-2X and OLYP functionals with the 6-311+G(d,p) basis set
- Complemented by coupled-cluster type and multi-reference RASPT2 calculations.

HÜCKEL-BAIRD HYBRID AROMATICITY

Is TMTQ aromatic in T_1?



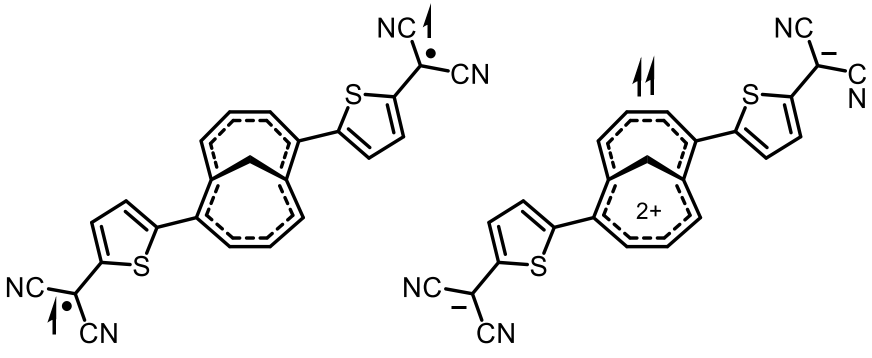
ACID plot:
Diatropic (aromatic) ring current



NICS scan:
Aromatic shape

→Yes it is aromatic according to MICD and NICS.

TMTQ-b and/or TMTQ-c are important. Are they equally important or is either dominating?



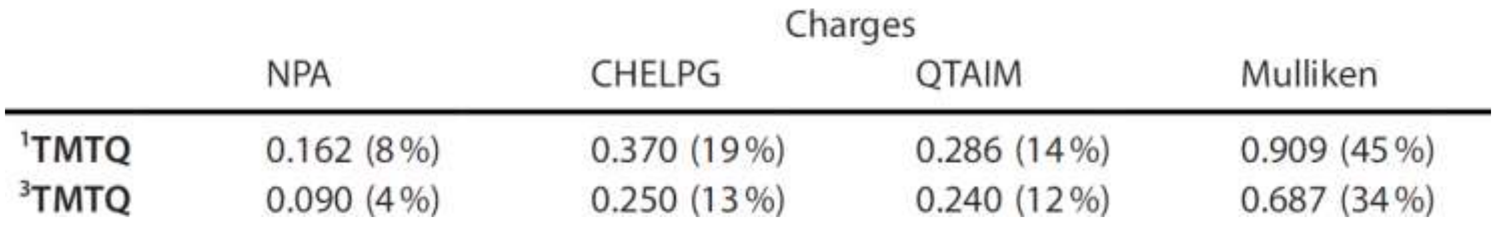
TMTQ-b **TMTQ-c**

HÜCKEL-BAIRD HYBRID AROMATICITY

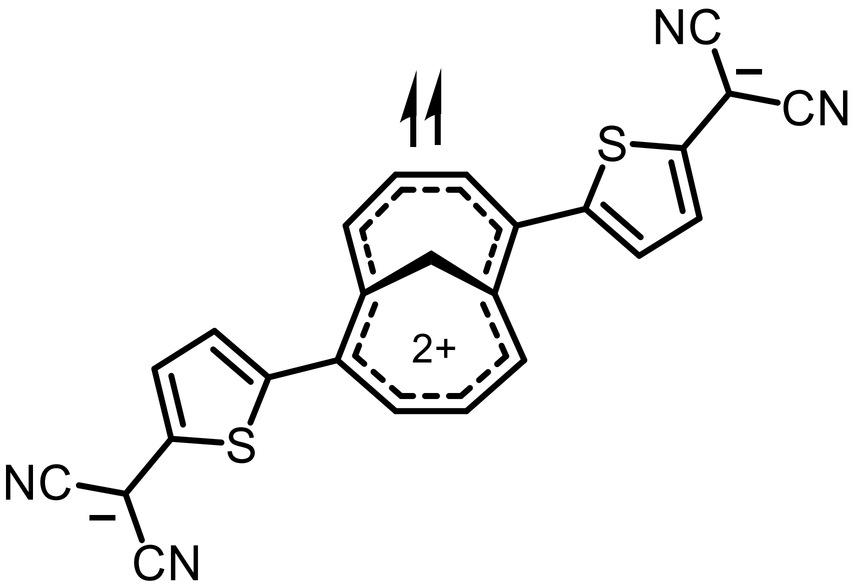
Is TMTQ aromatic in T_1?

Condition I for Baird-aromaticity:

A charge of +2 should be present on the M10 unit

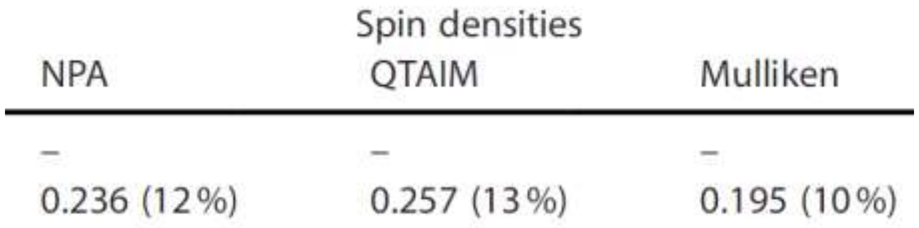


	Charges			
	NPA	CHELPG	QTAIM	Mulliken
^{1}TMTQ	0.162 (8%)	0.370 (19%)	0.286 (14%)	0.909 (45%)
^{3}TMTQ	0.090 (4%)	0.250 (13%)	0.240 (12%)	0.687 (34%)



Condition II for Baird-aromaticity

A spin of 2 should be present on the M10A unit



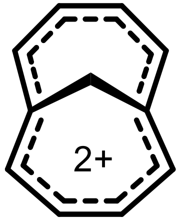
	Spin densities		
	NPA	QTAIM	Mulliken
	–	–	–
^{3}TMTQ	0.236 (12%)	0.257 (13%)	0.195 (10%)

HÜCKEL-BAIRD HYBRID AROMATICITY

Is TMTQ aromatic in T_1?

- **Electronic aromaticity index FLU was divided into separate contributions from α and β electrons and their difference $\Delta FLU_{\alpha\beta}$**
- **Significant $\Delta FLU_{\alpha\beta}$ values are expected for Baird-aromatic annulenes and values closer to zero for Hückel-aromatic annulenes**

	^{3}TMTQ	^{3}M10A^{2+}
FLU	0.0046	0.0058
FLU_α	0.0041	0.0029
FLU_β	0.0052	0.0145
$\Delta FLU_{\alpha\beta}$	-0.0010	-0.0116
$\Delta FLU_{\alpha\beta}/FLU$	-0.2233	-2.0005

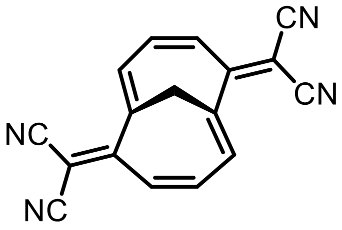


Fully (100%) Baird-aromatic

But TMTQ is only ~10% Baird-aromatic

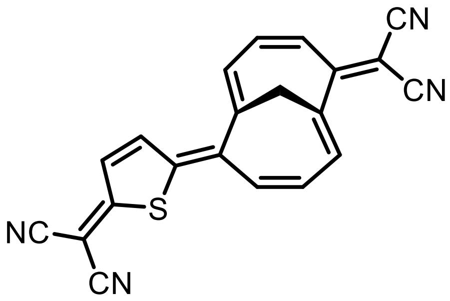
HÜCKEL-BAIRD HYBRID AROMATICITY

- **The smaller analogues MQ and TMQ show higher degree of Baird aromaticity**
- **They could be called hybrids which are simultaneously Hückel and Baird aromatic**



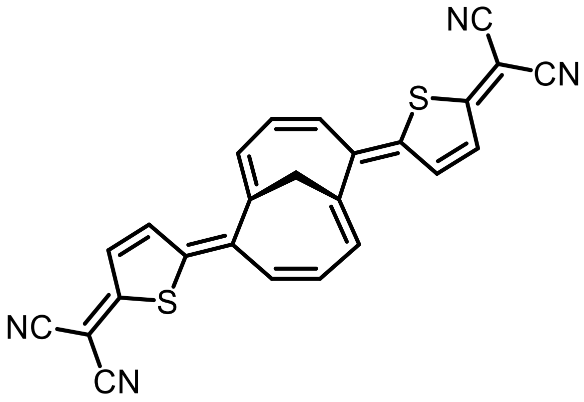
MQ

25%



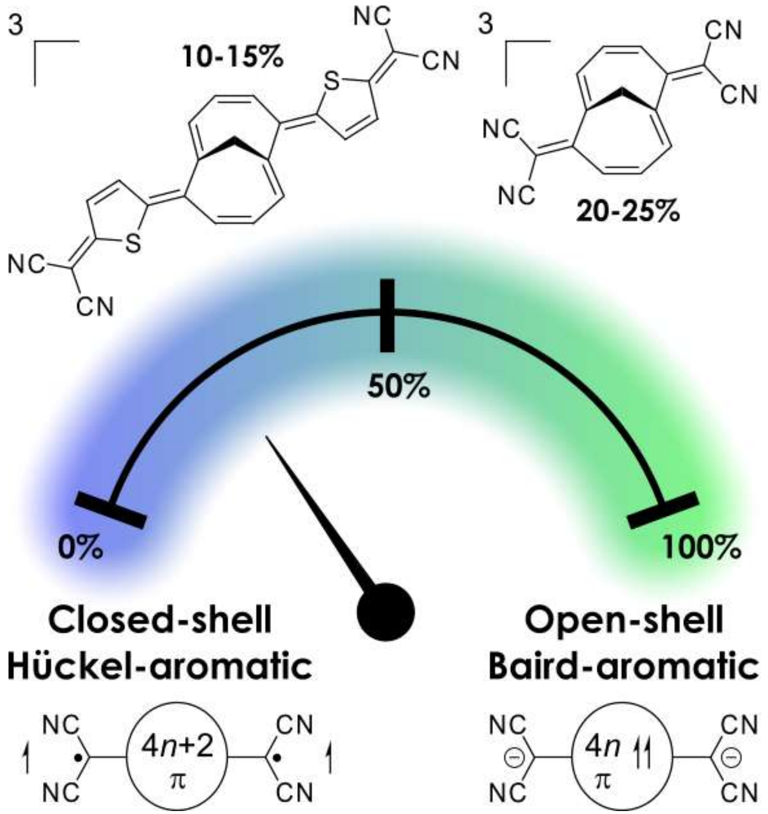
TMQ

18%



TMTQ

12%



LIMITATIONS:

- TO WHICH ELECTRONIC STATES CAN THE CONCEPTS WE APPLIED?
- AT WHAT RING SIZE ARE THE CONCEPTS NOT APPLICABLE ANYMORE?

