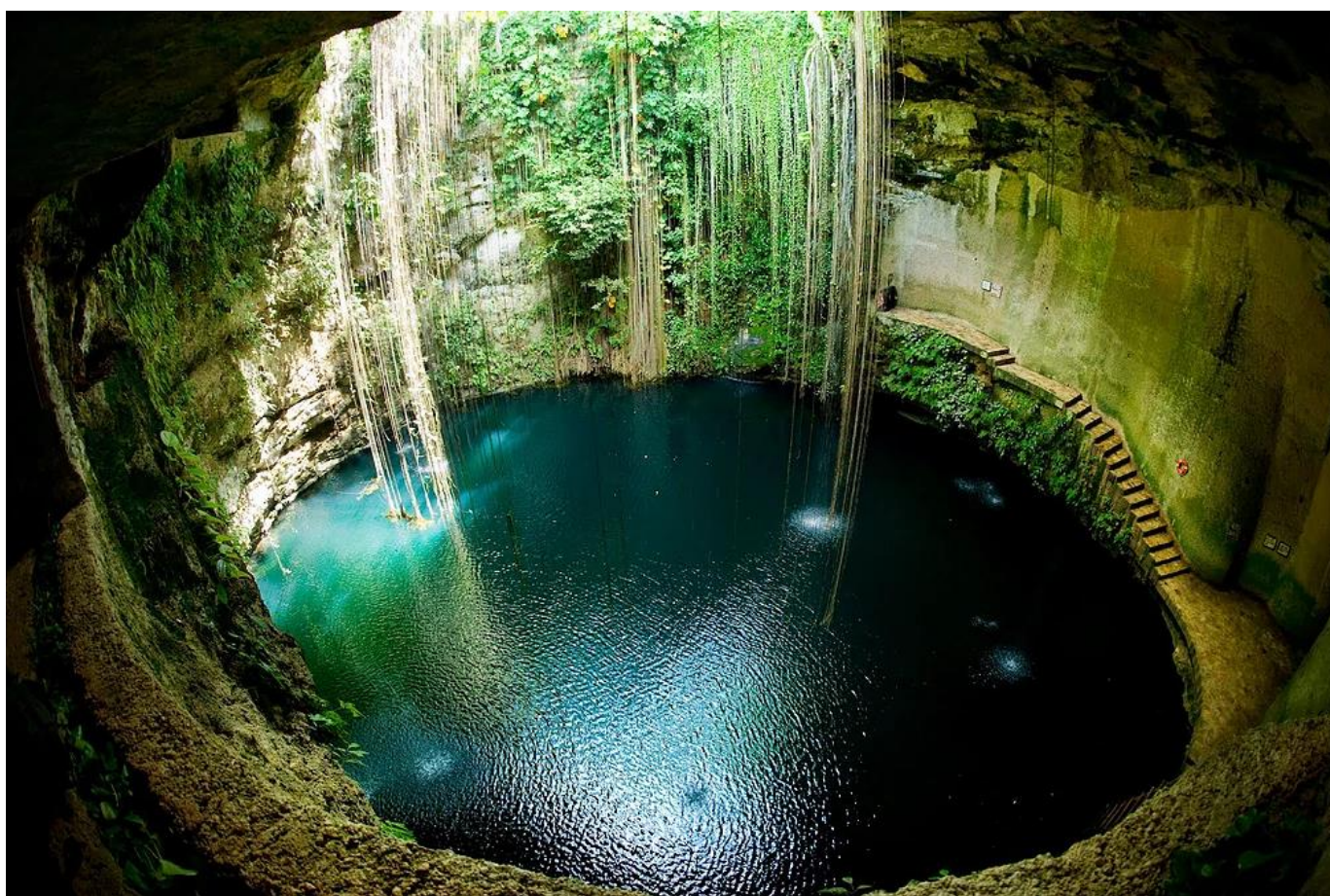

AROMAT CITY 2018

Riviera Maya, Mexico

ABSTRACT BOOK



November 28-December 1, 2018



Welcome to Aromaticity 2018!

The meaning of the term aromatic has changed over time, but it is still used in all areas of chemistry to define systems with similar behavior as benzene. As a concept, *aromaticity* is not directly accessible in experiments, but its consequences are. This experimental impossibility of measuring *aromaticity* has opened the door to many controversial issues and discussions around it. It is therefore not surprising to find many attempts to define this term according to the grounds of a variety of approaches. So, assigning an unequivocal and absolute meaning to *aromaticity* is risky. In view of these problems of subjectivity, it is remarkable that this concept is still useful to rationalize and understand the structure and reactivity of many molecular entities. In this meeting, experts (theorists and experimentalists) will discuss all aspects of aromaticity, in order to lay the foundations for an updated and *more comprehensive definition* of this concept by IUPAC.

So, on behalf of the Organizing Committee of *Aromaticity 2018*, we welcome you in Riviera Maya, which is located on one of the most beautiful beaches in Mexico. We are confident that the academic program and the attractive location will make Aromaticity 2018 an unforgettable event.

Gabriel Merino, Miquel Solà and Henrik Ottosson
Chairmen
Aromaticity 2018

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Scientific Program

Wednesday, November 28

8:00-9:00

Registration



Chairperson. Henrik Ottosson

8:30-9:00

Opening. Gabriel Merino and Henrik Ottosson

9:00-9:30

L1 Gabriel Merino

Centro de Investigación y de Estudios Avanzados. Mexico
The induced magnetic field

9:30-10:00

L2 Jordi Poater

Universitat de Barcelona. Spain
Role of aromaticity and H•••H interactions in the stability of polycyclic aromatic hydrocarbons

10:00-10:30

L3 Mercedes Alonso

Vrije Universiteit Brussel. Belgium
How and why aromaticity should be quantified in porphyrinoids?

10:30-11:00

L4 Hiroyuki Isobe

University of Tokyo. Japan
Rigid, cylindrical cycloarylenes: chirality and properties

11:00-11:30

Coffee Break



Chairperson. Miquel Solà

11:30-12:00

L5 Michael Haley

University of Oregon. USA
Indenofluorenes and ring-expanded analogues: from quinoidal electron-accepting materials to stable organic diradicals

12:00-12:30

L6 Juan Casado

Universidad de Málaga. Spain
Diradicals and their driving forces

12:30-13:00

L7 Israel Fernández

Universidad Complutense de Madrid. Spain
Aromaticity in metallabenzene: quantification and influence on reactivity

13:00-13:30

L8 Judy Wu

University of Houston. USA
Aromaticity-modulated noncovalent interactions: when counting electrons matter

13:30-15:30

Lunch



Chairperson. Dage Sundholm

15:30-16:00

L9 Patrick Bultinck

Ghent University. Belgium
Understanding the behaviour of the NICS_{zz}

16:00-16:30

L10 Fernando Cossío

Euskal Herriko Unibertsitatea. Spain
Aromatic stabilization in pericyclic transition structures

16:30-17:00

L11 Yoshimitsu Itoh

University of Tokyo. Japan
Energetic impact of Baird aromaticity on molecular dynamics

17:00-17:30

L12 Eduard Matito

Euskal Herriko Unibertsitatea. Spain
An aromaticity measure for macrocycles

17:30-18:00

Coffee Break

**Chairperson. Matthias Bickelhaupt****18:00-18:30****L13 Daniel Gryko**

University of Warsaw. Poland

Pyrrolo[3,2-B]pyrroles – electron-rich functional heterocycles

18:30-19:00**L14 Renana Poranne**

ETH Zurich. Switzerland

Additive aromaticity

19:00-19:30**L15 Anirban Misra**

University of North Bengal. India

Exocyclic aromaticity and its role in stabilizing organic radicals

19:30-20:30**Welcome cocktail****Thursday, November 29****Chairperson. Igor Alabugin****9:00-9:30****L16 Masaaki Nakamoto**

Hiroshima University. Japan

Tetrahedranes and cyclobutadienes: diradical character of *para*-phenylene-linked cyclobutadiene**9:30-10:00****L17 Matthias Bickelhaupt**

Vrije Universiteit Amsterdam. The Netherlands

Aromaticity: core criteria, physical basis... and fuzziness

10:00-10:30**L18 Yosadara Ruiz-Morales**

Instituto Mexicano del Petróleo. Mexico

Y-rule and extended Y-rule to determine the aromaticity of pericondensed and catacondensed polycyclic aromatic hydrocarbons

10:30-11:00**L19 Yasujiro Murata**

Kyoto University. Japan

Open-cage fullerenes toward the synthesis of endofullerenes and heterofullerenes

11:00-11:30**Coffee Break**



Chairperson. Anastassia Alexandrova

11:30-12:00

L20 Shigeru Yamago
Kyoto University. Japan
Aromaticity of cycloparaphenylene dications

12:00-12:30

L21 Roald Hoffmann
Cornell University. USA
Theorist intent on stabilizing molecules, molecules doing something else

12:30-13:00

L22 J. D. Tovar
Johns Hopkins University. USA
Dissecting aromaticity within borepin-based polycyclic aromatics

13:00-13:30

L23 Norihiro Tokitoh
Kyoto University. Japan
Heavier group 14 element analogues of aryl anions

13:30-15:30

Lunch



Chairperson. Marina Petrukhina

15:30-16:00

L24 Oscar Jiménez
Universidad de Guanajuato. Mexico
The effect of the (anti-)aromaticity in the reactivity of boron-containing compounds

16:00-16:30

L25 Aurelio Mateo
Universidad del País Vasco. Spain
Synthesis of giant monodisperse N-doped nanographenes

16:30-17:00

L26 Peter Karadakov
University of York. United Kingdom
Ground and excited state aromaticity and antiaromaticity: evidence from magnetic properties and valence-bond theory

17:00-17:30

L27 Fernando Langa
Universidad de Castilla. Spain
Molecular engineering of porphyrins for high performance organic solar cells

17:30-18:00
Coffee Break



Chairperson. Mercedes Alonso

18:00-18:30

L28 Lechosław Latos-Grażyński

University of Wrocław, Poland

Aromaticity switching in porphyrinoids and heteroporphyrinoids.

18:30-19:00

L29 Marina Petrukhina

University of Albany, USA

Reshaping carbon bowls and belts by multi-electron charging

19:30-19:30

L30 Dage Sundholm

University of Helsinki, Finland

Applications of the gauge-including currents method on large multi-ring molecules and nanostructures

19:30-21:00

Poster Session

Friday, November 30

Free Morning



Chairperson. Yasujiro Murata

15:30-16:00

L31 Yunlong Zhang

ExxonMobil Research and Engineering Company, USA

Abundant Natural Products from Heavy Oils: Novel Polynuclear Aromatic Hydrocarbons

16:00-16:30

L32 Henrik Ottosson

Uppsala University, Sweden

Scope and limitations of excited state aromaticity and antiaromaticity

16:30-17:00

L33 Laszlo Kürti

Rice University, USA

Transition metal-free C-H functionalization of aromatic rings: Organocatalytic atroposelective synthesis of biaryls

17:00-17:30

L34 Shohei Saito

Kyoto University, Japan
Excited state aromaticity of flapping COT materials

17:30-18:00

Coffee Break



Chairperson. Jonathan Sessler

18:00-18:30

L35 Masaichi Saito

Saitama University, Japan
Challenge to expand aromaticity –from π -aromaticity to $\sigma+\pi$ -double aromaticity-

18:30-19:00

L36 Amnon Stanger

Technion-Israel Institute of Technology, Israel
Some thoughts about aromaticity

19:00-19:30

L37 Alvaro Muñoz

Universidad Autónoma de Chile, Chile
Unifying planar and spherical aromatics. Shielding cone as common characteristic

Saturday, December 1



Chairperson. Fernando Cossío

9:00-9:30

L38 Anastassia Alexandrova

University of California Los Angeles, USA
Local aromaticity driving the formation of functional surface alloys and 2-D materials

9:30-10:00

L39 Igor Alabugin

Florida State University, USA
Redesigning cycloaromatization reactions: Interplay between aromaticity and antiaromaticity in the ground and excited states

10:00-10:30

L40 Guglielmo Monaco

Università degli Studi di Salerno, Italy
Magnetic indicators of aromaticity

10:30-11:00

L41 William Tiznado

Universidad Andrés Bello. Chile
On the search of aromatic silicon rings

11:00-11:30

Coffee Break



Chairperson. Israel Fernández

11:30-12:00

L42 Miquel Solà

Universitat de Girona. Spain
Combining and connecting rules. Toward a unified theory of aromaticity

12:00-12:30

L43 Minh Nguyen

KU Leuven. Belgium
The quasi-planar boron cluster B_{50} : Leap-frog formation and disk aromaticity

12:30-13:00

L44 Dirk Guldi

University of Erlangen-Nürnberg. Germany
Aromatic singlet fission materials – Up- and down-converting photons

13:00-13:30

L45 Arthur Winter

Iowa State University. USA
Role of antiaromaticity in ground state diradical carbocations

13:30-15:30

Lunch



Chairperson. Laszlo Kürti

15:30-16:00

L46 Jonathan Sessler

The University of Texas Austin. USA
Exploring aromaticity with expanded porphyrins

16:00-16:30

L47 Marija Baranac

University of Belgrade. Serbia
Does more aromatic mean more stable? The case of azaborines and their B/N-monosubstituted derivatives

16:30-17:00

L48 Haiping Xia

Xiamen University, China

Carbolong chemistry: a novel aromatic system

17:00-17:30

L49 Jun Zhu

Xiamen University, China

Aromaticity in organometallics and its application in N₂ activation

17:30-18:00

Coffee Break



18:00-19:30

R1 Henrik Ottosson and Igor Alabugin

Round-Table

ABSTRACTS

L1. THE INDUCED MAGNETIC FIELD

Gabriel Merino

Departamento de Física Aplicada, Centro de Investigación y de Estudios Avanzados, Unidad Mérida, México.
gmerino@cinvestav.mx

Aromaticity is an indispensable concept for explaining a variety of chemical behaviors, including reactivity, structural features, relative energetic stabilities, and spectroscopic properties. When interpreted as the spatial delocalization of π -electrons, it represents the driving force for the stabilization of many planar molecular structures. A delocalized electron system is sensitive to an external magnetic field; it responds with an induced magnetic field having a particularly long range. The shape of the induced magnetic field reflects the size and strength of the system of delocalized electrons and can have a large influence on neighboring molecules.