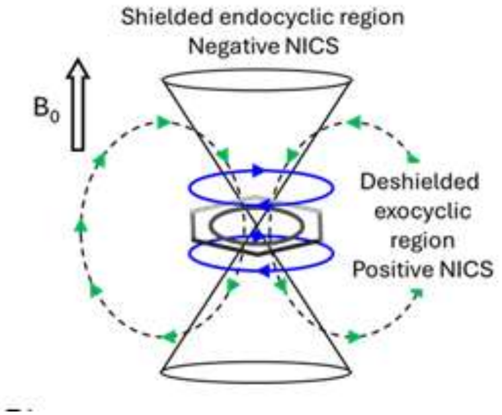
COMPLICATIONS:

- COMPUTATIONAL METHOD VARIATIONS (*e.g.* FUNCTIONALS) …
- AS WELL AS VARIATIONS BETWEEN AROMATICITY DESCRIPTORS

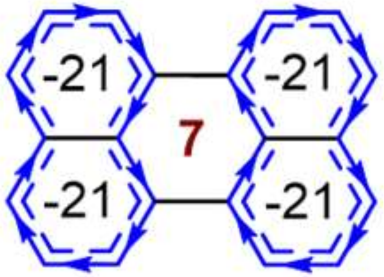
PITFALLS:

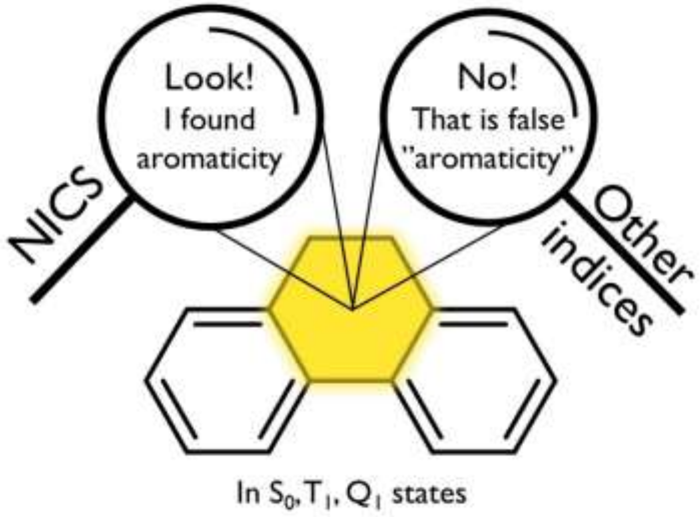
- COMPUTATIONAL: AROMATICITY INDICATORS FALSELY INDICATING AROMATICITY
- CONCEPTUAL: EXCITED STATE HÜCKEL-AROMATICITY INSTEAD OF BAIRD-AROMATICITY

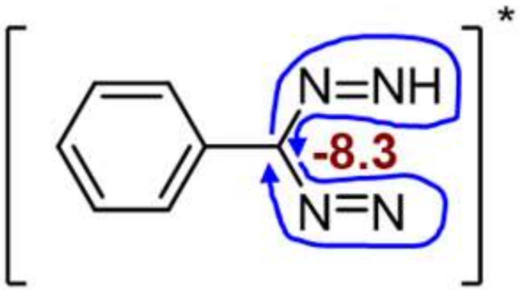
NICS – AN EASY-TO-USE AROMATICITY INDEX WITH A SEVERE PITFALL



- The Nucleus Independent Chemical Shift (NICS) is the negative of the shielding at a selected point in space.
- Does not contain information on how that shielding is generated.
- Shielding can originate from ring currents or from local currents at specific atoms or groups in a molecule.



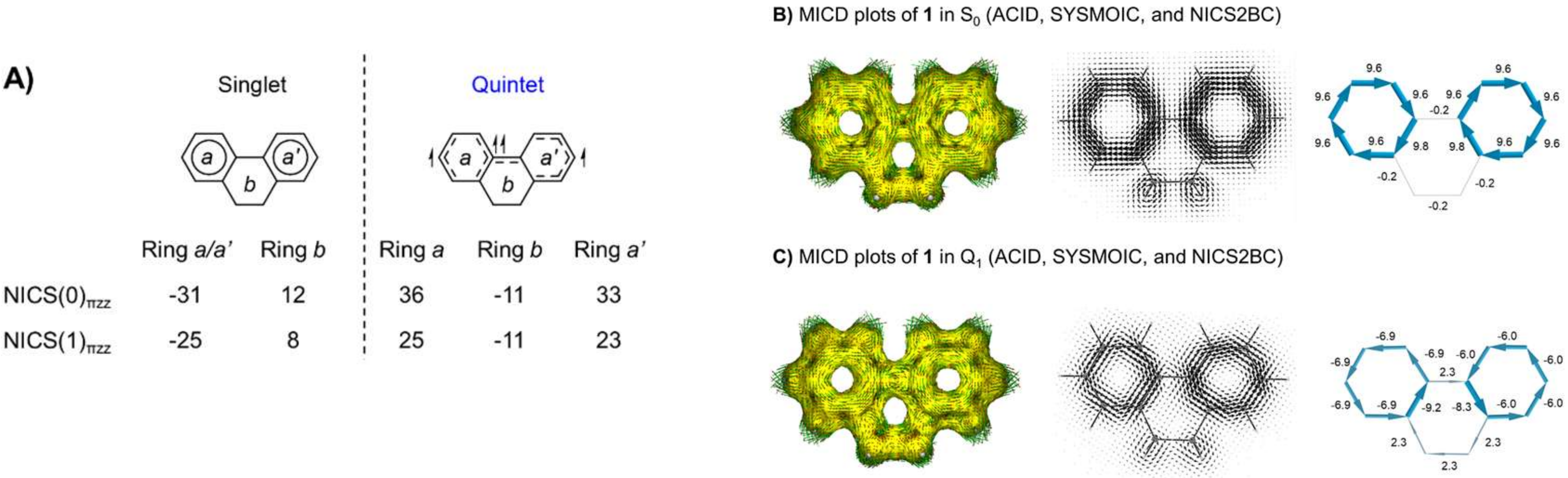




Mayer & Ottosson. *J. Phys. Org Chem. A*, **2025**, *39*, e70000

NICS – AN EASY-TO-USE AROMATICITY INDEX WITH A SEVERE PITFALL

- **NICS**; the partially saturated ring *b* has some antiaromatic character in S_0 and some aromatic character in the lowest quintet state Q_1
- **Is that a correct description of (anti)aromaticity in the two states?**



	Ring *a*/*a'*	Ring *b*	Ring *a*	Ring *b*	Ring *a'*
$NICS(0)_{\pi zz}$	-31	12	36	-11	33
$NICS(1)_{\pi zz}$	-25	8	25	-11	23

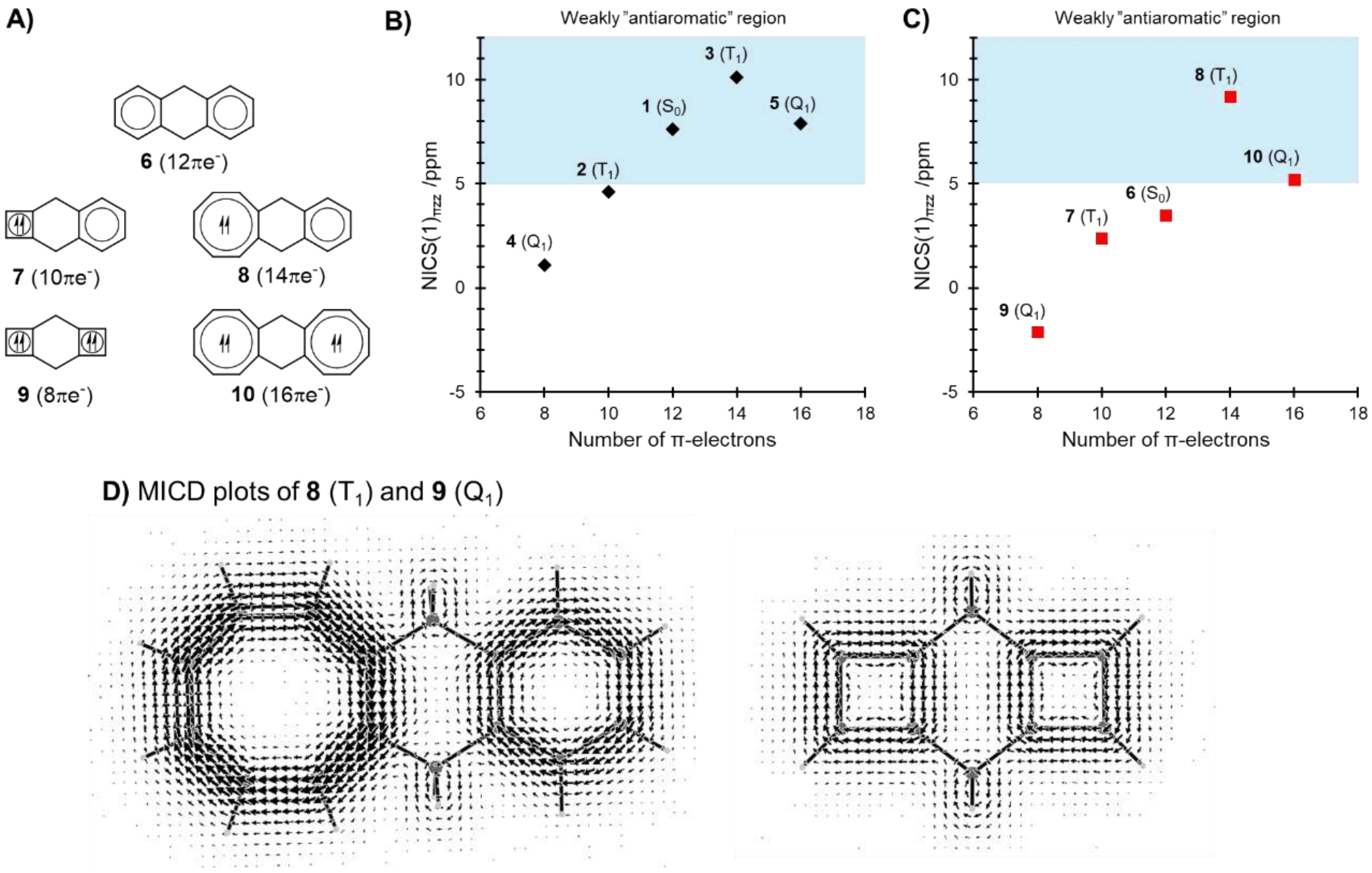
B) MICD plots of **1** in S_0 (ACID, SYSMOIC, and NICS2BC)

C) MICD plots of **1** in Q_1 (ACID, SYSMOIC, and NICS2BC)

Mayer & Ottosson. *J. Phys. Org Chem. A*, **2025**, *39*, e70000

NICS – AN EASY-TO-USE AROMATICITY INDEX WITH A SEVERE PITFALL

- **Large aromatic (diatropic) rings generate large deshielding regions**
- **False ”antiaromatic” character appear in small ring between two strongly diatropic rings.**



Mayer & Ottosson. *J. Phys. Org Chem. A*, **2025**, *39*, e70000

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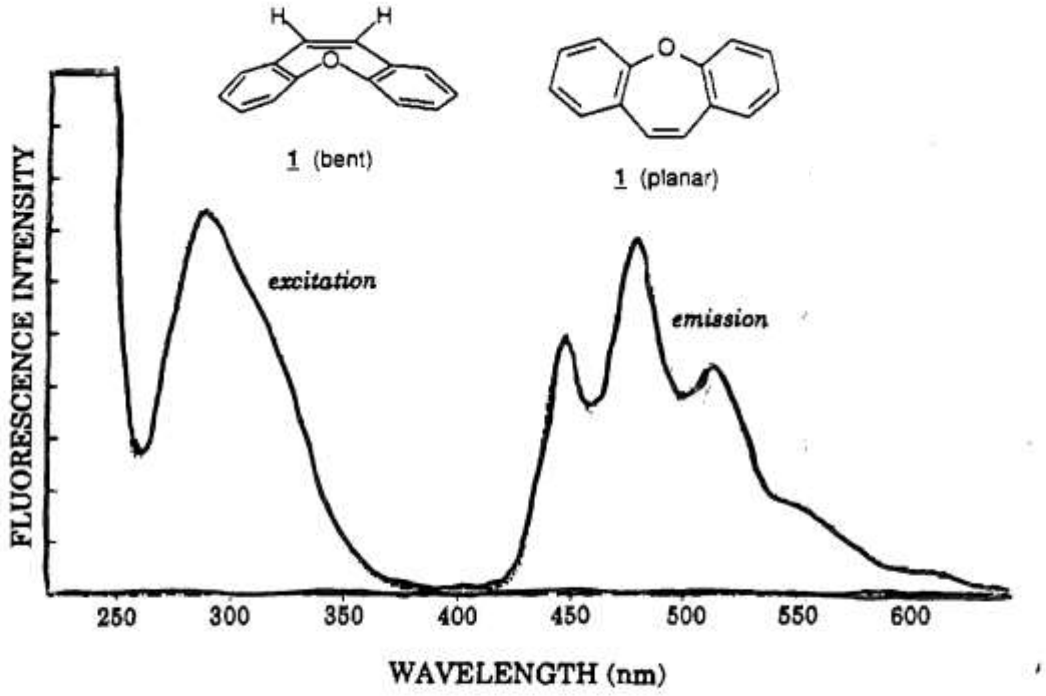
PITFALLS:

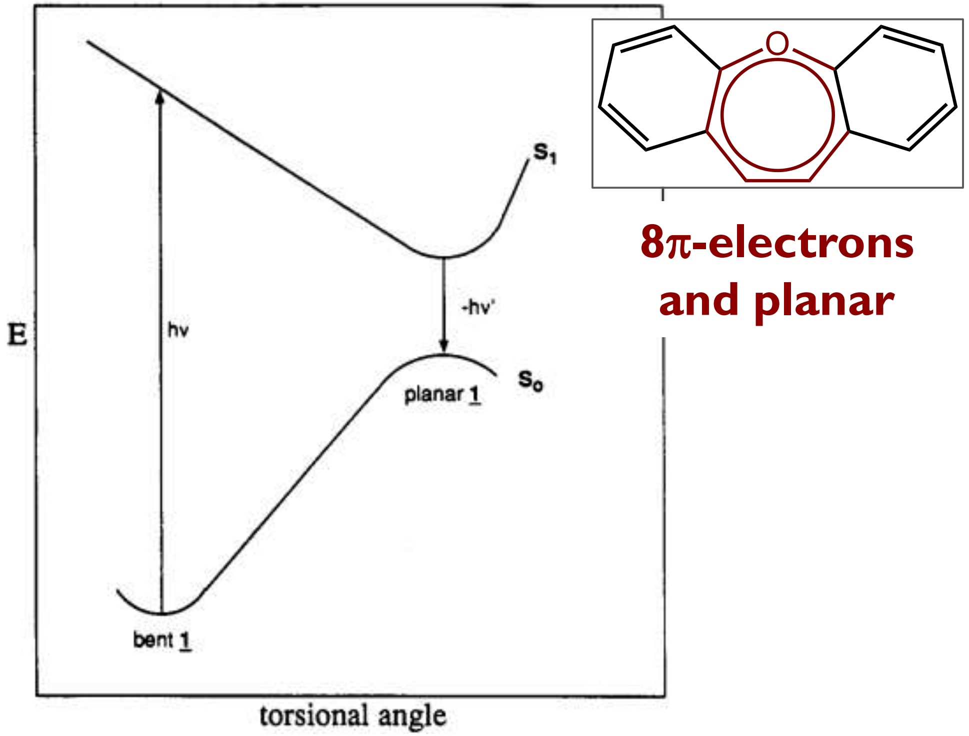
- EXPERIMENTAL: AN OBSERVED PROPERTY FALSELY INDICATES AROMATICITY
- CONCEPTUAL: EXCITED STATE HÜCKEL-AROMATICITY INSTEAD OF BAIRD-AROMATICITY

FIRST SPECTROSCOPIC EVIDENCE OF EXCITED STATE AROMATICITY … LATER COMPUTATIONAL SUPPORT

Large Stokes' shift in dibenz[*b*,*f*]oxepin

Shukla & Wan *J. Am. Chem. Soc.* **1993**, *115*, 2990.





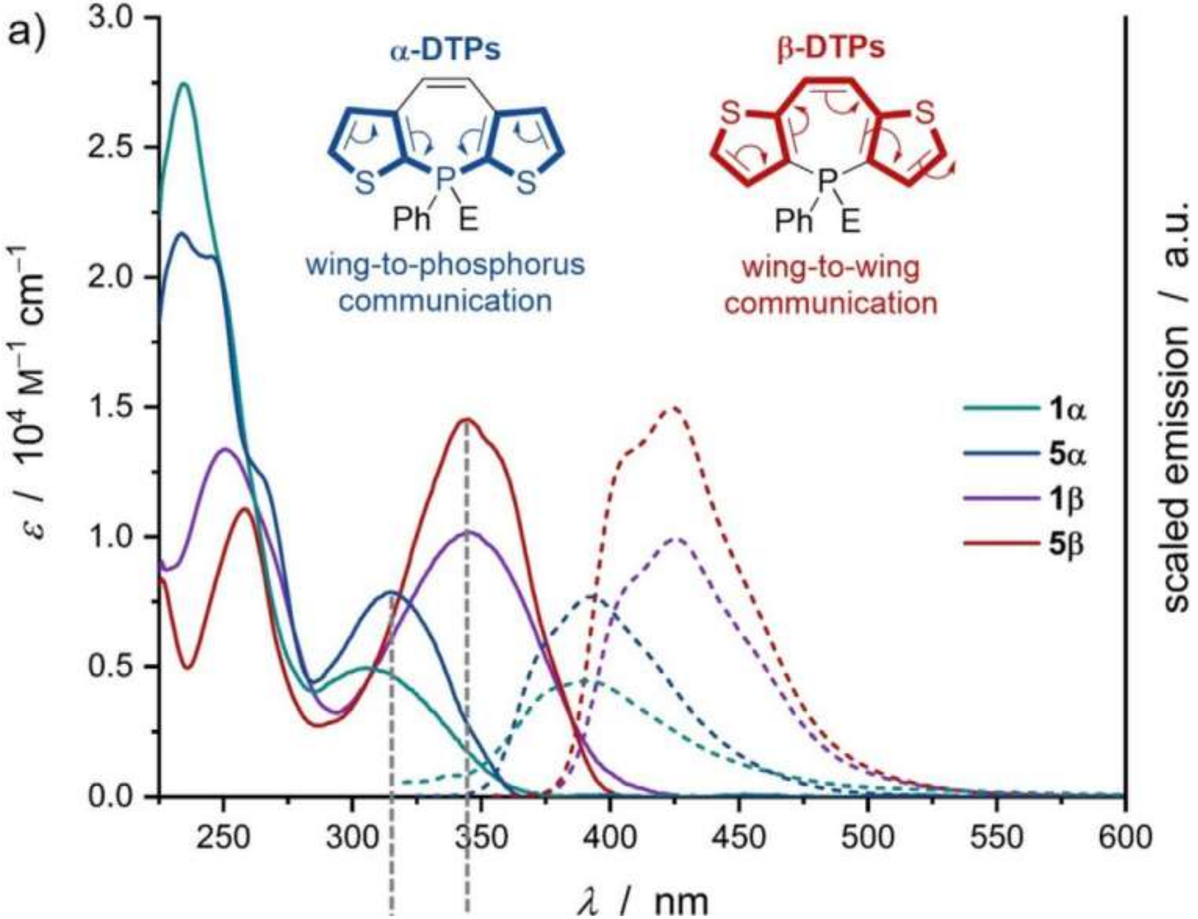
8π-electrons and planar

SPECTROSCOPIC PITFALL INDICATION OF EXCITED STATE AROMATICITY

Stokes' shifts in dibenzannelated P-containing 7-membered rings

Padberg *et al. Chem. Eur. J.* **2020**, *26*, 3474.

- **Compounds 1 have E = lone-pair while compounds 5 have E = O**
- **Both the compounds with trivalent and those with pentavalent P show strong Stokes' shift. It is concluded that it does not stem from gain of ESA.**



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VARIATION WITH (ANTI)AROMATICITY DESCRIPTOR

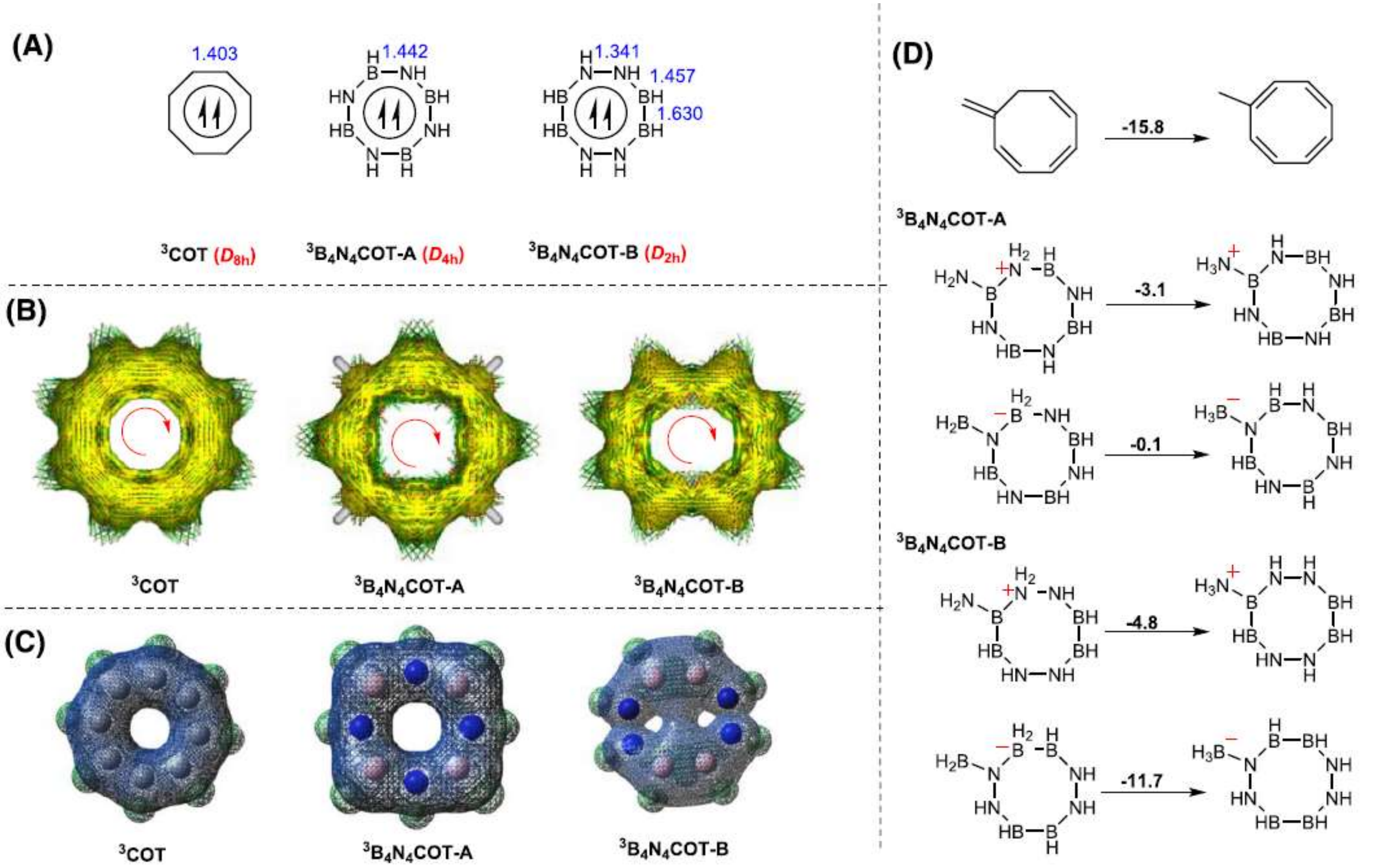
Received: 29 August 2022 | Revised: 5 October 2022 | Accepted: 11 October 2022
DOI: 10.1002/poc.4455

RESEARCH ARTICLE

Journal of Physical Organic Chemistry WILEY

Azaboracyclooctatetraenes reveal that the different aspects of triplet state Baird-aromaticity are nothing but different

Preethanuj Preethalayam[1] | Nathalie Proos Vedin[1] | Slavko Radenković[2] | Henrik Ottosson[1]



Preethalayam *et al.* *J. Phys. Org. Chem.* **2023**, *36*, e4455.