In 2004, we proposed using the induced magnetic field as a means of estimating the degree of electron delocalization and aromaticity in planar as well as in nonplanar molecules. We have since tested the method on aromatic, antiaromatic, and nonaromatic compounds, and a refinement now allows the individual treatment of core-, σ -, and π -electrons.

In this talk, I will discuss the use of the induced magnetic field as an analytical probe for electron delocalization and its application to a large series of molecules. In all cases, we have observed that planar structures show a high degree of electron delocalization in the π -electrons and, in some examples, also in the σ -framework.

Quantitatively, the induced magnetic field has contributions from the entire electronic system of a molecule, but at long range the contributions arising from the delocalized electronic π -system dominate. The induced magnetic field can only indirectly be confirmed by experiment, for example, through intermolecular contributions to NMR chemical shifts. We show that calculating the induced field is a useful method for understanding any planar organic or inorganic system, as it corresponds to the intuitive Pople model for explaining the anomalous proton chemical shifts in aromatic molecules. Indeed, aromatic, antiaromatic, and nonaromatic molecules show differing responses to an external field; that is, they reduce, augment, or do not affect the external field at long range. The induced field can be dissected into different orbital contributions, in the same way that the nucleus-independent chemical shift or the shielding function can be separated into component contributions. A result is a versatile tool that is particularly useful in the analysis of planar, densely packed systems with strong orbital contributions directly atop individual atoms.

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L2. ROLE OF AROMATICITY AND H...H INTERACTIONS IN THE STABILITY OF POLYCYCLIC AROMATIC HYDROCARBONS

J. Poater,¹ G. Merino,² C. Fonseca Guerra,³ F.M. Bickelhaupt,³ M. Duran,⁴ M. Solà⁴

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²Departamento de Física Aplicada, Centro de Investigación y de Estudios Avanzados, Mérida, 97310, México

³Department of Theoretical Chemistry & ACMM, Vrije Universiteit Amsterdam, Amsterdam, 1081HV, The Netherlands

⁴Institut de Química Computacional i Catàlisi & Departament de Química, Universitat de Girona, Girona, 17003, Spain

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We have quantum chemically analyzed how the stability of small and larger polycyclic aromatic hydrocarbons (PAHs) is determined by characteristic patterns in their structure. In particular, we focus on the effect of the nonbonded H...H interactions that occur in the bay region of kinked (or armchair) PAHs,^{1,2} but not in straight (or zigzag) PAHs. Model systems comprise anthracene, phenanthrene, and kekulene as well as derivatives thereof. Our main goals are: (1) to explore how nonbonded H...H interactions in armchair configurations of kinked PAHs affect the geometry and stability of PAHs and how their effect changes as the number of such interactions in a PAH increases; and (2) to examine the origin of such stabilizing/destabilizing interactions, with emphasis on their aromaticity.³

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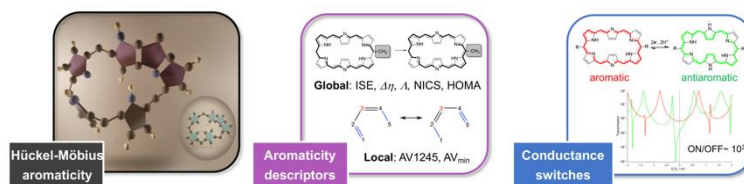
L3. HOW AND WHY AROMATICITY SHOULD BE QUANTIFIED IN PORPHYRINOIDS?

M. Alonso

General Chemistry Department (ALGC), Vrije Universiteit Brussel (VUB), 1050 Brussels, Belgium
e-mail: mercedes.alonso.giner@vub.be

Expanded porphyrins are recognized as the best test bed for exploring the concept of aromaticity,¹ since they provide congeneric macrocycles with $[4n+2]$ and $[4n]$ π -electrons and different π -conjugation topologies, including Möbius structures.² As such, these macrocycles have been used to verify experimentally the validity of Hückel and Möbius aromaticity rules as well as the Baird's aromaticity rules in polycyclic systems.¹ Nevertheless, aromaticity is not an observable and its evaluation is challenging. Aromaticity is currently described as a multidimensional phenomenon, implying that it cannot be quantified using a single aromaticity descriptor. Besides, expanded porphyrins contain multiple π -conjugation pathways and, accordingly, one of the main issues to describe their aromaticity concerns the selection of the macrocyclic conjugation pathway. In this talk, I will present a multidimensional approach to assess Hückel and Möbius aromaticity in expanded porphyrins, based on global and local descriptors rooted on the energetic, magnetic, reactivity, structural and electronic criteria.^{3,4} By using these descriptors, the validity of the widely-used annulene model to describe the aromaticity of porphyrinoids will be discussed as well as the structure-property relationships between molecular topology, number of π -electrons and aromaticity.

In the second part of the talk, I will emphasize the importance of quantifying aromaticity in porphyrinoids. Through our recent research, aromaticity emerges as a guiding concept to rationalize the photophysical and transport properties, allowing us to devise different selection rules for UV-vis spectroscopy and transmission.⁵ Together, our findings demonstrate how the concept of the reversal of aromaticity can be exploited to create a novel type of single-molecule switching devices with high performance.⁶



References

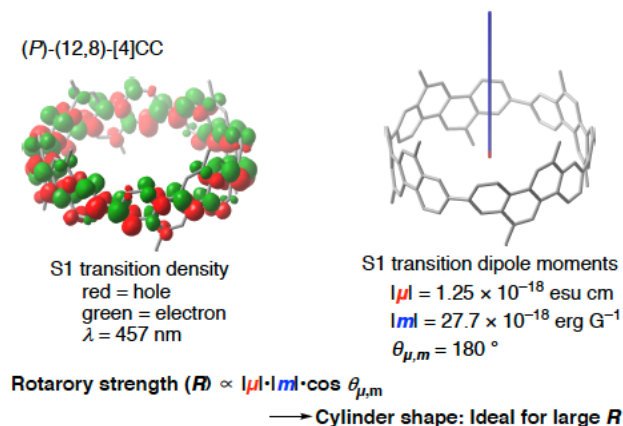
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L4. RIGID, CYLINDRICAL CYCLOARYLENES: CHIRALITY AND PROPERTIES

Hiroyuki Isobe

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ERATO Isobe Degenerate π -Integration Project
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Rigid, cylindrical aromatic molecules have attracted interest of scientists, initially due to their unique structures as segments of carbon nanotubes. We are particularly interested in the rigid, cylindrical cycloarylenes and have intensively studied molecular shapes (cylinder/non-cylinder),¹ flexibility/rigidity and chirality² to understand relationships between molecular structures and properties. In the presentation, I wish to report some of interesting observations of circular dichroism and circularly polarized luminescence, which may be unique to conjugated systems on cylinders.³



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L5. INDENOFLOURENES AND RING-EXPANDED ANALOGUES: FROM QUINOIDAL ELECTRON-ACCEPTING MATERIALS TO STABLE ORGANIC DIRADICALS

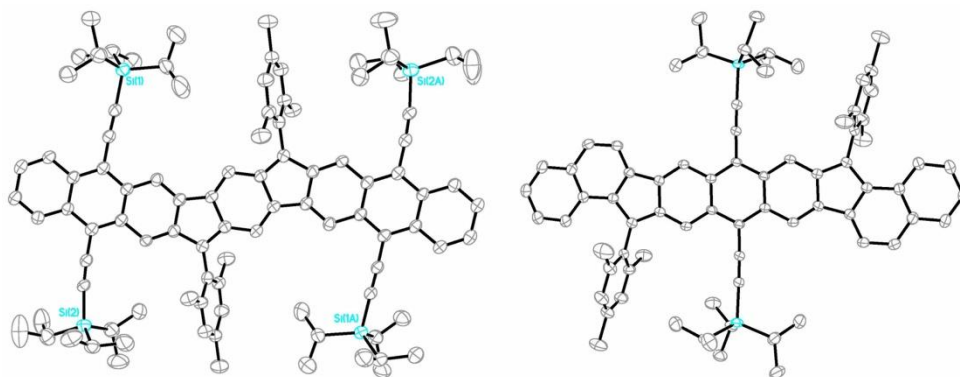
Michael M. Haley

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This talk will present our synthetic, structural, computational and materials studies of a new class of carbon-rich, electron-accepting molecules based on the indenofluorene (IF) skeleton.¹ Access to the fully conjugated, 20 π -electron, formally anti-aromatic, pentacyclic ring system is accomplished using a variety of intermediate diones. These molecules in turn can be prepared via a simple three-step process (Suzuki cross-coupling, oxidation, Friedel-Crafts acylation). Optimization of their synthesis now permits access to IF derivatives in multigram quantities. We have shown that thin films or single crystals of several different IF scaffolds can serve as an active layer in organic field effect transistors (OFETs) that exhibit ambipolar behavior. Current studies are focused on varying the antiaromaticity of the indacene unit by systematic alteration of the outer benzene groups with other aromatic units as well as on increasing the diradical character of the framework by expansion of the quinoidal core.



References

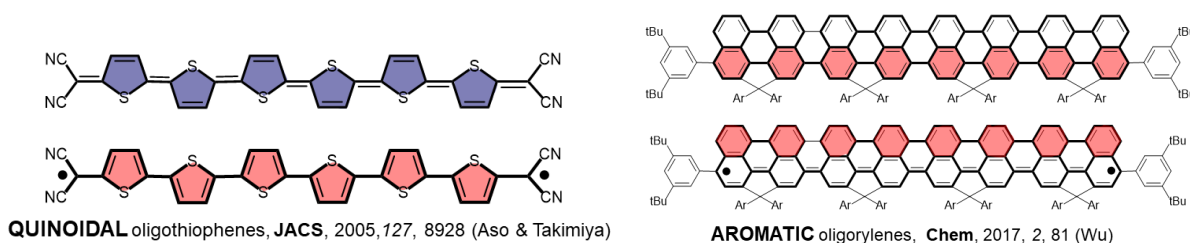
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L6. DIRADICALS AND THEIR DRIVING FORCES

Juan Casado

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Several series of aromatic and quinoidal compounds, such as oligothiophenes (Scheme 1), oligophenylene-vinylenes, oligoperylenes (oligophenyls) and graphene nanoribbon derivatives, are studied in the common context of the capability to stabilize diradical structures.^{1,2,3,4} In this work, we try to clarify how several driving forces (i.e., thermodynamic and entropic) are responsible for the generation of diradical and diradicaloid structures.



Scheme 1. Left: Quinoidal oligothiophenes and their conversion into aromatic diradicals. Right: Aromatic oligorylenes and their conversion into non-aromatic diradicals.

A combination of different types of molecular spectroscopies (i.e., electronic absorption, electronic emission, excited state absorption, vibrational Raman, vibrational infrared, etc.) as well as hybridized with thermal and pressure-dependent techniques are shown to provide important information about the origin of the formation and stabilization of diradicals. From a conceptual point of view, we analyze these properties in the context of the oligomer approach which is the study of the evolution of these spectroscopic quantities as a function of the oligomer size.

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L7. AROMATICITY IN METALLABENZENES: QUANTIFICATION AND INFLUENCE ON REACTIVITY

Israel Fernández

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The aromatic nature of metallabenzene complexes has attracted the interest of both experimental and theoretical chemists from the very beginning. Indeed, the seminal report by Thorn and Hoffmann in 1979 predicted that metallabenzenes might be synthesized as stable molecules on the basis of the computed electron delocalization within the six-membered ring.¹ Only three years later, Roper and co-workers prepared the first metallabenzene, an osmabenzene complex.²

Since then, different methods have been applied to estimate the aromaticity strength of these organometallic species. However, the presence of the transition metal fragment hampers a reliable quantification of their aromaticity. In this talk, we shall discuss these difficulties and present a method based on the Energy Decomposition Analysis (EDA) to directly estimate the aromaticity strength of metallabenzenes.³ In addition, the influence of the aromaticity of these species on their Diels-Alder reactivity shall be also discussed.⁴

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L8. AROMATICITY-MODULATED NONCOVALENT INTERACTIONS: WHEN COUNTING ELECTRONS MATTER

Judy Wu

University of Houston, Department of Chemistry

judyicwu@gmail.com

Aromaticity and hydrogen bonding interactions are traditionally considered to be largely separate chemical concepts. We are showing, however, that their reciprocal effects are significant and provide insights to understanding puzzling problems pertaining molecular recognition, assembly, proton-coupled electron transfer, and even enzyme catalysis. According to the AMHB relationship, hydrogen-bonding interactions that increase cyclic $4n+2$ π electron delocalizations (enhanced aromaticity) in heterocycles are strengthened, while those that decrease (reduced aromaticity) cyclic $4n+2$ π electron delocalization are weakened. We also show that, at specific excited states, these trends *reverse* following Baird's Rule for excited-state aromaticity ($4n\pi e$) and excited-state antiaromaticity ($4n+2\pi e$). Representative examples will be discussed.