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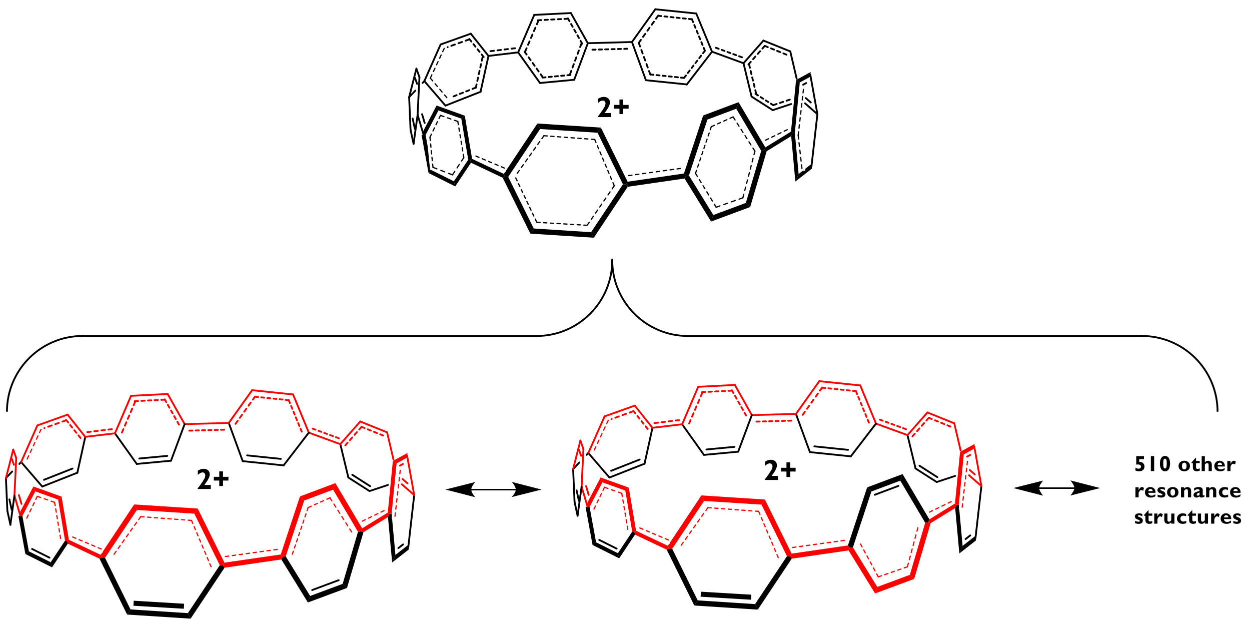
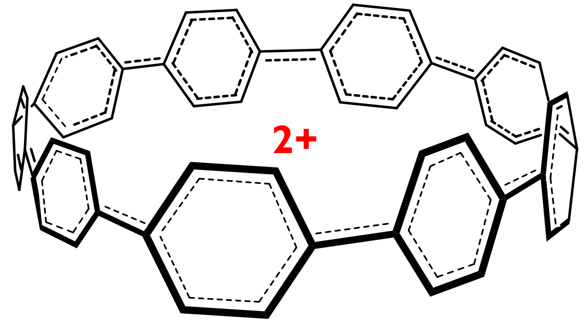
THE T_1 STATES OF [*n*]CPPs IN THE ZILBERG-HAAS INTERPRETATION

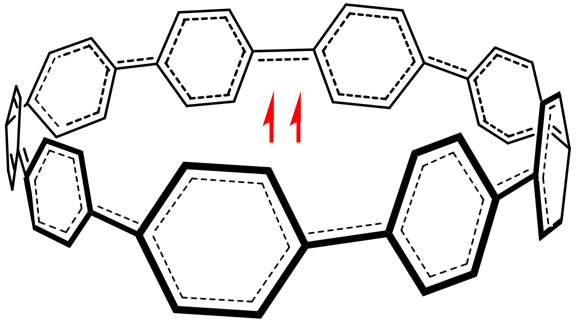


Red path: A cycle with 4 × 9 - 2 = 34 π-electrons, thus potentially Hückel-aromatic.

[9]CPP dication: A Hückel-aromatic cycle with 4 × 9 - 2 π-electrons.



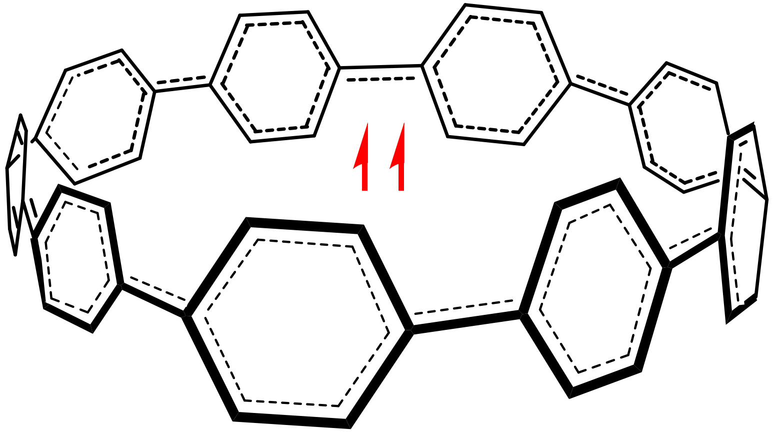
T_1 state [9]CPP: A Hückel-aromatic cycle with 4 × 9 - 2 π-electrons plus two non-bonding π_α-electrons, **i.e., Baird-aromatic**.



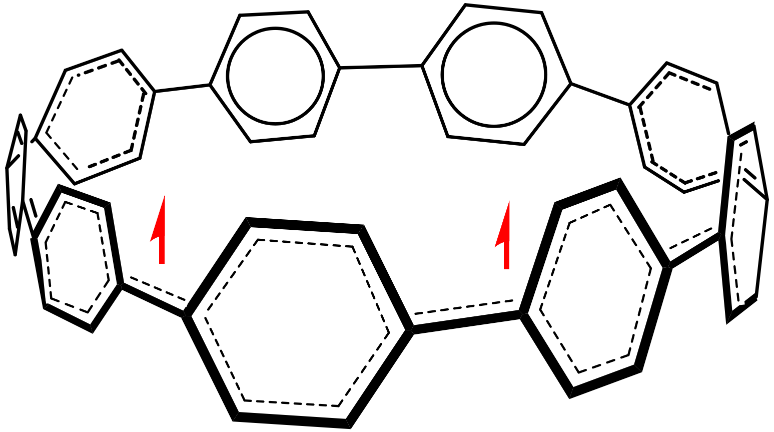
Ayub, El Bakouri, Smith, Jorner, & Ottosson. *J. Phys. Chem. A*, **2021**, *125*, 570.

CAN [*n*]CPPs ALSO BE AROMATIC "CHAMELEONS"?

T_1 state Baird-aromatic [9]CPP



T_1 state non-aromatic [9]CPP

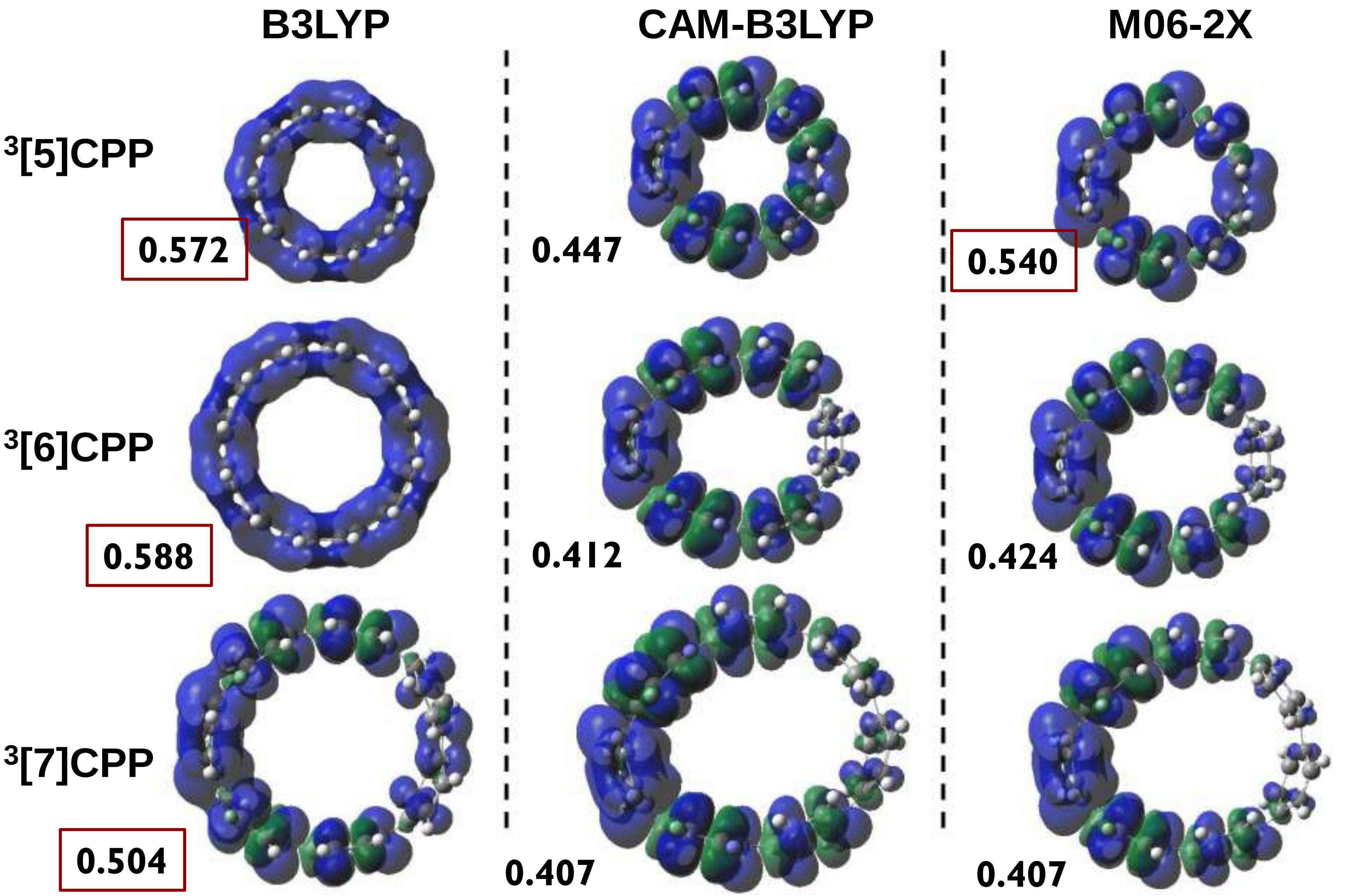


When does Baird-aromaticity in the macrocycle win over local Hückel-aromaticity of individual benzene rings?