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L9. UNDERSTANDING THE BEHAVIOUR OF THE NICS_{zz}

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The Nucleus Independent Chemical Shift (NICS) is one of the most used indices to assess aromaticity, in part due to the ease with which it can be calculated. Concerns about local contributions (primarily from the σ framework) prompted Schleyer et al. to propose more “refined” indices, such as the zz -component of the NICS (also called NICS_{zz}).¹

In this talk, we will show that there is no simple one-to-one relationship between NICS_{zz}-values and current density maps.² As such, we can construct diatropic and paratropic current density maps that both have the same NICS_{zz}-value.

The existence of this many-to-one mapping is a consequence of the fact that the NICS_{zz} is the result of an integration over the entire space. As such, it also no longer explicitly contains the information needed to quantify the separate contributions arising from underlying current density patterns.

We will show that these contributions can be revealed by resolving the NICS_{zz} into orbitals, sign, and positions. Our analysis of benzene in terms of these resolutions shows that the same underlying current density can lead to highly complex shielding patterns that vary greatly depending on the position of the NICS_{zz}-probe.

As such, our results indicate that any analysis solely based on NICS_{zz}-values can lead to results that are difficult to interpret, even if the system under study is considered to be well-known.

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L10. AROMATIC STABILIZATION IN PERICYCLIC TRANSITION STRUCTURES

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Although the concept of aromaticity usually refers to stable cyclic molecules, it can be extended to cyclic transition structures connecting reactants and products in a given elementary step.¹ Among the different criteria to describe aromaticity, geometric, magnetic and energetic criteria have proved to be especially useful. In transition structures, synchronicity can be considered as an extension of geometric criteria.² Magnetic and energetic criteria can be readily extended to transition structures by choosing adequate reference systems.³ These considerations are especially relevant in pericyclic reactions.⁴ In our presentation, several aspects concerning aromaticity criteria and competitive pericyclic reactions will be discussed, highlighting the multidimensional character of aromaticity.

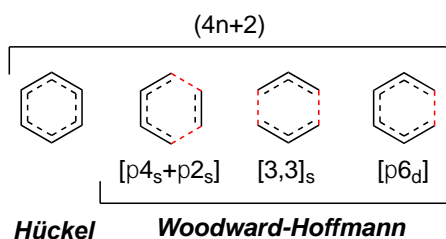


Figure 1. Formal equivalence between the Hückel $4n+2$ rule of aromaticity and the Woodward-Hoffman rules for allowed pericyclic reactions.

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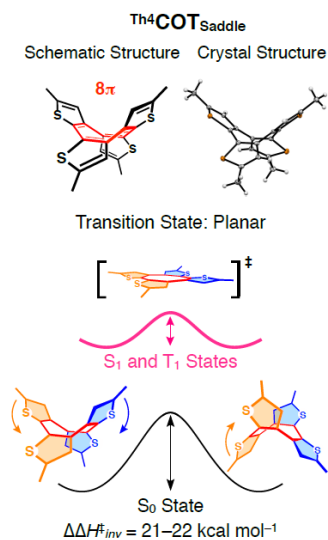
L11. ENERGETIC IMPACT OF BAIRD AROMATICITY ON MOLECULAR DYNAMICS

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Aromaticity is one of the most important concepts in organic chemistry that can explain the stability of planar conformations found in some specific cyclic π -conjugated molecules. In the electronic ground state, such molecules with $4n+2$ π -electrons prefer to be planar (Hückel's rule 1) because the resulting electronic conjugation leads to an energetic stabilization. The stabilization effect by Hückel aromaticity is estimated to be 29 kcal/mol based on heats of formation.² On the other hand, in the electronic excited state, it is known that cyclic π -conjugated molecules with $4n$ π -electrons prefer to be planar (Baird's rule 3). However, the energetics of the Baird aromaticity has been elusive before our study.

Recently, we reported the first experimental evaluation of the energetic impact of Baird aromaticity using thiophene-fused [8]annulene ($\text{Th}^4\text{COT}_{\text{Saddle}}$).⁴ $\text{Th}^4\text{COT}_{\text{Saddle}}$ is chiral and can be optically resolved by chiral HPLC. We found that the racemization of this compound is highly accelerated by photo irradiation. This is due to the energetic stabilization of the planar transition state of the ring inversion process by the emergence of Baird aromaticity at the electronic excited state. The activation enthalpy of the racemization under photo irradiation was 21–22 kcal/mol lower than that under dark. This value corresponds to the energetic impact of Baird aromaticity. This suggests that the Baird aromaticity can not only affect the single molecular dynamics but also its assembling behavior.



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L12. AN AROMATICITY MEASURE FOR MACROCYCLES

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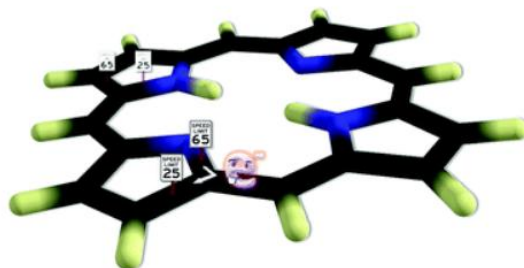
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We introduce a new electronic aromaticity measure, AV1245,¹ consisting of an average of the 4-center multicenter indices (MCI) along the ring. AV1245 measures the extent of transferability of the delocalized electrons between bonds 1–2 and 4–5, which is expected to be large in conjugated circuits and, therefore, in aromatic molecules. AV1245 is a size-extensive measure carrying a low computational cost that grows linearly with the number of ring members; it does not rely on reference values and it does not present limitations concerning the nature of the atoms. Unlike current multicenter delocalization indices,² AV1245 is especially suited to study the conjugation in large circuits such as those occurring in expanded porphyrins or polymeric chains.^{3,4} Different statistical quantities based on this index are presented and discussed in the context of porphyrins and expanded porphyrins.



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L13. PYRROLO[3,2-B]PYRROLES – ELECTRON-RICH FUNCTIONAL HETEROCYCLES

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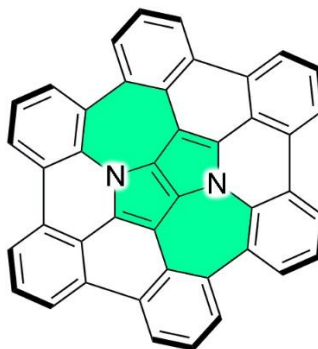
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Recently we have discovered and optimized the first practical synthesis of non-fused pyrrole[3,2-*b*]pyrroles *via* domino reaction of aldehydes, primary amines, and butane-2,3-dione. Six bonds are formed in heretofore unknown tandem process, which gives rise to substituted pyrrole[3,2-*b*]pyrroles – the ‘missing link’ on the map of aromatic heterocycles. Unparalleled simplicity and versatility of this one-pot reaction, non-chromatographic purification and superb optical properties (including strong violet, blue or green fluorescence both in solution as well as in the solid state), brought these molecules from virtual non-existence to the intensively investigated area functional π -systems. The parent 1,4-dihydro-pyrrolo[3,2-*b*]pyrroles served as building block to construct various π -expanded analogs including diindolo[2,3-*b*:2',3'-*f*]pyrrolo[3,2-*b*]pyrroles. These compounds constitute the most electron-rich ladder-type heteroacenes known to date - E_{HOMO} was located at $\sim(-4.6)$ eV. Strongly fluorescent diindolo[2,3-*b*:2',3'-*f*]pyrrolo[3,2-*b*]pyrroles represent the longest ladder-type heteroacenes and the only existing compounds bearing the 1,4,5,8-tetrahydropyrrolo[3,2-*b*]pyrrolo[2',3':4,5]pyrrolo[2,3-*d*]pyrrole core.



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L14. ADDITIVE AROMATICITY

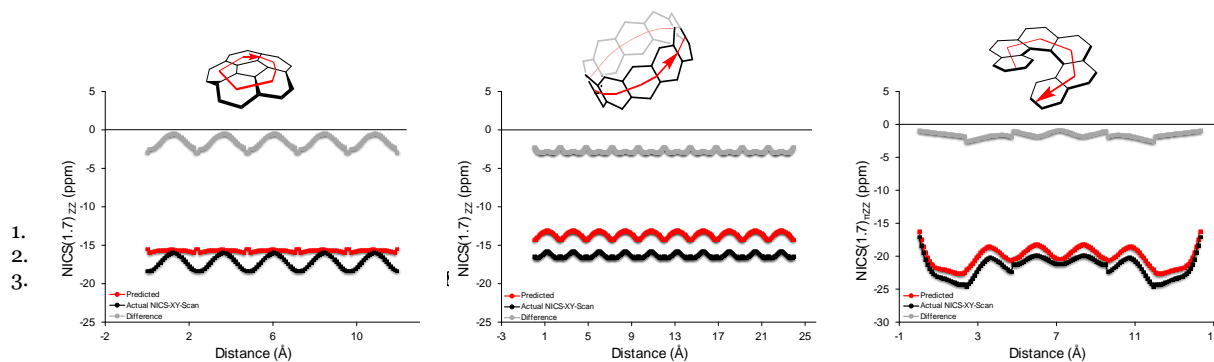
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Aromaticity is a fundamental property that is key to understanding the reactivity and behavior of a wide range of compounds, from simple reagents to complex materials. Despite ongoing investigations spanning over 150 years, it is still not definitively clear what aromaticity is and what it entails. Thus, the search for additional insight and for general, robust indices to quantify aromaticity, continues.

Recently, we demonstrated for the first time that the magnetic manifestation¹ of aromaticity is an additive property. Using NICS-XY-Scans² as building blocks within an additivity scheme,³ we showed that it is possible to generate full NICS-XY-Scans and predict the aromatic profiles of polycyclic aromatic hydrocarbons at a fraction of the computational cost. The additivity scheme was shown to work in 1- and 2-dimensional, all-carbon systems.

We now report that the additivity scheme has been expanded to include heterocyclic and anti-aromatic moieties. Furthermore, we have successfully applied the method to 3-dimensional structures, which are challenging to treat with existing computational methods. These developments prove the technique useful for predicting the aromaticity of a wide range of PAHs of various functionalities.



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L15. EXO-CYCLIC AROMATICITY AND ITS ROLE IN STABILIZING ORGANIC RADICALS

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Aromatic molecules are known to be stable and the domain of aromaticity has been expanded from polycyclic aromatic hydrocarbons, heterocycles to all-metal aromatic systems. The advent of a plethora of such stable molecular systems with outstanding properties keeps the option open for the addition of new types of molecules to this family. Here, we show a novel class of stable molecules where the parent ring adopts aromaticity in an unusual fashion depending upon the nature of the substituent. Cyclic conjugation is conventionally considered to be the principal factor for aromaticity, while maintaining the well-known aromatic electron count rule in a planar molecule. In the proposed molecular system, aromaticity is manifested through an 'exo-cyclic' conjugation to attain the magic number to form the aromatic 'sextet'.¹ The aromatic stabilization energy is calculated through a recently developed phenomenological model.² The stability of the molecules is established through density functional and *ab-initio* calculations. Thus, in this endeavor we design and establish a novel mode of aromatic conjugation in an unambiguous way.³ Furthermore, we observe that such systems play a key role in stabilizing organic radicals in a unique way.⁴

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L16. TETRAHEDRANES AND CYCLOBUTADIENES: DIRADICAL CHARACTER OF PARA-PHENYLENE-LINKED CYCLOBUTADIENEMasaaki Nakamoto,¹ Akira Skiguchi²¹Department of Chemistry, Hiroshima University,

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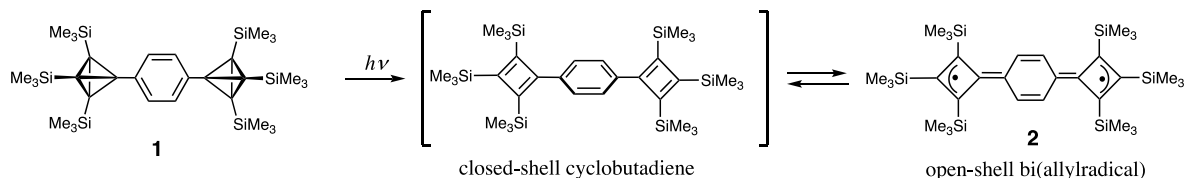
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Cyclobutadiene is a molecule with four π -electrons in its planar four-membered ring. Although cyclobutadiene derivatives are known to be reactive species due to the antiaromaticity, their electronic properties such as thermally accessible triplet state have been investigated experimentally and theoretically.¹

One of the practical approaches to the stable cyclobutadienes is the introduction of bulky substituents such as trimethylsilyl group. Since cyclobutadiene is a valence isomer of tetrahedrane molecule, we developed the synthesis of isolable cyclobutadiene derivatives via photoreaction of corresponding silyl-substituted tetrahedranes.² Recently, we have demonstrated that the photoreaction provides the practical approach to the stable cyclobutadienes because of the excited state aromaticity of four π -electrons ring system.

By using this strategy, the para-phenylene-linked cyclobutadiene derivative having diradical character was synthesized for the first time. In this presentation, the molecular structure in the solid state and diradical nature in a solution of compound 2 will be discussed.

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L17. AROMATICITY: CORE CRITERIA, PHYSICAL BASIS... AND FUZZINESS

F. M. Bickelhaupt

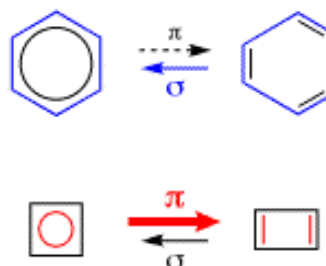
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Aromaticity is a powerful and ubiquitous concept, in organic chemistry, and beyond. It has physically well-defined core criteria: (i) a high symmetry, cf. double-bond delocalization; (ii) high thermodynamic stability; and (iii) low reactivity. In my lecture, I will discuss why (i), (ii) and (iii) are the core criteria for aromaticity. And I will point out why this does not rule out a role for additional criteria, such as magnetic properties that show up, e.g., in NMR spectroscopy.

Furthermore, I will focus on geometry as one of the primary and most direct indicators of aromaticity and antiaromaticity: a regular structure with delocalized double bonds (e.g., benzene) is symptomatic of aromaticity whereas a distorted geometry with localized double bonds (e.g., 1,3-cyclobutadiene) is characteristic of antiaromaticity.



I present an MO model of aromaticity that explains, in terms of simple orbital-overlap arguments, why this is so. This MO model is based on accurate Kohn-Sham DFT analyses of the bonding in benzene, 1,3-cyclobutadiene and various other cyclic molecules. In particular, I will show that the propensity of the π electrons is always, i.e., in both aromatic and antiaromatic molecules, to localize the double bonds, against the delocalizing force of the σ electrons. Interestingly, the π electrons nevertheless decide about the localization or delocalization of the double bonds (see illustration). I will point out the connection with larger aromatic ring systems, with aromatic transition states in pericyclic reactions, and with aliphatic ring systems.

L18. Y-RULE AND EXTENDED Y-RULE TO DETERMINE THE AROMATICITY OF PERICONDENSED AND CATACONDENSED POLYCYCLIC AROMATIC HYDROCARBONS

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There are pericondensed polycyclic aromatic hydrocarbons (peri-PAHs) that have more than one Clar structure, with the highest number of resonant sextets, and in these cases the Clar's rules cannot identify which is/are the most important Clar structure(s) that represent(s) the π -electronic density distribution. The problem of the number and location of aromatic sextets in peri-PAHs involves the very concept of aromaticity. An easy to apply heuristic topological rule, named the Y-rule, to determine the π -electronic density distribution, in terms of resonant sextets and localized double bonds, in pericondensed polycyclic aromatic hydrocarbons will be presented and discussed. The Y-rule extends the sextet-double bond description of Clar's model for peri-PAHs and generates Clar type structures. The final π -electronic distribution obtained with the Y-rule corresponds to the superposition of the most important Clar structures. The Y-rule has been applied to numerous benzenoid PAHs and cyclopenta-fused PAHs and its surprisingly good agreement with other, more sophisticated, theoretical assessments of local aromaticity (in particular, the Schleyer's NICS values) will be discussed. The Y-rule contributes towards the solution to the problem of the misrepresentation of the π -electronic density distribution in benzenoid PAHs, where there is a practice of drawing a circle inside of each hexagonal ring. This practice should be discouraged, and actually represents a misuse of the circle notation to depict aromatic sextets. General features of the Y-rule, including the limits of its applicability, will be discussed. The Y-rule can only be applied to pericondensed PAHs, where there are internal triple bridgehead carbon atoms, also referred as Y-carbons, attached to three hexagonal rings. Therefore, the Y-rule has been extended to be applied to catacondensed PAHs. The extended Y-rule will also be presented and discussed.

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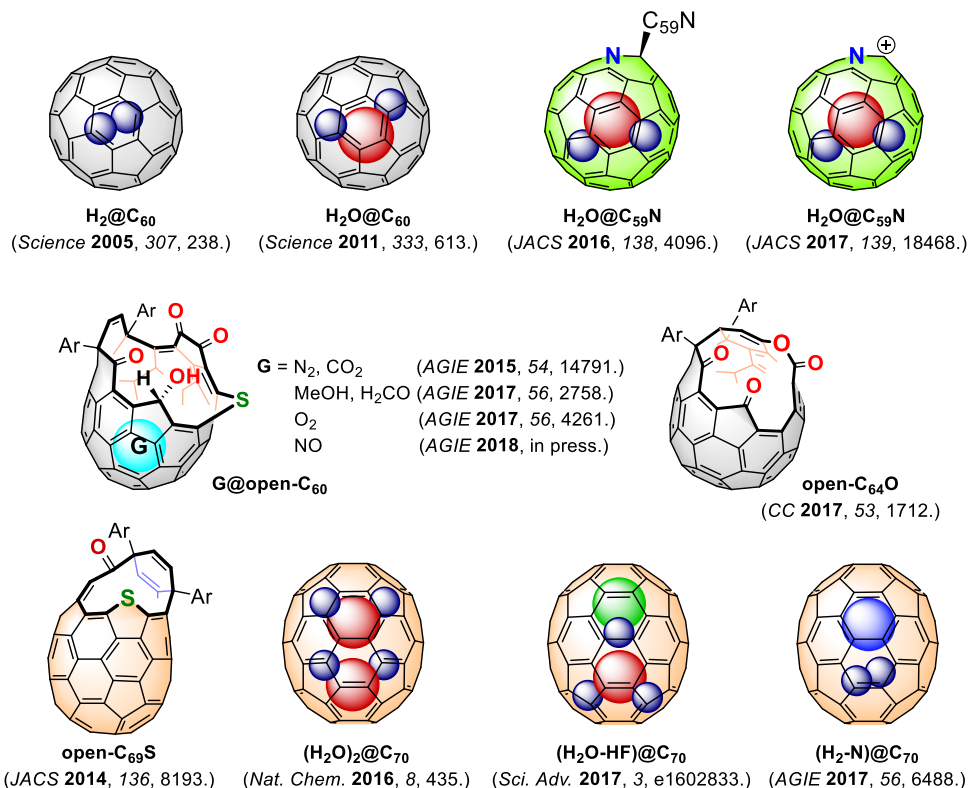
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L19. OPEN-CAGE FULLERENES TOWARD THE SYNTHESIS OF ENDOFULLERENES AND HETEROFULLERENES

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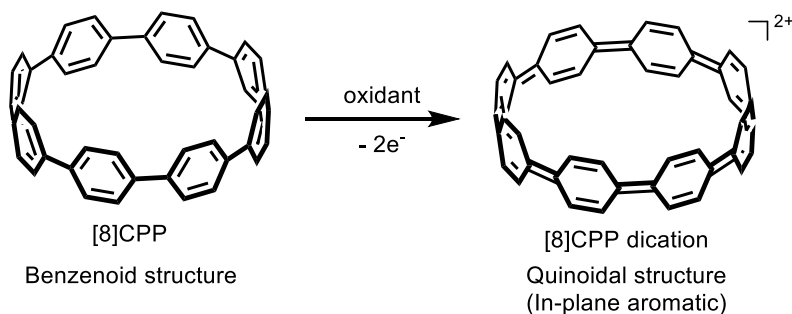
Open-cage fullerene derivatives are synthesized as isomerically pure forms by the reactions starting from pristine C_{60} and C_{70} . They are the precursors for heterofullerenes in which one of the carbon atoms is replaced with a hetero atom. Furthermore, in the case that their openings are large enough for a small molecule to pass through into the carbon cage, molecule-encapsulated ones become available. Escape of the small molecule can be prevented by making a stopper on the opening and fully suppressed when the opening is completely closed to regenerate the original fullerene cages. In this talk, several open-cage fullerene derivatives as well as endohedral fullerenes encapsulating a molecule will be presented. Also, doubly-encapsulated C_{70} will be introduced.



L20. AROMATICITY OF CYCLOPARAPHENYLENE DICATIONS

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Cycloparaphenylenes (CPPs) are hoop-shaped conjugated hydrocarbons possessing the simplest cyclic structural unit of armchair carbon nanotubes. Recent successful bottom-up organic synthesis including our group enables elucidation of their unique physical properties.¹ During the course to clarify their redox properties,² we could successfully isolate their radical cations and dications (Scheme 1). While the neutral CPPs take benzenoid structure in which each paraphenylene unit preserves aromatic character, but the dications possess quinoid structure and has in-plane aromaticity. This aromatic stabilization can explain the unusual stability of CPP dications. Detail results will be discussed.³



Scheme 1. Generation of [8]CPP dication from [8]CPP.

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L21. THEORISTS INTENT ON STABILIZING MOLECULES, MOLECULES DOING SOMETHING ELSE

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Basic ideas about thermodynamic stability and metastability, and on kinetic persistence of molecules in various phases of matter will be reviewed. I will describe some personal quests for stabilization, in the service of illustrating one or another chemical principle. And how molecules consistently foil (forgive the anthropomorphism) our good ideas and find ingenious escape routes. These case studies will include benzene dimers, halobenzenes, and zwitterionic aromatic systems. If time permits, I will discuss some quite stable systems, mostly two- and three-dimensional, that are waiting to be made. And instances where one might want to design instability.

L22. DISSECTING AROMATICITY WITHIN BOREPIN-BASED POLYCYCLIC AROMATICS

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Borepin rings are seven-membered rings bearing six pi-electrons analogous to the tropylium ion where one of the carbons is replaced by a tricoordinate boron. The seven p-orbitals in the circuit are able to foster an aromatic current, albeit a weak one. Our group maintains an interest in molecules/materials with extended pi-electron delocalization facilitated by weakly aromatic subunits that can enable facile polarization or otherwise stabilize charge-carrying species without costly dearomatization penalties. In this regard, we have prepared and studied several borepin cores fused with different arenes in order to assess the extent of “aromaticity competition” within the polycyclic cores, much in the style of Mitchell’s fused variants of the dimethyldihydropyrene core, whereby the borepin ring protons serve as suitable reporters for local aromaticity within the borepin core. To augment this analysis, we show through various NICS XY-Scans and through ACID plots how the local aromaticity and the global ring currents vary as a function of ring fusion. We find a distinct lack of sigma-aromaticity contribution from the borepin units in these molecules which makes them an interesting case study for aromatic character in polycyclic compounds.

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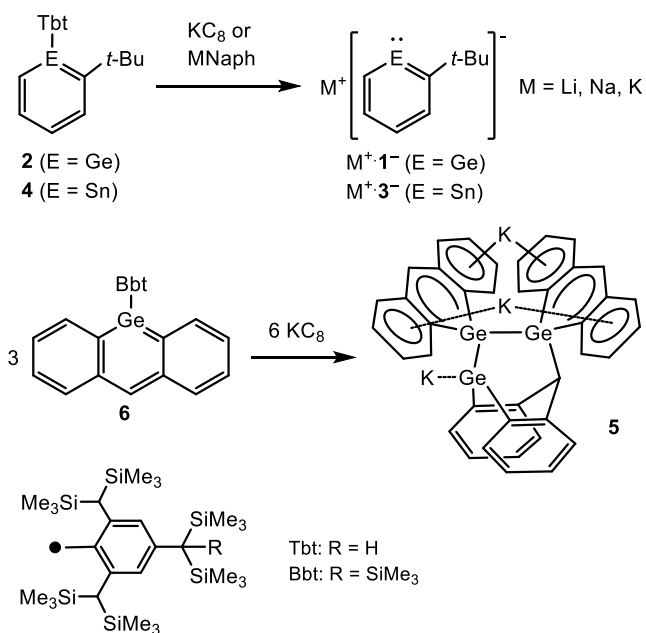
L23. HEAVIER GROUP 14 ELEMENT ANALOGUES OF ARYL ANIONS

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We have recently reported the synthesis and isolation of 2-*tert*-butylgermabenzenylpotassium ($K^+\cdot\mathbf{1}^-$), the first example of heavy phenyl anion, *i.e.*, a germanium analogue of phenylpotassium, by the reaction of 1-Tbt-2-*tert*-butylgermabenzene **2** with KC_8 .¹ Spectroscopic and X-ray crystallographic analysis together with theoretical calculations revealed that $K^+\cdot\mathbf{1}^-$ exhibits not only aromatic character due to the C_5Ge system but also germylene character due to the delocalization of negative charge on the five ring carbon atoms.¹ $Li^+\cdot\mathbf{1}^-$ and $Na^+\cdot\mathbf{1}^-$ were also synthesized from **2** in order to elucidate the effect of the counter ion on the properties of germabenzenyl anion, and $Na^+\cdot\mathbf{1}^-$ was fully characterized by NMR spectroscopy and X-ray diffraction analysis.²

These results are of great interest from the viewpoints of not only the synthesis and isolation of new germabenzenyl anions but also the systematic comparison for heavy arylmetals having different alkali metals, because such an approach is very scarce even in the chemistry of carbon analogues.