Ayub, El Bakouri, Smith, Jorner, & Ottosson. *J. Phys. Chem. A*, **2021**, *125*, 570.

BAIRD-AROMATICITY IN T_1 STATE [*n*]CPPs: SIZE AND METHOD VARIATION

- Spin densities and HOMA values in fair agreement.
- **Break-point for strong Baird-aromaticity is between [6]- and [7]CPP with B3LYP, and before [5]CPP with CAM-B3LYP (and M06-2X).**
- **Yet, [5]CPP is still Baird-aromatic with HOMA using M06-2X.**



UDFT/6-311+G(d,p)

BAIRD-AROMATICITY IN T$_1$ STATE [*n*]CPPs: SIZE AND METHOD VARIATION

- Spin densities and NICS in fair agreement.
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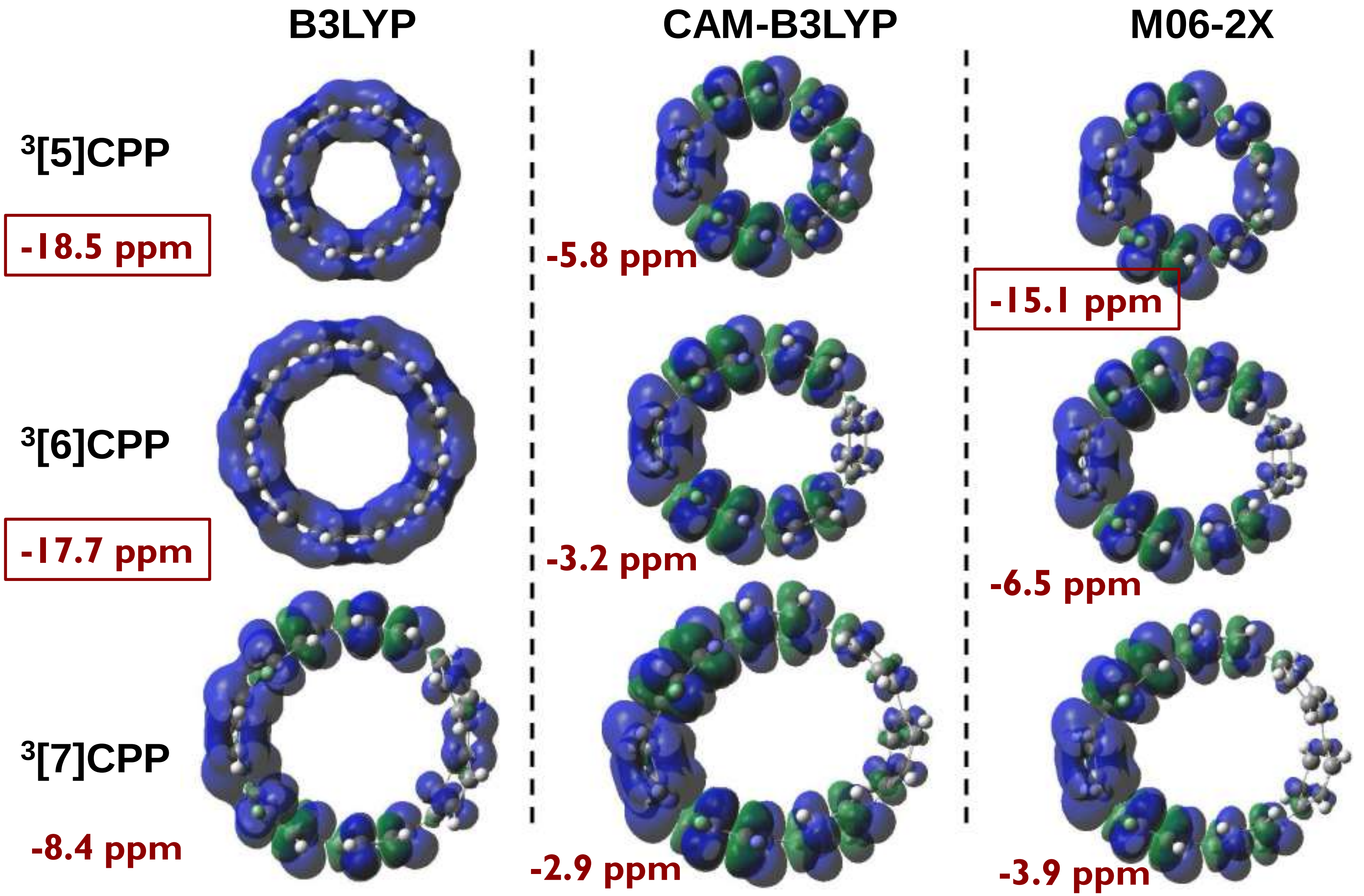

UDFT/6-311+G(d,p)

UCCSD(T)/cc-pVTZ CALCULATIONS OF T_1 STATE [5]CPP

Run high-quality single-point UCCSD(T) calculations at optimal UDFT geometries to check which UDFT gives the best geometry

State	T_1		
Geometry	B3LYP	CAM-B3LYP	M06-2X
BLYP ref wave function	0.0	0.9	-0.1
ROHF ref wave function	0.0	5.2	2.3

Relative energies in kcal/mol.

State	T_1		
Geometry	B3LYP	CAM-B3LYP	M06-2X
BLYP ref wave function	0.017	0.023	0.022
ROHF ref wave function	0.013	0.018	0.015

Findings:

- The T_1 state geometry of [5]CPP at CAM-UB3LYP level is far from the optimal UCCSD(T) geometry.
- Whether UB3LYP or UM06-2X T_1 state geometry gives the lowest UCCSD(T) energy depends on the reference wave function used.
- T_1 diagnostics values of the UCCSD wavefunction reveal low multi-configurational character except for calculations using BLYP reference based on the CAM-B3LYP and M06-2X geometries.

Ayub, El Bakouri, Smith, Jorner, & Ottosson. *J. Phys. Chem. A*, **2021**, *125*, 570.

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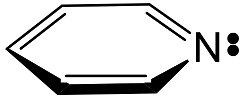
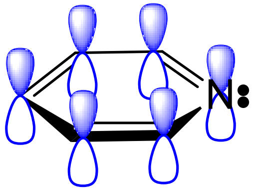
THE n,π* STATES OF HETEROAROMATICS: ARE THEY AROMATIC, NONAROMATIC OR ANTIAROMATIC?

HETEROAROMATICS IN THEIR LOWEST n,π* AND π,π* STATES

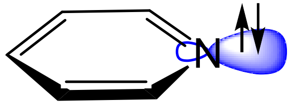
Explore aromatic character of the α and β spins separately

Pyridine in S_0



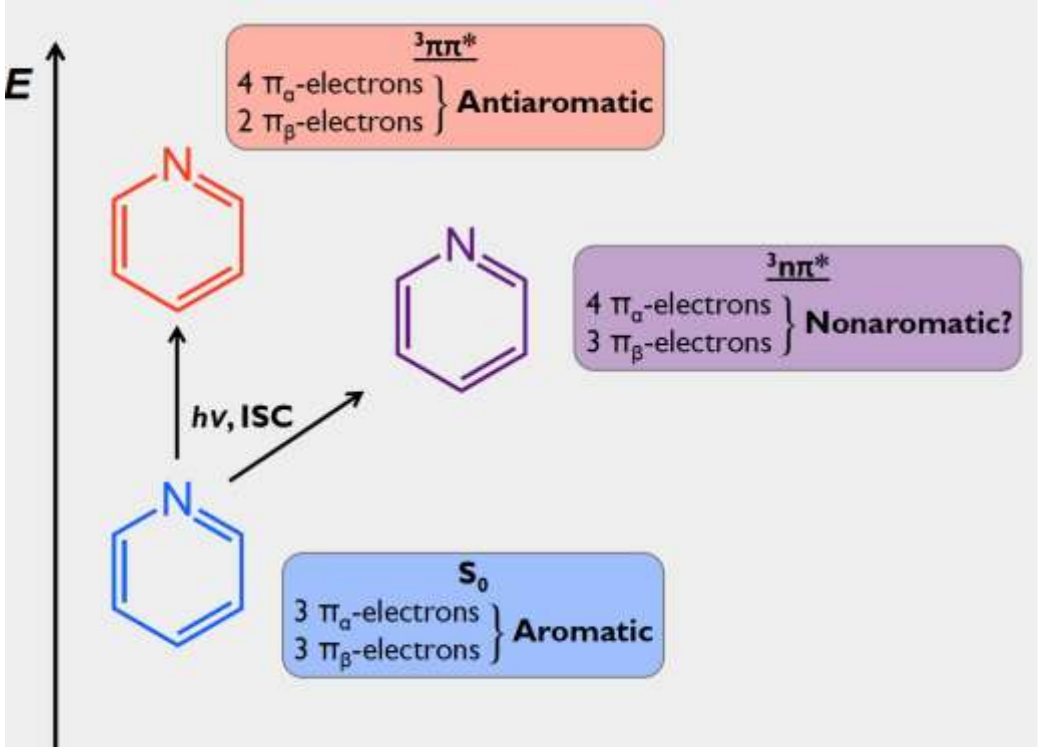


6 π-electrons

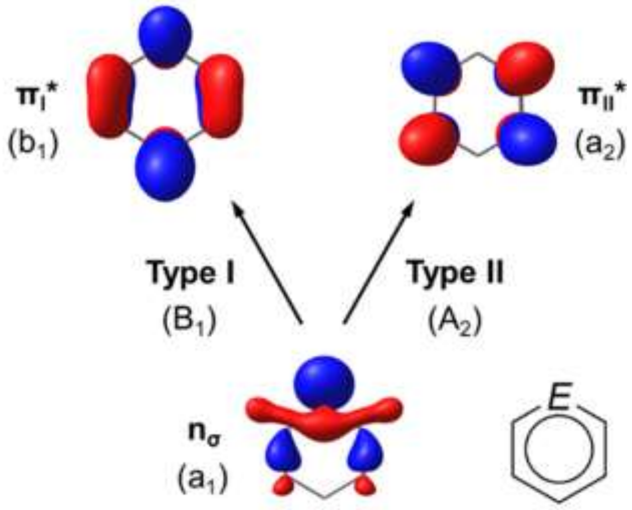


2 electrons in in-plane lone-pair

π,π* *versus* n,π* states



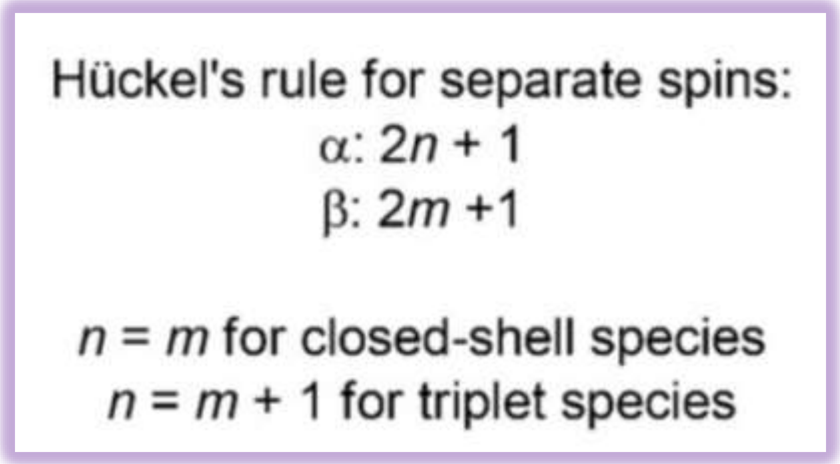
Two types of n,π* states



The B_1 states are lowest in nearly all cases

Proos Vedin, Escayola, Radenković, Solà & Ottosson. *J. Phys. Chem. A*, **2024**, *128*, 4493