Furthermore, stannabenzenylpotassium $K^+\cdot\mathbf{3}^-$ was also synthesized as a stable compound starting from the corresponding stannabenzene **4**. In the case of Bbt-substituted 9-germaanthracene **6**, its reaction with KC_8 resulted in the formation of a unique trimer **5** of the initially formed germaanthracenylpotassium.³



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L24. THE EFFECT OF THE (ANTI-)AROMATICITY IN THE REACTIVITY OF BORON-CONTAINING COMPOUNDS

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Boroles are unsaturated, extremely electron-deficient, pentacyclic molecules with four π -electrons. Due to their photophysical characteristics and isoelectronic relationship to the cyclopentadienyl cation, boroles are of fundamental interest. Thus, in this talk we present our contribution in this field, where many differently substituted, nonannulated borole derivatives have been isolated and characterized experimental and computationally in terms of their aromaticity.¹ Furthermore, we have analyzed the aromaticity in BN heterocycles, which have been recently rekindled partly due to their potential for applications in biomedical research and materials science. Thus, we report on the reaction mechanism proposed by using DFT methodology and some aromaticity studies.²

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L25. SYNTHESIS OF GIANT MONODISPERSE N-DOPED NANOGRAPHENES

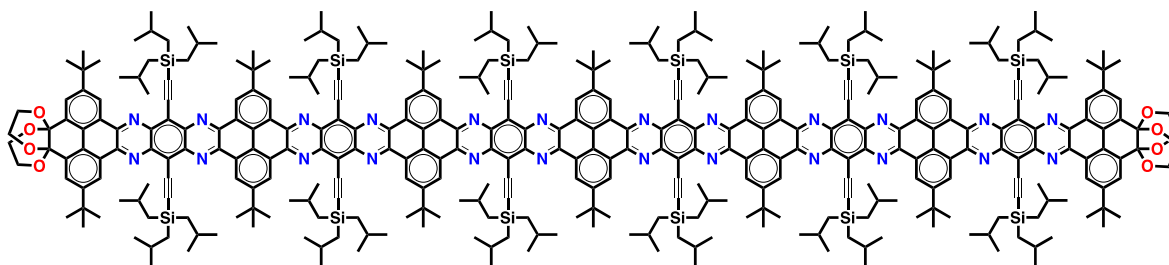
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The discovery of fullerenes, nanotubes, and graphene has stimulated the exploration of synthetic low-dimensional carbon nanostructures. Nanographenes are large monodisperse polycyclic aromatic hydrocarbons that extend in size beyond the nanometer, which show unique electronic, optical and mechanical properties with a lot of potential for electronics, photonics, and energy conversion, among others.^[1] The properties of nanographenes are highly dependent on several structural variables such as the number of fused rings and their arrangement, and also the presence of heteroatoms in the structure. The synthesis of extended nanographenes is still a challenging task that requires dealing with insoluble intermediates and products, which overall makes synthesis, purification, characterization and processing difficult, slowing down the exploration of their fundamental properties and the development of potential applications.

We have recently developed an iterative approach that assembles a small molecular building block into nanographenes of different sizes. In this lecture, such new approach will be showcased by describing the synthesis of several giant monodisperse N-doped nanographenes that extend beyond 5 nm in size.^[2]



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L26. GROUND AND EXCITED STATE AROMATICITY AND ANTIAROMATICITY: EVIDENCE FROM MAGNETIC PROPERTIES AND VALENCE-BOND THEORY

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Two rather different approaches: (i) the analysis of magnetic properties such as nucleus-independent chemical shifts (NICS), proton shieldings, magnetic susceptibilities and isotropic magnetic shielding contour plots and isosurfaces, and (ii) spin-coupled generalized valence bond (SCGVB) theory are shown to provide robust theoretical tools for identifying ground and excited state aromaticity and antiaromaticity and establishing their effects on chemical bonding. Examples include a discussion of the profoundly different shielding distributions in the ground (S_0) states of benzene (C_6H_6) and square cyclobutadiene (C_4H_4) which can be viewed as aromaticity and antiaromaticity “fingerprints” that are reproduced in other electronic states of the two molecules and allow classification of these states as aromatic (S_0 and S_2 for C_6H_6 , T_1 and S_1 for C_4H_4) or antiaromatic (S_0 and S_2 for C_4H_4 , T_1 and S_1 for C_6H_6). S_2 C_6H_6 is predicted to be even more aromatic than S_0 C_6H_6 . As isotropic shielding isosurfaces and contour plots show very clearly the effects of aromaticity and antiaromaticity on chemical bonding, these can be considered, arguably, as the most succinct visual definitions of the two phenomena currently available. A recent example of an application of SCGVB theory to aromaticity is provided by the study of the monocyclic cyclononatetraenyl cation, $C_9H_9^+$, which vindicates, in a surprising level of detail, essential features of Heilbronner’s ideas for the electronic structure of Möbius annulenes such as the arrangement of overlapping carbon 2p atomic orbitals along a Möbius strip, leading to a phase inversion between the first and last orbitals. In the SCGVB description, the aromaticity of this Möbius system with eight π electrons follows from the extensive resonance between VB structures.

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L27. MOLECULAR ENGINEERING OF PORPHYRINS FOR HIGH PERFORMANCE ORGANIC SOLAR CELLS

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Porphyrins are stable π -aromatic molecules and excellent electron donors frequently used as building blocks in artificial photosynthesis; their solubility, optical, photophysical and electrochemical properties can be tailored by substitution in the periphery or inner metal complexation. Porphyrins possess an intense Soret band at 400-450 nm and moderate Q bands at 500-650 nm; one hopeful way to overcome the problem relating to the poor light-harvesting properties of porphyrins is to modify the electronic structures of porphyrins, so that one can match the light-harvesting properties with the solar energy spectrum.

Porphyrin-based molecules have been explored for a long time as the active materials in dye-sensitized solar cells and the highest efficiency achieved is 13%. Nevertheless, until the last few years, this family of molecules has been scarcely explored as donor materials in bulk heterojunction (BHJ) organic solar cells (OSCs).

Believing that porphyrin-based molecules should play a more important role in BHJ OSCs) we started a few years ago a project in this field using a careful structural optimization. Here I'll present our last results achieving efficiencies close to 10%.

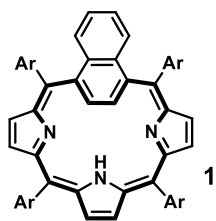
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L28. AROMATICITY SWITCHING IN PORPHYRINOIDS AND HETEROPORPHYRINOIDS

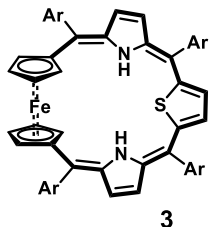
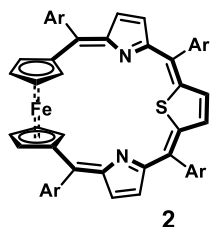
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An effective strategy to study the phenomenon of aromaticity is through the synthesis of new molecules, which are specifically designed to test various aspects of the theory or to pose new problems. Aromaticity of porphyrinoids can be influenced by a variety of structural modifications, such as peripheral substitution, covalent linking of multiple macrocycles, ring expansion or contraction, and introduction of non-pyrrolic subunits. Such modifications can profoundly affect the molecular and electronic structure eventually determining the macrocyclic aromaticity as demonstrated by the investigated

family of porphyrinoids including carbaporphyrinoids represented by 1,4-naphthiporphyrin **1**. Our studies have been focused on the physical manifestations of aromaticity, with a special emphasis on ^1H NMR spectroscopy. The aim of the presentation is to provide a description of porphyrinoid aromaticity and its connection with linking mode of arene moieties, tautomeric equilibria, intramolecular rearrangements, reversible peripheral modifications, oxidation state or coordination. The selected processes act as peculiar reversible switches of aromaticity. Thus, deprotonation of 1,4-naphthiporphyrin **1** forced the folded - extended macrocyclic transfer changing the macrocyclic aromaticity. A figure-eight A,D-di-p-benzi[28]hexaphyrin exhibits an unprecedented controlled switching between several Möbius and Hückel π -delocalization modes. Similarly, the palladium complexes of vacataporphyrin reveal Hückel aromaticity or Möbius antiaromaticity of analogous [18]annulene applying a butadiene fragment as a specific topology selector. Aromaticity switching between antiaromatic 28π -electron, aromatic 26π - and 18π -electron systems was presented for azulene-1,3-diyl-strapped A,D-dithiahexaphyrin. The direct transmission of



metallo-macrocyclic π -electron conjugation across a d -electron metallocene brought to light the novel aspects of aromaticity. Magnetic properties of ferrocenothiaporphyrin **2** and dihydroferrocene-thiaporphyrin **3**, *i.e.* of molecules which combine structural features of metallocenophanes and porphyrinoids, demonstrate the redox- or conformation-switchable macrocyclic antiaromatic and aromatic properties.

L29. RESHAPING CARBON BOWLS AND BELTS BY MULTI-ELECTRON CHARGING

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Curved polycyclic aromatic hydrocarbons such as carbon π -bowls and belts that represent fragments of fullerenes and nanotubes attract significant attention of experimental chemists and theoreticians due to their unique properties and potential as new carbon-rich materials. Importantly, they are able to acquire multiple electrons in stepwise reduction reactions, producing sets of curved carbanions with variable negative charges. A systematic evaluation of structural and electronic consequences stemming from addition of multiple electrons to carbon π -bowls and belts has become the focus of our research programs. We use a combination of X-ray crystallography, theory, magnetism and spectroscopy to unravel changes in molecular geometry, aromaticity, charge delocalization and coupling pathways of non-planar nanocarbons upon their stepwise charging with electrons. Several systems having different framework topologies, variable sizes and symmetry will be discussed, stimulating our fundamental understanding of curved polyaromatics and advancing their applications as multi-electron storage materials.

L30. APPLICATIONS OF THE GAUGE-INCLUDING CURRENTS METHOD ON LARGE MULTI-RING MOLECULES AND NANOSTRUCTURES

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The basic features of the gauge-including magnetically induced currents (GIMIC) method will be presented.¹ The GIMIC method has been used in studies of current densities of Möbius twisted annulenes,² helical annulenes, and carbon nanotube tori. The applicability of Hückel's aromaticity rule on Möbius twisted molecules is discussed. GIMIC calculations on the carbon nanotube tori yielded structural conditions for sustaining global diatropic and paratropic ring currents in the tori. GIMIC calculations have been performed on multi-ring molecules such as porphyrinoids and [8]circulenes in order to determine the aromatic pathways and aromatic properties of these classes of molecules.^{3,4,5} Calculations on antiaromatic molecules show that closed-shell molecules sustaining a strong paratropic ring current can be paramagnetic.⁶

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L31. ABUNDANT NATURAL PRODUCTS FROM HEAVY OILS: NOVEL POLYNUCLEAR AROMATIC HYDROCARBONS

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Heavy oils are enriched with aromatic hydrocarbons, but characterization of their chemical structures has been a great challenge due to their tremendous diversity. Recently, with the advent of molecular imaging with non-contact atomic force microscopy (nc-AFM), molecular structures of petroleum have been imaged and a diverse range of novel PNA structures was revealed. Understanding these structures is important in order to understand their chemical reactivities, and conversion or formation pathways. Ongoing studies on aromaticity of non-alternant aromatic hydrocarbons provided insights into their intrinsic structural patterns which is essential to reconcile the small number of structures from single molecule imaging and to predict infinite number of diverse molecules in a bulk sample. The contrast mechanism for the AFM bond-like structures will also be discussed by studying a few aromatic molecules in order to facilitate the identification of unknown molecules and understand the relationship of image with molecular structure.

L32. SCOPE AND LIMITATIONS OF EXCITED STATE AROMATICITY AND ANTIAROMATICITY

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Aromaticity and antiaromaticity in the lowest $\pi\pi^*$ excited states of annulenes have received growing attention in the last years.¹ Annulenes with $4n$ π -electrons are aromatic in the first $\pi\pi^*$ triplet state (T_1) while those with $4n+2$ are antiaromatic (Baird's rule),² and this relationship often applies also to the lowest singlet excited state (S_1) of small annulenes.³ Yet, the scope and limitations of the excited state aromaticity and antiaromaticity concepts need to be explored further. In a photoreactivity study we observed that the photochemical ring-opening of the cyclopropyl (cPr) group of cPr-substituted annulenes was hampered for T_1 state aromatic annulenes (Figure 1A) while it is facilitated for T_1 state antiaromatic ones.⁴ But to what extent do the concepts apply to more complex molecules, *e.g.*, poly-cyclic conjugated hydrocarbons? We found that T_1 antiaromaticity of many polycyclic aromatic hydrocarbons localize to certain hexagons.⁵ Conversely, in polycyclic anti-aromatic hydrocarbons with central $4n\pi$ -electron units the T_1 aromaticity can localize to the $4n\pi$ -electron unit provided Hückel-aromatic π -sextets can form in hexagons that are disjoint to the central $4n\pi$ -electron unit.⁶ Thus, Baird's and Clar's rules can be combined. We also discovered the existence of T_1 state homoaromaticity (T_1 aromaticity involving through-space conjugated linkages), yet, its strength varies markedly between different molecules.⁷

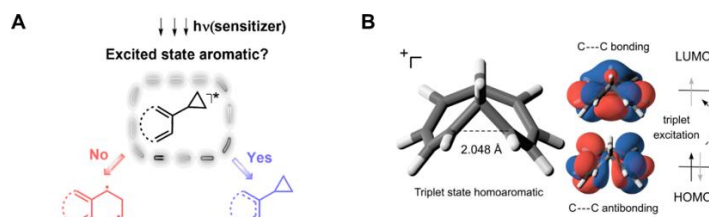


Figure 1: (A) The cyclopropyl group differentiates excited state aromatic cycles from excited state non/antiaromatic ones. (B) Attainment of excited state homoaromaticity leads to large structural changes.