HETEROAROMATICS IN THEIR LOWEST n,π* AND π,π* STATES



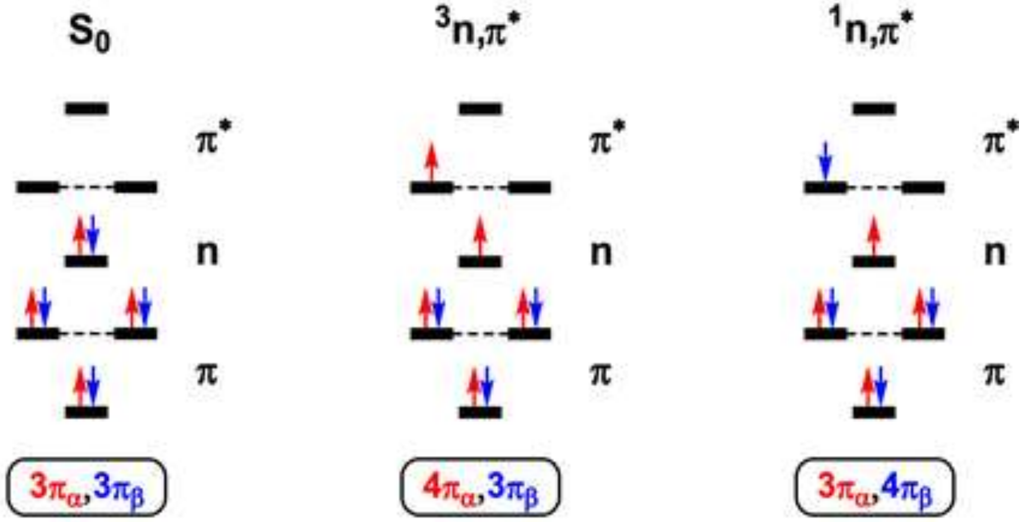
Hückel's rule for separate spins:
α: 2*n* + 1
β: 2*m* +1

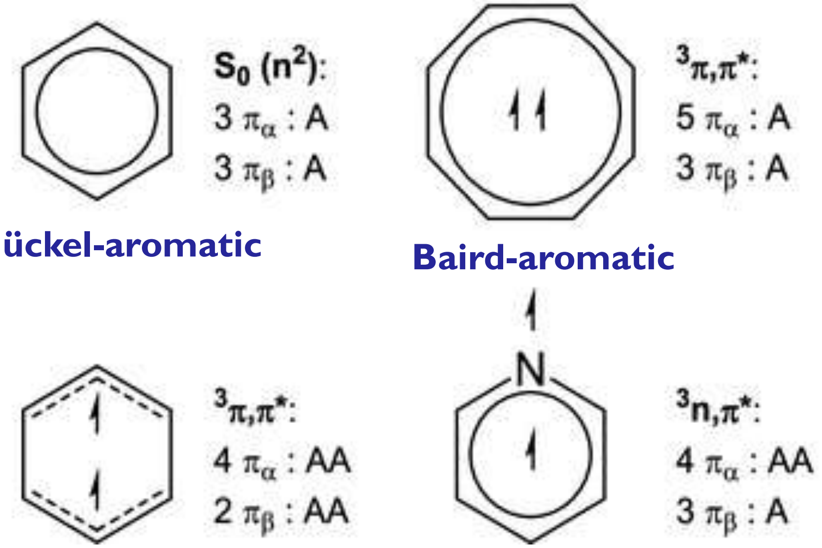
n = *m* for closed-shell species
n = *m* + 1 for triplet species

Mandado's rule:

Mandado, Graña & Pérez-Juste

J. Chem. Phys. **2008**, *129*, 164114





Hückel-aromatic

Baird-aromatic

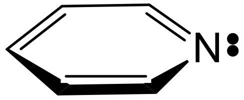
Baird-antiaromatic

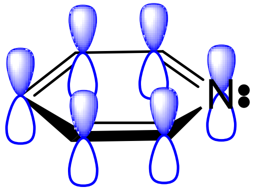
Nonaromatic?

Proos Vedin, Escayola, Radenković, Solà & Ottosson. *J. Phys. Chem. A*, **2024**, *128*, 4493

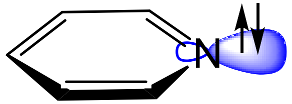
HETEROAROMATICS IN THEIR LOWEST n,π* AND π,π* STATES

Pyridine in S_0



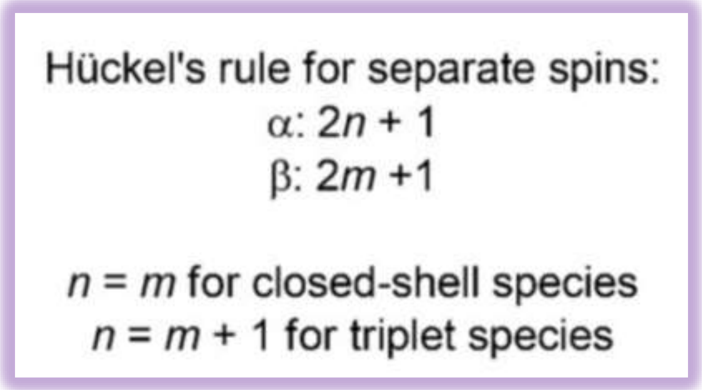


6 π-electrons



2 electrons in an in-plane lone-pair

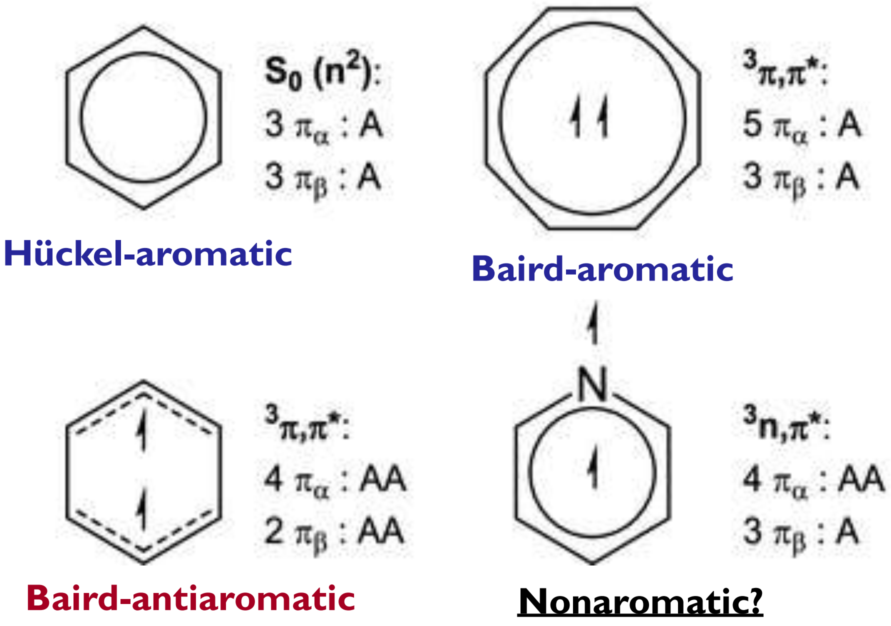
π,π* *versus* n,π* states
Explore aromatic character of α and β spins separately



Hückel's rule for separate spins:
α: $2n + 1$
β: $2m + 1$

$n = m$ for closed-shell species
$n = m + 1$ for triplet species

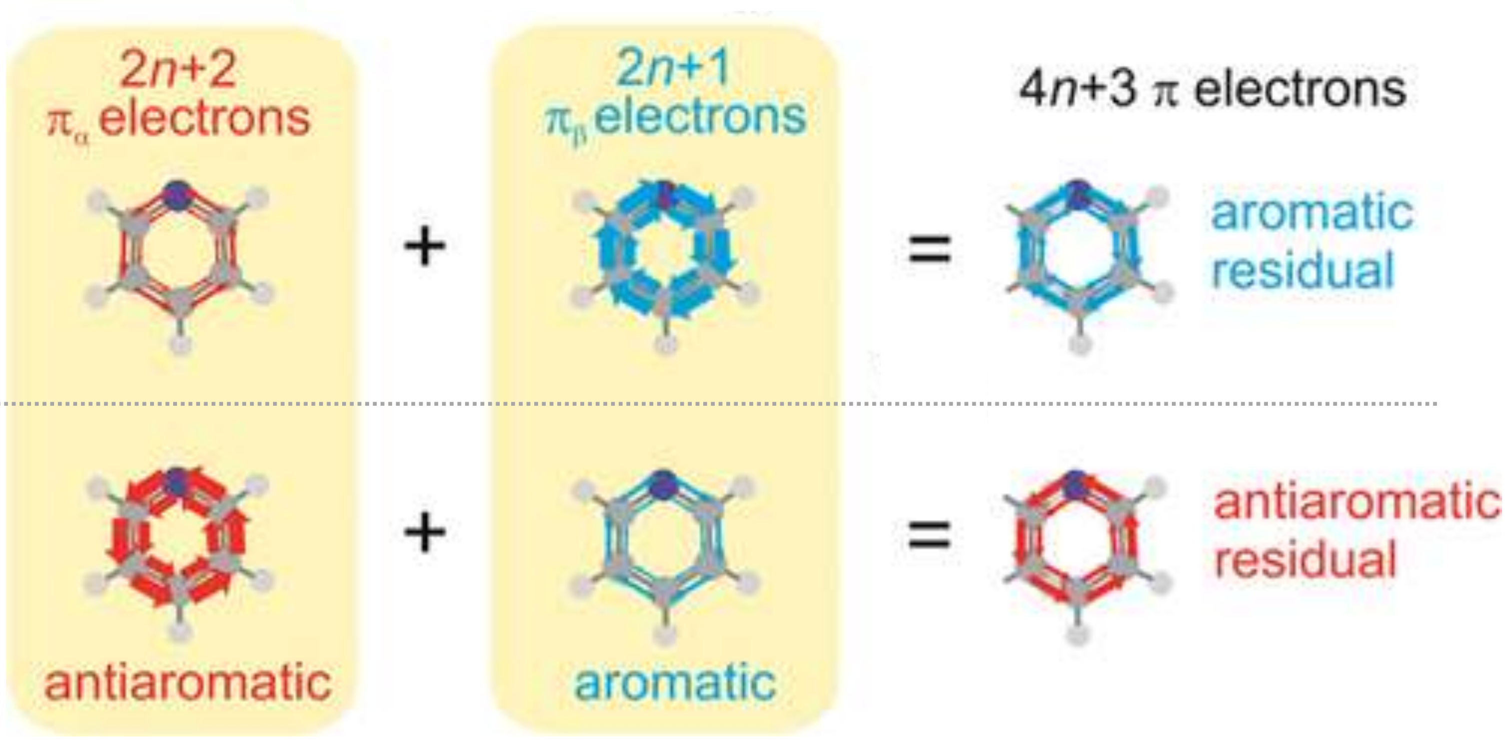
Also called Mandado's rule
Mandado, Graña & Pérez-Juste
J. Chem. Phys. **2008**, *129*, 164114



Proos Vedin, Escayola, Radenković, Solà & Ottosson. *J. Phys. Chem. A*, **2024**, *128*, 4493

HETEROAROMATICS IN THEIR LOWEST n,π* STATES

The aromatic, nonaromatic or antiaromatic character of n,π* states
depends on residual between the π_α and π_β spin components.