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L33. TRANSITION METAL-FREE C-H FUNCTIONALIZATION OF AROMATIC RINGS: ORGANOCATALYTIC ATROPOSELECTIVE SYNTHESIS OF BIARYLS

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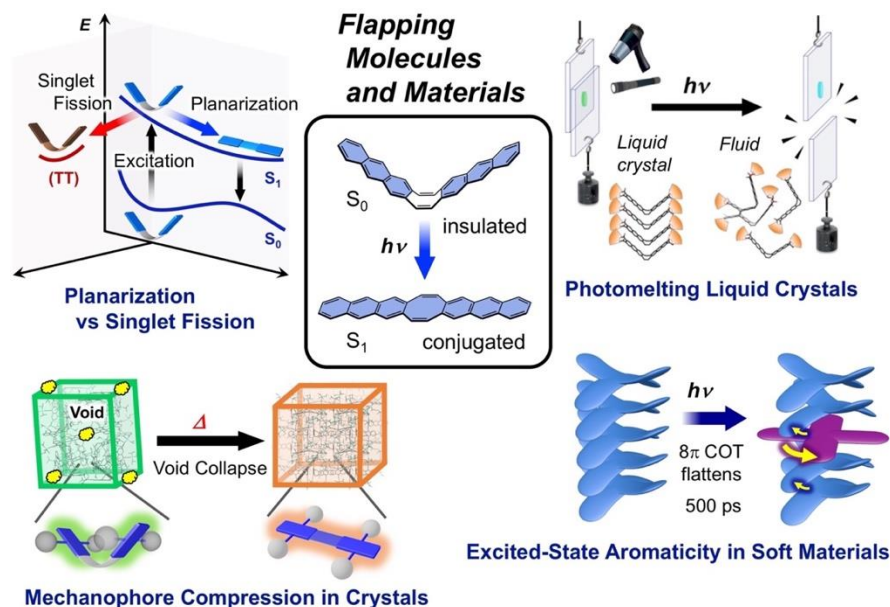
The Kürti lab has been exploring several fundamentally new strategies for the transition-metal-free direct C-H arylation of arenes, in particular the organocatalytic atroposelective synthesis of 1,1'-linked functionalized biaryls. Without exaggeration it can be stated that axially chiral non-racemic biaryls (e.g., BINAP, BINOL, BINAM and their derivatives) have become the most successful class of ligands used in catalytic enantioselective processes. In this presentation we will describe how achiral *N,N'*-diaryl hydrazines can be used as substrates in the presence of chiral acid catalysts to achieve the first catalytic atroposelective synthesis of 1,1'-linked-2,2'-diamino biaryls by utilizing a highly atom-economical [3,3]-sigmatropic rearrangement (i.e., diaza-Cope rearrangement). This sigmatropic rearrangement approach is a complete departure from existing strategies towards the catalytic asymmetric synthesis of biaryls and it has the following advantages: (1) the biaryl linkage (new C-C bond) is formed directly; (2) there is no need for halogens or other replaceable substituents; (3) the two reacting C(sp²)-H bonds are not activated; (4) no carbenes, C-centered radicals, carbocations or carbanions are involved; (5) small chiral organic molecules are utilized as catalysts that can activate the N-N bond; (6) the use of expensive transition metals and ligands is avoided; (7) both atropisomers may be accessed by using either enantiomer of the catalyst and (8) the catalysts can be recovered and used again without losing activity. Computational studies on the transition state, rational catalyst design as well as the mode of chirality transfer will be presented. A related process, the [3,3]-rearrangement of *N,O*-biaryl hydroxylamines, will also be discussed along with the organic acid catalyzed direct arylation of unprotected 2-naphthols to afford racemic as well as enantiomerically enriched, non-C₂-symmetrical 1,1'-linked functionalized biaryls. Our studies revealed that in catalytic enantioselective processes where sequential chirality-transfer steps are involved, the highest level of enantio-induction will most likely take place in those cases where the catalyst does not "miss/skip" an opportunity to transfer chiral information.

L34. EXCITED STATE AROMATICITY OF FLAPPING COT MATERIALS

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Flapping molecules (FLAP) bearing a fused 8π ring at the center have been recently recognized as an emerging class of photoresponsive systems. The FLAP molecules were reported as key structures that show a V-shaped-to-planar conformational change in the lowest singlet excited state (S_1), emitting fluorescence (FL) with large Stokes shift.¹ Along with this line, we have demonstrated the utilities of FLAP as photofunctional materials such as photoresponsive liquid crystals showing excited-state aromaticity,² light-melt adhesive,³ molecular viscosity probes,⁴ singlet fission chromophores,⁵ and conformationally flexible mechanophores.⁶ In this presentation, the latest progress of FLAP molecular series and new photofunctional materials based on their dynamic motion will be introduced.



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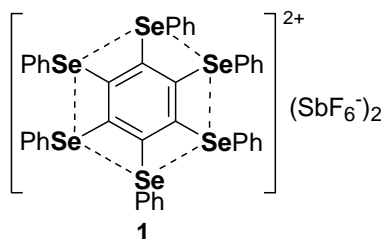
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L35. CHALLENGE TO EXPAND AROMATICITY—FROM π -AROMATICITY TO $\sigma+\pi$ -DOUBLE AROMATICITY

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Since the discovery of benzene, aromaticity has been utilized to explain unique properties of benzene and its derivatives. The aromaticity arises from delocalized π -orbitals composed of $(4n + 2)$ π -electrons and is found to be retained even in lead-bearing cyclic compounds.^{1,2} To expand the aromaticity, we decided to elucidate whether different types of aromaticity coexisted in a single molecule. Since theoretical prediction on a hypothetical molecule possessing σ - and π -double aromaticity was reported,³ experimental evaluation based on bench-stable σ - and π -double aromatic compounds has remained targeted.⁴ Inspired by the previous report on the synthesis of a hexaiodobenzene dication,⁵ though, which is still controversial,⁶ we independently designed a hexaselenylbenzene dication as a possible σ - and π -double aromatic compound, which was predicted by our previous quantum-chemical calculations of a model compound.⁷ We herein report the synthesis of dication salt of hexakis(phenylselenyl)benzene and its X-ray characterization.⁸ The σ - and π -double aromatic character is also discussed.

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L36. SOME THOUGHTS ABOUT AROMATICITY

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Aromaticity is a working concept in chemistry, despite the fact that it is not well defined and that there are no “aromaticity units”. Aromaticity is thus assessed by properties that aromatic systems are supposed to have, for example, energy, geometry, magnetic properties, electron density, number of π electrons, etc. Most of the criteria are not general and some have suffered from criticism because of different reasons. The two criteria that seem to be accepted by the vast majority of chemists are energy (aromatic stabilization energy) and magnetic criteria, which are based on the fact that, under external magnetic field, delocalized electrons form ring current which produce its own induced magnetic field. These conditions are necessary but not sufficient, since there are many stabilizing mechanisms and there are non-aromatic systems that show induced ring currents.

The paper will discuss some new findings regarding NICS _{π ,zz} – one of the most popular methods for assessing magnetic aromaticity. A new method that is based on integration of NICS _{π ,zz} will be presented. The quantitative relations between ASE and magnetic criteria will be discussed.

L37. UNIFYING PLANAR AND SPHERICAL AROMATICS. SHIELDING CONE AS COMMON CHARACTERISTIC

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After one and half century since Kekule's seminal work on the rationalization of benzene structure, this molecule continues to delight attracting interest of chemist communities.¹ This small cyclic hydrocarbon is indubitable one of the more relevant example of a prototypical planar aromatic molecule, displaying a characteristic induced magnetic field opposing or shielding the external field, resulting in long-ranged shielding cone.²⁻⁴ A relevant extension of the concept of *aromaticity* is the realization of three-dimensional aromatic systems, involving a *spherical aromatic* behaviour. Here we unravel a common property linking planar and spherical aromaticity, among other species, by showing their characteristic shielding cones (Figure 1).^{6,7} It is found that for planar aromatics, the cone is reserved only for a perpendicularly applied field, whereas for spherical aromatic compounds, it remains similar under different orientation of the external field.

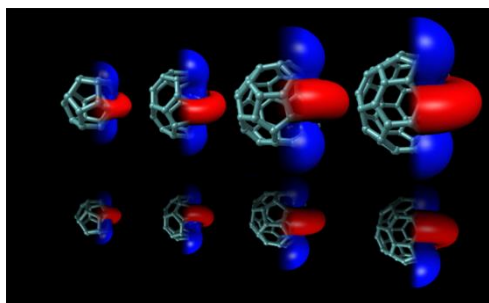


Figure 1. The shielding cone in fullerenes.

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L38. LOCAL AROMATICITY DRIVING THE FORMATION OF FUNCTIONAL SURFACE ALLOYS AND 2-D MATERIALS

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The focus of the talk will be multi-fold aromaticity in bulk interfaces and 2-D materials. The local phenomenon of aromaticity will be showing to stabilize the extended materials, and lead to specific structures and interesting functionalities, such as catalysis, anti-poisoning effects, and unusual conductivity and magnetism. We will discuss surface alloys of transition metals: borides, carbides, and nitrides of importance to catalysis, in which the local multi-fold aromaticity stabilizes the unusual square planar coordination of the main group element and leads to a varying degree of surface reconstruction. Aromaticity also stabilizes the top monolayers of these surface alloys as stand-alone 2-D materials, retaining the structure up to 1,800 K, and possessing conductivity and sometimes magnetism. We will also present a newly predicted 2-D phase of planar boron, forming on the surface of W. This π -phase has two conjugated aromatic systems, and as such possesses anisotropic electrical conductivity. On the fundamental level, we will demonstrate how, in order to obtain a meaningful local bonding picture for a material, it is necessary to not only discover the local bonding elements, but also to connect them to energy, in order to relate to properties.

L39. REDESIGNING CYCLOAROMATIZATION REACTIONS: INTERPLAY BETWEEN AROMATICITY AND ANTIAROMATICITY IN THE GROUND AND EXCITED STATES

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This talk will discuss the strange world of cycloaromatization reactions – the processes where cyclization is coupled with the loss of a chemical bond and formation of either a diradical or a zwitter-ion. High reactivity of such species is used in the enediyne antibiotics, the most potent class of anticancer agents produced by nature. Success of cycloaromatization reactions depends on the interplay of aromaticity with other electronic effects. This talk will discuss how cycloaromatization processes can benefit from electron injection, Au-catalysis and photochemical excitation.

L40. MAGNETIC INDICATORS OF AROMATICITY

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Among the many indicators of aromaticity, those based on the magnetic response are certainly among the oldest, and some of them, like ring current strengths and the many manipulations of shielding and magnetizability tensors, are almost invariably found in any investigation on aromatic molecules. The most popular of those indicators is certainly the nucleus independent chemical shift (NICS), which has captured the attention of non-specialists due to the wide availability of software for its computation.¹ For monocycles, NICS well correlates with energy-based indicators of aromaticity, and it is possible to devise quantitative measures of aromaticity. Despite its frequent effectiveness, there are cases where spurious factors affect the NICS,² and it is likely that, with the diffusion of software for the computation and the visualization of ab initio ring current strengths, the latter will replace NICSs in many cases.

A major concern is that both NICS and ring current strengths can be expected to probe local aromaticity at most, and it is unclear whether, in the study of polycyclics, they can be used to assess the aromaticity of the whole molecule. As both these indicators are eventually rooted in the current density tensor, we have approached that problem starting from it. By use of the anisotropy of that tensor,³ which we have recently re-defined taking care of its asymmetric character,⁴ we realized that it is indeed possible to recover the Hückel delocalization energy in a set of diverse aromatic and non-aromatic polycyclic hydrocarbons.

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L41. ON THE SEARCH OF AROMATIC SILICON RINGS

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Since 1981 when West, Fink, and Michl isolated and characterized a bright orange-yellow crystalline solid named tetramesityldisilene, which contains a sterically stabilized Si=Si double bond, chemists were greatly motivated on discovering silicon compounds analogous to organic molecules, especially aromatic silicon compounds. Unfortunately, silicon compounds, analogous to the benchmark aromatic compound (benzene), have not yet been reported; instead, non-flat Si₆ rings are still preferred. Nonetheless, some exceptional cases of aromatic silicon ring compounds have already been reported. An example of this is the synthesized lithium silicide Li₁₂Si₇, which is made up of planar Si₅ rings (stacked in one-dimensional columns) and trigonal planar Si₄ stars (located in the planes between the Si₅ rings). Each pentagonal silicon-ring is rationalized as a negatively charged Si₅⁶⁻ species, which is π -isoelectronic to the well-known aromatic systems, i.e. benzene, cyclopentadienyl anion, and tropylium cation. Additionally, in 2009, some of us reported the lowest energy structures of the Li_{7-x}Si₅^{1-x} (x = 0, 1, 2) clusters, which consist in a Si₅⁶⁻ pentagonal ring interacting with the corresponding Li⁺ cations. More recently, after exploring their potential energy surface, our high-level quantum chemical computations strikingly show that the lowest energy structures of the (Li₆Si₅)₂₋₅ systems are comprised of 2-5 Si₅⁶⁻ aromatic units and surrounded by Li⁺ counterions, respectively. These gas phase viable compounds are the pioneer reported cases of oligomers made by flat aromatic silicon rings. Moreover, based on the key evidence that these oligomers are energetically favored and that their silicon rings aromaticity is thoroughly preserved, we propose the Li₆Si₅ cluster as a potential assembly unit to build silicon-lithium nanostructures, thus opening new paths to design Zintl compounds at the nanoscale level. We also report different approaches to energetically favor the planar and aromatic Si₆ ring (benzene analog). In particular, we find that the saturation of the bridging and apical positions of the hexagonal ring with counterions shortens the energy gap between the aromatic and the lowest-energy isomer.