The two extremes

An n,π* state with
***aromatic* character**

An n,π* state with
***antiaromatic* character**

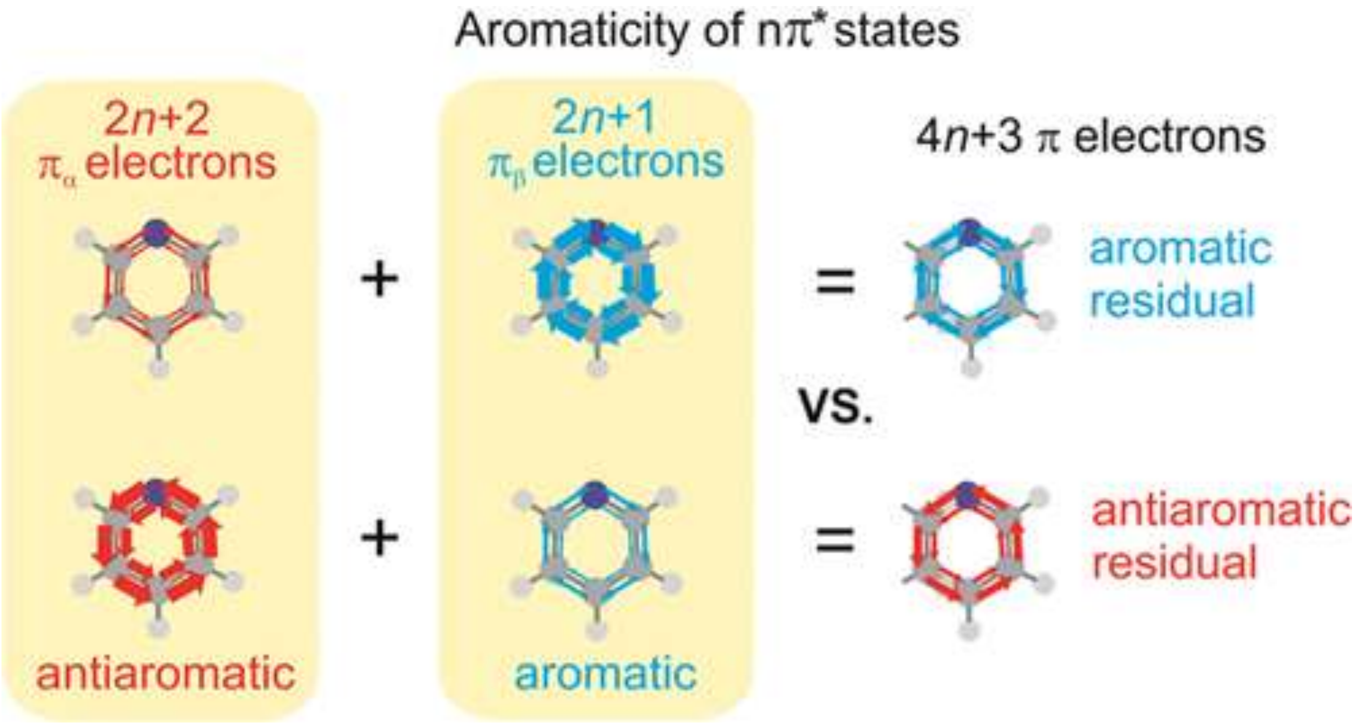
But this (anti)aromatic character varies with descriptor used.

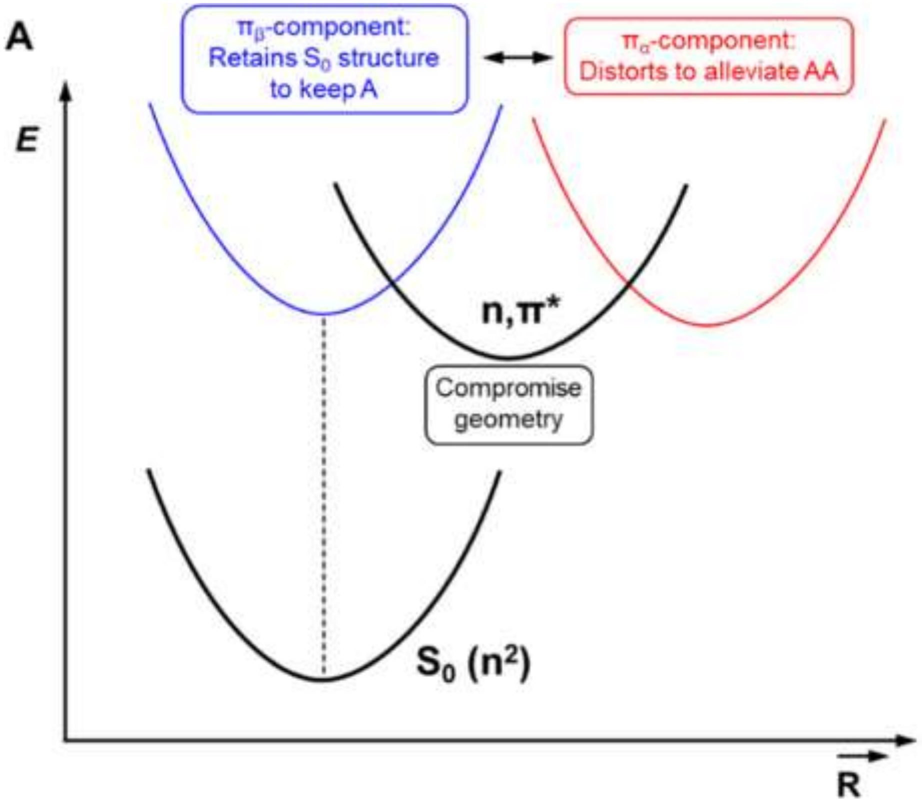
Proos Vedin, Escayola, Radenković, Solà & Ottosson. *J. Phys. Chem. A*, **2024**, *128*, 4493

HETEROAROMATICS IN THEIR LOWEST n,π* STATES

The (anti)aromatic character of n,π* states depends on <u>the residual between the π_α and π_β spin components.</u>

A tug-of-war between an aromatic and an antiaromatic component





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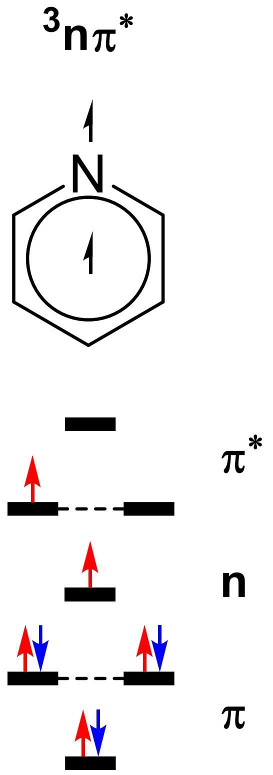
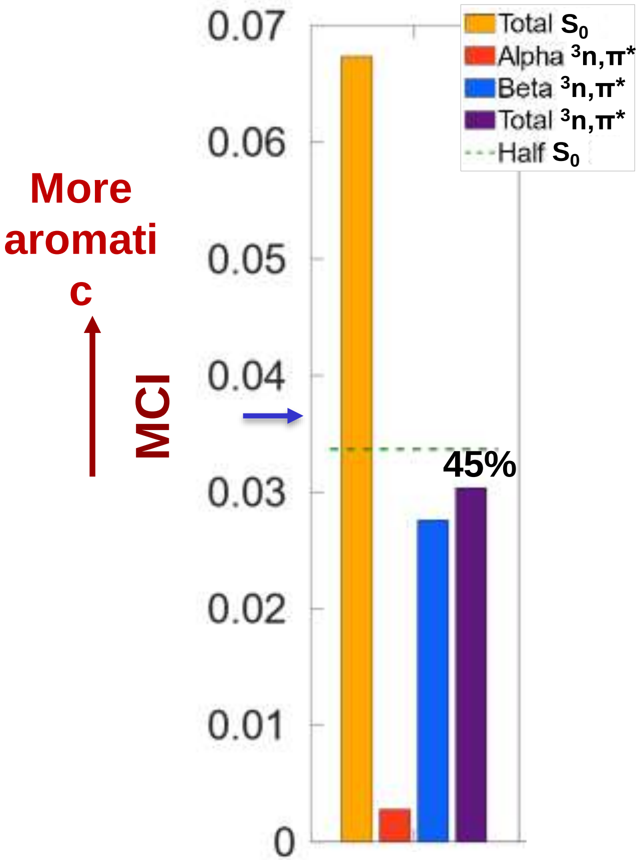
PYRIDINE IN ITS ^{3}n,π* STATE: SPIN-SEPARATED DESCRIPTIONS

UCAM-B3LYP/6-311+G(d,p)



4 π_α**: AA**
3 π_β**: A**

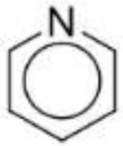
Electronic descriptor



^{3}n,π* of pyridine

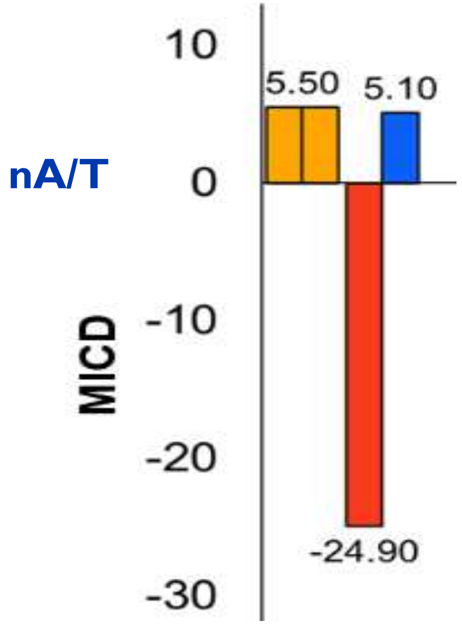
- **Slight leaning towards antiaromaticity according to electronic MCI, but**
- **Strong antiaromaticity according to magnetic NICS and MICD**