L42. COMBINING AND CONNECTING RULES. TOWARD A UNIFIED THEORY OF AROMATICITY

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Many of the quintessential aromatic compounds present high symmetry. Although not all aromatic species are symmetric, the most archetypal aromatic compounds are highly symmetric and possess degenerate highest-occupied molecular orbitals. These orbitals can be fully occupied resulting in a closed-shell structure or can be same-spin half-filled. This closed-shell or same-spin half-filled electronic structure, which provides an extra stabilization, is the origin of several rules of aromaticity such as the Hückel $4n+2$ rule,¹⁻⁴ the lowest-lying triplet excited state Baird's rule,^{5,6} or the $4n$ rule followed by monocyclic conjugated hydrocarbons in a Möbius-type conformation.^{7,8} These rules of (anti)aromaticity are nicely connected in the Ottosson's cube.⁹ In the case of polycyclic conjugated hydrocarbons (PCH) the above mentioned rules do not necessarily apply. One of the most successful attempts to generalize Hückel's rule to benzenoid PCH is the so-called Clar's π -sextet rule.¹⁰ In 1984, Glidewell and Lloyd (GL) reported an extension of this rule to polycyclic conjugated hydrocarbons having rings with any even number of carbon atoms in their structure. Examples of the combination of some of these rules performed in our group will be discussed and the validity of some of these rules will be assessed. Finally, we will briefly refer to the connection between Hückel's rule and the $4n+2$ Wade-Mingos' rule in *closo* boranes,^{11,12} and to the extension of Hirsch's rule¹³ and the Jellium model¹⁴ to open-shell systems.

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L43. THE QUASI-PLANAR BORON CLUSTER B₅₀: LEAP-FROG FORMATION AND DISK AROMATICITY

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The pure B₅₀ boron cluster has recently been found to exhibit a quasi-planar shape rather than a 3D structure as its neighboring sizes. In this talk we discuss the high thermodynamic stability of this structure in terms of the two stabilizing factors: i) B₅₀ is formed from a leap-frog operation starting from B₁₀, and ii) its 32 π valence electrons populate a disk configuration of $[(1\sigma)^2(1\pi)^4(1\delta)^4(2\sigma)^2(2\pi)^4(1\gamma)^4(1\phi)^4(2\delta)^4(1\varphi)^4]$ that satisfy the electron count of disk aromaticity. Relationships to other quasi-planar or bowl-shaped boron clusters will also be discussed.

L44. AROMATIC SINGLET FISSION MATERIALS – UP- AND DOWN-CONVERTING PHOTONS

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The Shockley-Queisser limit places an upper bound on solar conversion efficiency for a single p-n junction solar cell at slightly more than 30%. To surpass this limit, multi-exciton generation is being explored in inorganic semiconductors, while singlet fission (SF) is being investigated in arrays of conjugated organic molecules. In an optimal SF process, the lowest singlet excited state of one molecule (S_1) that is positioned next to a second molecule in its ground state (S_0) is down-converted into two triplet excited states (T_1) each residing on one of the two adjacent molecules. The two triplet states initially form a correlated pair state $^1(T_1T_1)$, which then evolves into two separated triplet states ($T_1 + T_1$). As such, the energetic requirement for SF is $E(S_1) \geq 2 \times E(T_1)$.

We have set our focus in recent years on intramolecular SF in molecular materials and their studies in solution rather than on intermolecular SF investigations in crystalline films. Implicit in intramolecular SF is a resonant, direct excitation of the SF material. In pentacene dimers linked by a myriad of molecular spacers, SF takes place with quantum yields of up to 200%. In addition, all key intermediates in the SF process, including the formation and decay of a quintet state that precedes formation of the pentacene triplet excitons, have been identified. This approach is, however, limited to the part of the solar spectrum, where, for example, the pentacene dimers feature a significant absorption cross-section. To employ the remaining part of the solar spectrum necessitates non-resonant, indirect excitation of the SF materials via either up- or down-conversion. For example, the up-conversion approach is realized with singlet excited states in pentacene dimers, which are accessed by two-photon absorptions (TPA). TPA is then followed in the second step of the sequence by an intramolecular SF – similar to what is seen upon resonant, direct excitation. Quite different is the down-conversion approach, which is based on an intramolecular Förster resonance energy transfer (FRET) and thereby the (photo)activation of the SF material. FRET requires the use of a complementary absorbing chromophore and enables funneling its excited state energy unidirectionally to the SF performing pentacene dimer. Again, SF completes the reaction sequence.

L45. ROLE OF ANTIAROMATICITY IN GROUND STATE DIRADICAL CARBOCATIONS

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Carbocations are widely viewed to be closed-shell singlet electrophiles. Here, we show that computations indicate that azulenyl-substituted carbocations have triplet ground states. This triplet ground state for azulenyl carbocations stands in striking contrast to the isomeric naphthenyl carbocation, which is a normal closed-shell singlet with a large singlet–triplet gap. Furthermore, substitution of the azulenyl carbocation can substantially alter the energy gap between the different electronic configurations and can manipulate the ground state towards either the singlet or the triplet state depending on the nature and location of the substituent. A detailed investigation into the origin of this spin state reversal, including NICS calculations, structural effects, substitution patterns, orbital analysis, and detailed linear free-energy relationships allowed us to distill a set of principles that caused these azulenyl carbocations to have such low-lying diradical states. The fundamental origin of this effect mostly centers on singlet state destabilization from increasing antiaromatic character, in combination with a smaller, but important, Baird triplet state aromatic stabilization. We find that azulene is not unique, as extension of these principles allowed us to generate simple rules to predict an entire class of analogous non-alternant carbocation and carbanion structures with low-energy or ground state diradical states, including a purely hydrocarbon triplet cation with a large singlet–triplet gap of 8 kcal/mol. Although these ions have innocuous-looking Lewis structures, these triplet diradical ions are likely to have substantially different reactivity and properties than typical closed-shell singlet ions.

L46. EXPLORING AROMATICITY WITH EXPANDED PORPHYRINS

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Expanded porphyrin is a term we introduced into the literature in 1988 to describe larger homologues of natural and synthetic tetrapyrrolic macrocycles. Expanded porphyrins, along with many other contracted, isomeric, and core-modified porphyrin analogues, are now known. Expanded porphyrins, in particular, have seen application in areas as diverse as anion recognition and transport, self-assembly, liquid-liquid ion extraction, photodynamic therapy, and anticancer drug development. In recent years expanded porphyrins have helped increase our understanding of aromaticity and antiaromaticity. In this lecture, an update on recent systems that have helped us understand the determinants that allow switching between aromatic and antiaromatic forms in large heteroannulenes will be presented using examples from our laboratory. Also discussed will be systems that support unexpected electronic configurations, including unusual $[4n + 1]$ π -electron semi-aromatic peripheries or which support expanded porphyrin-based self-assembly. New work involving so-called 3D-aromaticity will also be presented.

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**L47. DOES MORE AROMATIC MEAN MORE STABLE?
THE CASE OF AZABORINES AND THEIR *B/N*-MONOSUBSTITUTED
DERIVATIVES**

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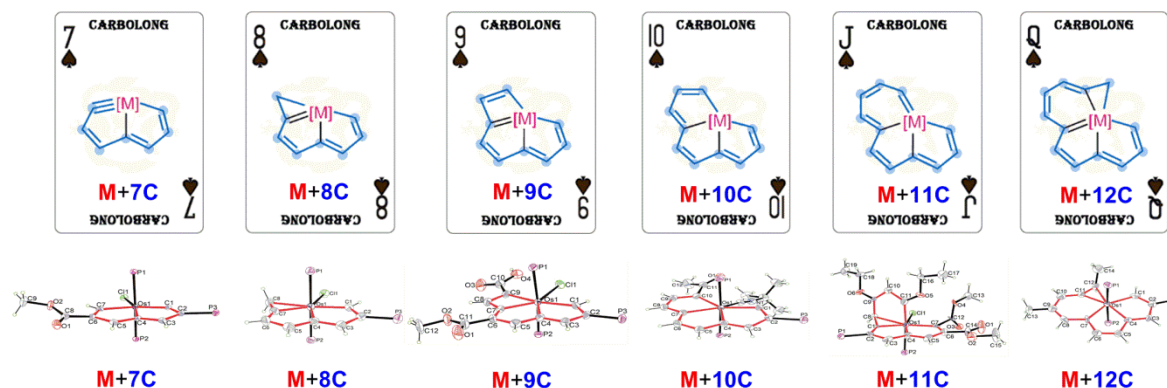
Aromaticity is an important concept in chemistry associated with enhanced thermodynamic stability of cyclic conjugated molecules, relative to acyclic structural analogues, and their special chemical reactivity (substitution instead of addition reaction) which retain the cyclic conjugation. Commonly, more aromatic compound is considered as more stable. However, this is not always the case and exceptions to this traditional thought render aromaticity as a kind of stabilizing effect and stability as a global molecular property. In this presentation, the case of the three isomeric azaborines and their *B/N*-monosubstituted derivatives will be discussed. These compounds feature one BN unit instead of the CC unit in benzene. The two units are isoelectronic, but the BN one is more polar. The BN substitution pattern, as well as substituent position can lead to different trend of aromaticity and stability.

L48. CARBOLONG CHEMISTRY: A NOVEL AROMATIC SYSTEM

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The development of new aromatic systems has long been a fundamental and fascinating topic in chemistry. Recently, we have developed a novel class of metal-containing aromatics, named as “carbolong complexes”, by chelating transition metals with carbon chains of 7 to 12 carbon atoms.¹ In particular, these complexes exhibit remarkable aromaticity. For example, **M+7C** displays unprecedented Craig Möbius aromaticity,² while **M+8C** demonstrates dominant σ -aromaticity.³ All these metalla-aromatics exhibit excellent thermodynamic stability; they are persistent even when the solid sample were heated to 100 °C in air. More importantly, these metallaaromatics have unique optoelectronic, photoacoustic and photothermal properties. Most of them could achieve luminescence phenomena such as aggregation induced emission enhancement, large Stokes shifts and long lifetime, broad absorption from the ultraviolet-visible to the near-infrared region, suggesting promising application in medical chemistry and material science.



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L49. AROMATICITY IN ORGANOMETALLICS AND ITS APPLICATION IN N₂ ACTIVATION

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Aromaticity, one of the most fundamental concepts in chemistry, has attracted considerable attention from both theoreticians and experimentalists. However, besides metallabenzenes, other transition metal-involved aromatics are less developed. Here, we report the magic rule of transition metals in several metallaaromatics by density functional theory calculations. Specifically, Craig-type Möbius aromaticity, σ -aromaticity dominating in an unsaturated ring, hyperconjugative aromaticity and adaptive aromaticity are achieved due to an introduction of transition metals.¹⁻⁵ In addition, the application of aromaticity in N₂ activation will be also discussed.

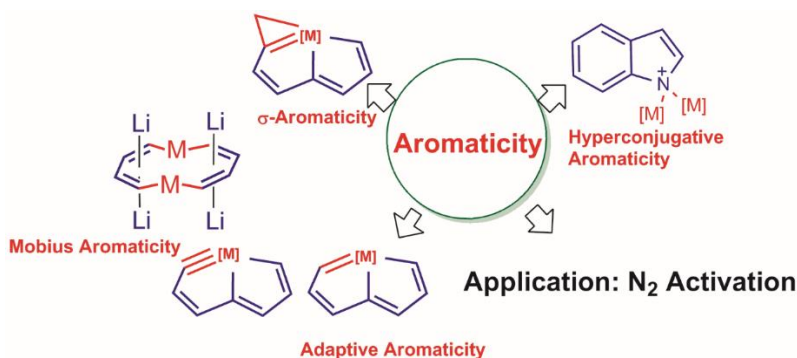


Figure 1. Schematic illustration of some unconventional aromaticity and its application in N₂ activation.

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P1. MOLECULAR HELMHOLTZ COILS

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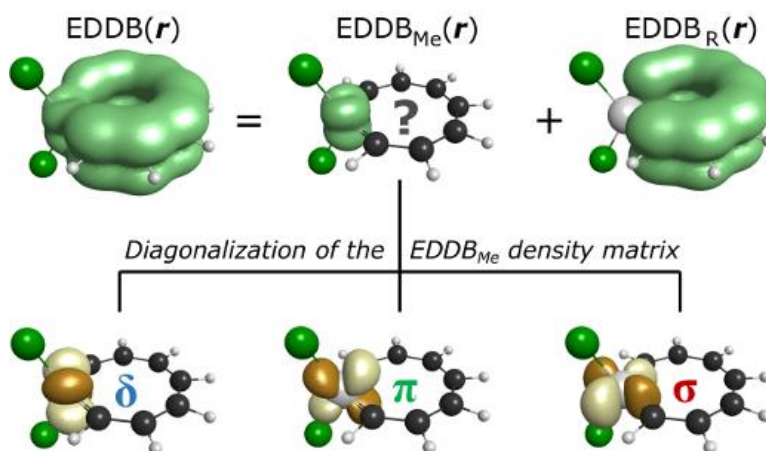
How to build a molecular Helmholtz coil? To evaluate the nature of feasible homogeneity as classical electrodynamics predicts in an ideal case, the induced magnetic field is computed in systems comprised by two stacked π - π hydrocarbon rings in such a way that they satisfy the condition of a Helmholtz coil, namely, that the distance between rings coincides with the ring radius. The systems are constructed using planar rings with formula C_nH_n ($n = 6 - 10$). The magnetic responses are dissected into molecular orbital contributions. The results show uniform π -magnetic responses for dimers with $n = 8-10$, independently of the induced field intensity. Conversely, σ -electrons are more localized, therefore, their induced currents do not flow along the entire structure and Helmholtz homogeneity is not present. Our work provides a solid way to rationalize and design coils at the molecular scale.

P2. AROMATICITY OF METALLACYCLES: HÜCKEL OR MÖBIUS?