Magnetic descriptors



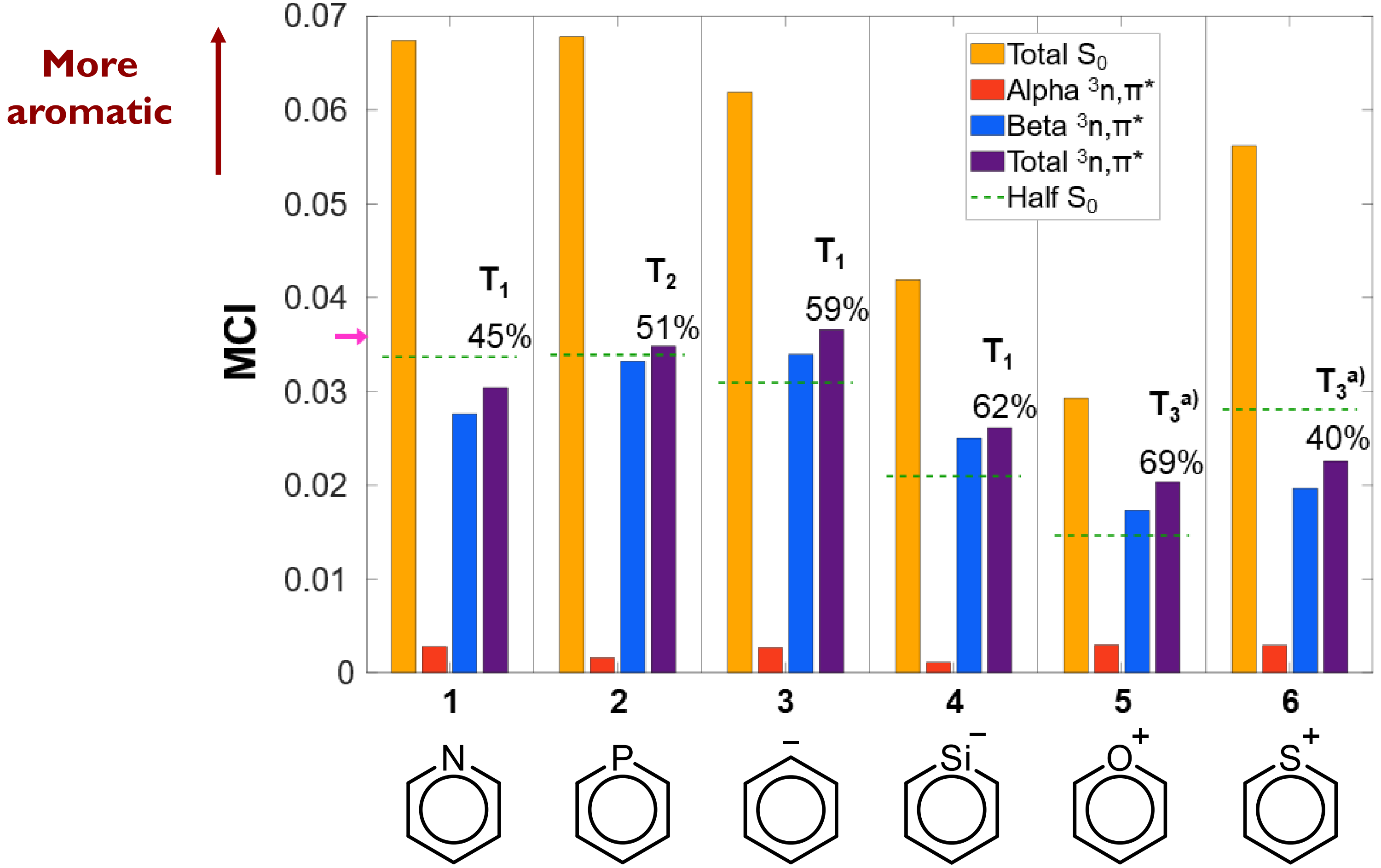
NICS(1)$_{zz}$

S_0: -29.1
^{3}n,π*: 53.3



Proos Vedin, Escayola, Radenković, Solà & Ottosson. *J. Phys. Chem. A*, **2024**, *128*, 4493

SIX-MEMBERED RING (6-MR) MONOHETEROAROMATICS IN ^{3}n,π*



UCAM-B3LYP/6-311+G(d,p)

- **The MCI value of benzene in S_0 (0.072) is used as a reference for strong aromaticity**
- **$MCI_\alpha(T_1)$ which corresponds to $4\pi_\alpha$-electrons (antiaromatic) is close to 0**
- **$MCI_\beta(T_1)$ which corresponds to $3\pi_\beta$-electrons (aromatic) is ~$MCI(S_0)/2$**
- **$MCI(T_1)_{tot}$ ~ $MCI(S_0)/2$ for a nonaromatic ^{3}n,π*. Examples are compounds 1 & 2**
- **$MCI(T_1)_{tot}$ >> $MCI(S_0)/2$ for an ^{3}n,π* with aromatic residual. Example is 3**
- **$MCI(T_1)_{tot}$ << $MCI(S_0)/2$ for an ^{3}n,π* with antiaromatic residual. Example is 6.**

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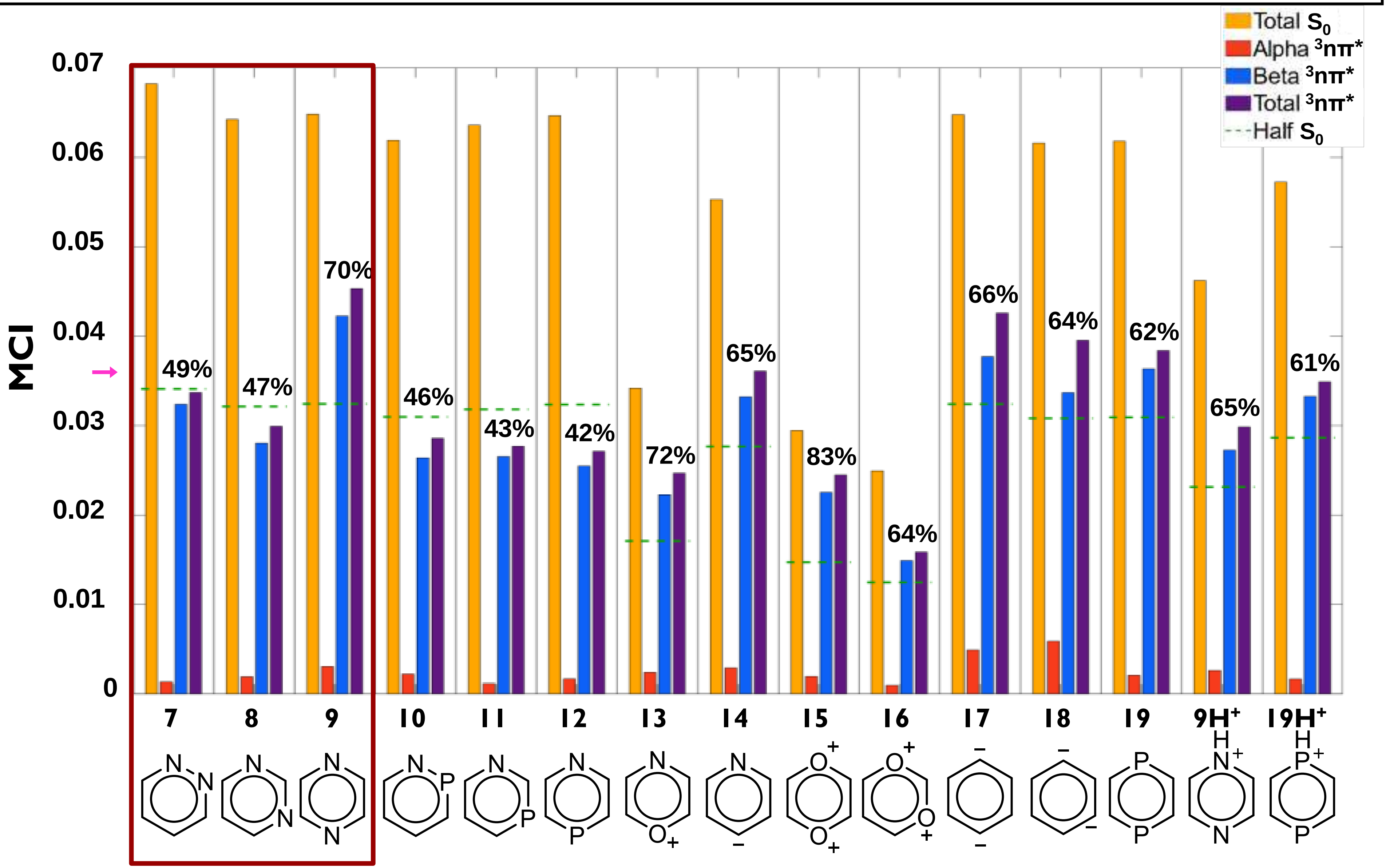
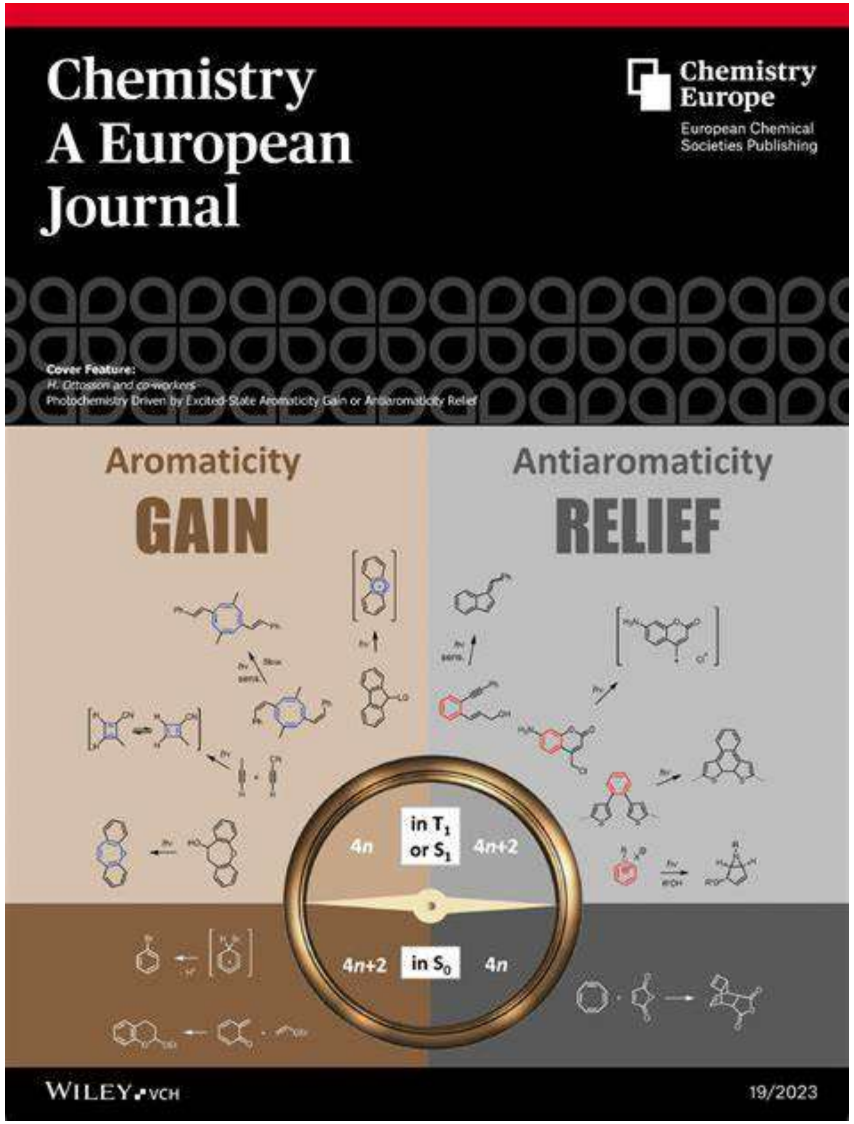
SIX-MEMBERED RINGS (6-MR) WITH TWO HETEROATOMS

- **Some diheteroaromatics have aromatic $^3n\pi^*$ states, e.g., pyrazine 9.**
- **Stems from the π_β component which is more aromatic in $^3n\pi^*$ than in the S_0 state.**



FLOWCHART FOR INVESTIGATIONS OF TENTATIVE EXCITED STATE (ANTI)AROMATICITY EFFECTS



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Cover Feature:
H. Ottosson and co-workers
Photochemistry Driven by Excited-State Aromaticity Gain or Antiaromaticity Relief

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Yan, Slanina, Bergman & Ottosson,
Chem. Eur. J. **2023**, *29*, e202203748

A critical stance needed:

- **Limitations, complications and pitfalls should be unravelled.**
- **There are computational method limitations and pitfalls (e.g., NICS values can be misinterpreted).**
- **ESA & ESAA not only Baird-type; molecules can be excited state Hückel-aromatic.**

1
Run quantum chemical calculations with methods that *properly* describe the excited state in question.

2
Explore *the different aspects* of excited state (anti)aromaticity by suitable descriptors, and openly describe differences in the results.

3
Is the ring in question *really* Baird-aromatic or Baird-antiaromatic?
Use qualitative MO or VB theory to find alternative ways to rationalize the computational results and test these.