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Metallacycles play a crucial role in organic synthesis where they frequently appear as reaction intermediates. The properties and catalytic reactivity of metallacycles are known to be determined by aromatic stabilization.^{1,2} Unfortunately, quantitative analysis and interpretation of the aromaticity phenomenon involving transition metals has been a major challenge for a long time owing to availability of several different d-type orbitals contributing to the resonance in aromatic ring.^{3,4} In this work we propose a method that not only allows one to quantify and visualize cyclic delocalization in metallacycles, but also to determine the contribution of each d-type orbital from the metal atom to the chemical resonance. Our approach is based on the recently developed electron density of delocalized bonds method (EDDB),⁵ and relies on decomposition of the total EDDB(r) density into two fragments representing metal and carbon ring, EDDB_{Me}(r) and EDDB_R(r) respectively, followed by diagonalization of the EDDB_{Me} density matrix to get the corresponding d -orbital contributions to the aromatic stabilization. We use our method to study selected metallacycles with 8π -electrons and different bonding topologies.



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P3. INDUCED MAGNETIC FLUX ANALYSIS IN PLANAR CYCLIC MOLECULES

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Fundamental concepts as the chemical bond, electronegativity or electron delocalization (ED) have not a simple definition and always are immersed in controversy.¹ In particular, the ED cannot be measured through an experiment, hence, in an effort to quantify it, several criteria have been introduced, of which the magnetic ones are among the most popular such as the NICS² or the induced magnetic field³ (\mathbf{B}^{ind}). The systems with delocalized electrons (aromatic) are sensible to external magnetic fields, they respond with an induced current density that produces the \mathbf{B}^{ind} . In this sense, we can compute the magnetic flux associated with the induced field (Φ^{ind}). Therefore, in this work we calculated the induced magnetic flux that crosses the molecular ring surface. Since, the magnetic flux depends on the area, we define the quantity “induced magnetic flux per area unit” (Φ^{ind}/A). Thus, Φ^{ind}/A was obtained in order to quantify the diamagnetic (or paramagnetic) character of several mono- and polycyclic molecules as a way to diagnose the ED degree. Furthermore, we analyzed the orbital contributions to the \mathbf{B}^{ind} as well as for Φ^{ind} . Our calculations show that the valence contributions to the magnetic flux (Φ^{ind}) describe correctly electron delocalization of the systems, even better than NICS and \mathbf{B}^{ind} in the case of polycyclic molecules (See Table 1). Hence, we propose a new parameter to diagnose ED in terms of magnetic quantifications of induced fluxes.

Table 1. $\Phi_{\sigma}^{\text{ind}}/A$, $\Phi_{\pi}^{\text{ind}}/A$ y Φ^{ind}/A in ppm for monocyclic molecules.

	$\Phi_{\text{core}}^{\text{ind}}/A$	$\Phi_{\sigma}^{\text{ind}}/A$	$\Phi_{\pi}^{\text{ind}}/A$	Φ^{ind}/A
Benzene	-14.73	3.00	-32.18	-43.90
Al ₄ ²⁻	-7.07	-42.98	-5.25	-55.28
Cyclobutadiene	-11.34	18.61	41.24	48.51
Cyclopentadienyl cation	-12.22	2.99	165.55	156.33
Borazine	-21.48	11.70	-9.94	-19.73

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P4. AROMATICITY OF NOVEL EXPANDED PORPHYRINS

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Since the first report of sapphyrin by Woodward in 1966, significant efforts have been made in developing and characterizing expanded porphyrins.^{1,2} In addition to many of their interesting properties, expanded porphyrins exhibit flexible electronic properties in that they can be aromatic or anti-aromatic depending on the number of π -electrons and their topology. We and others have exploited this dynamic nature to develop several novel expanded porphyrins. Recently, our group in conjunction with collaborators reported the so-called naphthorosarin, an annulated expanded porphyrin. This system demonstrated proton-promoted redox switching (PCRS), where the addition of HCl was found reduce the anti-aromatic $[4n]$ π -electron species to the corresponding $[4n+1]$ π -electron radical species. Similar treatment with HI produced a fully aromatic $[4n+2]$ π -electron form. Initial efforts to generalize this to several porphyrinoids proved unsuccessful. However, we were able to prepare a novel, highly rigidified expanded porphyrin analogue, namely octaphyrin(1.0.1.0.1.0.1.0), that exhibited similar PCRS behavior. On a different note, we have found that the aromatic nature of expanded porphyrins can be modified through metal coordination. For example, we reported a metal complexation-based strategy that permits access to highly stable expanded porphyrin-type quinoidal polycyclic aromatic hydrocarbons (PAH). In this instance, the double insertion of Pd(II) cations into what was dibenzo[g,p]chrysene-fused bis-dicabacarrole (bis- H_3) was found to produce a stable bis-Pd species that undergoes facile benzenoid-quinoid transformation. This opens the door to a generalized approach to the design of quinodial PAH structures with long wavelengths and solvatochromic absorption features. We also found that the reaction between amethyrin and a non-aqueous silylamide uranyl cation source ($UO_2[N(SiMe_3)_2]_2$) under anaerobic conditions affords a bench-stable uranyl complex. UV-vis spectroscopy, cyclic voltammetry, as well as proton NMR spectroscopic analyses provided support for the conclusion that all six pyrrole subunits participate in coordination of the uranyl dication and that, upon complexation, the amethyrin-core undergoes a 2-electron oxidation to yield a formal 22 π -electron aromatic species. This work and new studies of expanded porphyrins will be highlighted in this presentation.

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P5. THE EFFECT OF EXOCYCLIC SUBSTITUENTS AND π -SYSTEM LENGTH ON THE ELECTRONIC STRUCTURE OF CHICHIBABIN DIRADICALOIDS

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Since the synthesis of Chichibabin's diradicaloid polycyclic hydrocarbons in 1907, the nature of their electronic structure and that of their derivatives have been a recurring topic of debate for both theoretical and experimental chemists.¹ These compounds are getting special attention owing the tunable character of its ground state (GS) that can be singlet (open- or closed-shell) or triplet, depending on the elongation of the π -system and the exocyclic substituents.² These molecules have either a triplet GS or a small singlet-triplet energy gap.

To analyze the effect of the size and exocyclic substituents on the nature of the GS of Chichibabin's hydrocarbons, we have selected a number of them with different substituents in the exocyclic carbon atoms and different ring chain lengths. Several DFT functionals and CCSD(T) together with cc-pVXZ (X=D,T) basis sets were used for the optimization of the smallest systems, whereas the largest species are "only" treated at DFT level of theory. The aromaticity of the resulting electronic structures was evaluated with NICS, PDI, I_{ring} , and MCI aromaticity indices. Our results show that the shortest π -systems (one or two rings) have a singlet GS. However, systems with three to five rings favor triplet GS. Electron-withdrawing groups (EWG) in the exocyclic carbons tends to stabilize the triplet state, while electron-donating groups (EDG) have slightly destabilize the triplet state. In general, the compounds present small singlet-triplet energy gaps, and in particular, the ones with two rings and EW substituents present the smallest singlet-triplet energy gaps.

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P6. DFT AROMATICITY STUDY OF CARBON-RING ALLOTROPE STRUCTURES

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First, an aromaticity study of monocyclic conjugated carbon-ring allotrope structures was carried out, alternating simple and triple bonds, obtained by geometric optimization of carbon chain pairs with the molecular modeling software *DMol³* of Biovia Materials Studio, which uses methodology based on Density Functional Theory, with GGA / PW91 functional, spin non-restricted; at the level of self-consistent field electron (SFC), with DND analogous to 6-31G* basis. The study was fundamented on the geometrical criterion: the bonds lengths and the planarity of the molecule, and on the electronic criterion: the energy difference between HOMO and LUMO orbitals, the molecular potential, hardness and electrons π , where the main reactivity of the aromatic compounds is the electrophilic substitution.

Second, an aromaticity study of planar rings of 14 and 16 carbons with mixed simple, double, and triple bonds, inserted in planar molecules $C_{20}H_3$, $C_{22}H_3$, $C_{22}H_4$, respectively; corresponding to $4N + 2$ and $4N$ according to the Hückel aromaticity rules in complex conjugation. The methodology used is the molecular modeling software *DMol³* of Biovia Materials Studio, based on Density Functional Theory, with *GGA/VWN – PB* functional for SCF spin non-restricted, and DND similar to 6-31G * basis.

The creation of new carbon structures and their analysis of aromaticity provides us with chemical characteristics that will determine its molecular structure and its operation which can be used in design and development of materials with new technologies.

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P7. GLOBAL AND LOCAL AROMATICITY OF EXPANDED PORPHYRINS THROUGH MAGNETIC RESPONSE ISOSURFACES

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The aromaticity of some expanded porphyrins has been analyzed according to the magnetic criteria, performing three-dimensional mapping of the z component of the magnetically induced magnetic field (B_{zz}^{ind}).¹ The studied systems consist in Hückel, Twisted and Möbius aromatic expanded porphyrins. The results show, in a graphical way, the existence of global and local long-range effects, which in turns allows to characterize the global and local aromatic character of these macrocycles. Besides, it is also possible identifies characteristic topological patterns due the main conjugation pathway coming from the [N]-annulene model.²

Additionally, it is introduced an alternative strategy to quantifies local and global aromaticity, by identifying the ring bifurcation critical points (3,-1) of the scalar B_{zz}^{ind} property. This approximation was inspired by the aromaticity scale proposed by Santos et. al. some years ago,³ which is based in the ring bifurcation values of the Electron localization function (ELF) identified through topological analysis of this function.

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P8. CORRELATION BETWEEN AROMATICITY (BY NMR) AND STABILITY AND COMPATIBILITY OF COLOMBIAN CRUDE OILS

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Crude oils are complex colloidal systems that possess Saturates, Aromatics, Resins and Asphaltenes compounds (SARA). Aromatics dissolve the paraffins and the asphaltenes and resins help stabilize asphaltenes, whose stability is one of the most important factors in the petroleum industry.¹ Asphaltenes are the fraction of petroleum that precipitates with n-heptane and is soluble in toluene, its chemical structure is not resolved yet but they are molecules with an aromatic core with aliphatic chains as substituents (aromaticity factor > 0.5) and depending of the number of aromatic rings and their polycondensation have been classified as continental type or archipelago type (Figure 1). According to the chemical structure of the asphaltenes and SARA composition they make the crude oils stable and compatible when they are mixed with other crude oils.

The goal of this work was to study the effect of aromaticity (measured by NMR) on stability (measured as I_N Instability Number) and compatibility (measured as Mix Solubility Number- S_{BN}) of sixteen Colombian crudes representing approx. 50% of the country's current production. Different chemometric methods (PCA, MLR, PLS) were used to correlate the aromatic structure with the properties of interest.

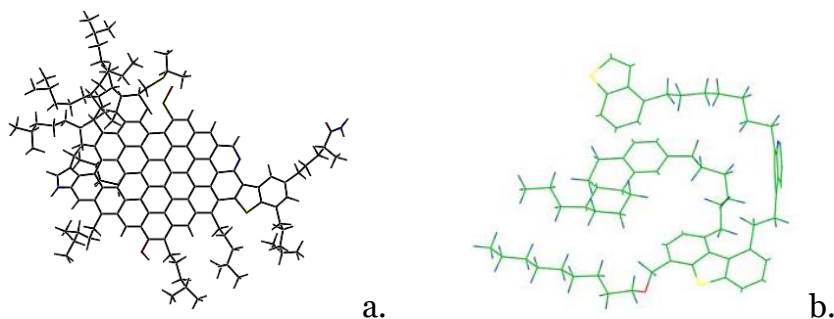


Figure 1. Continental (a) and archipelago (b) type structures of asphaltenes [2].

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P9. EXCITED STATE STRUCTURES AND AROMATICITY OF DIBENZ-ANNELATED 8π -ELECTRON HETEROCYCLIC COMPOUNDS

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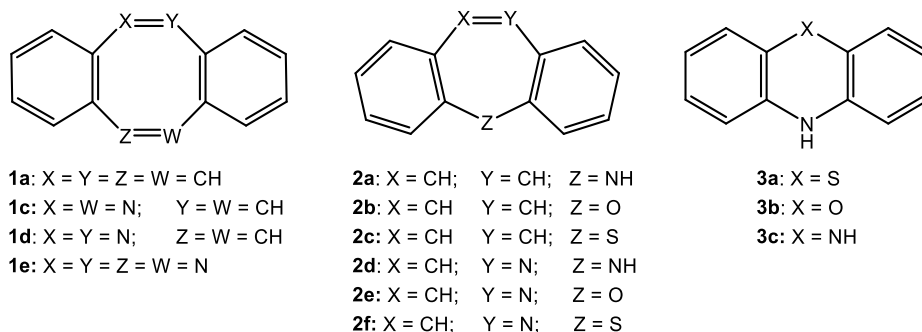
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Gain of excited state aromaticity, as given by Baird's $4n$ rule, is a driving force for photoreactivity as well as changes in excited state structures and other properties.⁵ Dibenzannelated molecules with central 8π -electron rings are interesting to investigate as they are found in diverse organic substance classes, such as antipsychotics (*e.g.* quetiapine, chlorpromazine and loxapine) and photofunctional materials (*e.g.* molecular viscosity probes and photoresponsive liquid crystals).⁶ In the ground state, these molecules usually adopt non-planar and nonaromatic tub-shaped geometries. However, in the first excited states (S_1 and T_1) they may adopt planar structures associated with Baird aromaticity.⁷ We now report on a quantum chemical study focused on how the position, type, and number of heteroatoms in the central 8π -electron ring (Scheme 1) affect the S_1 and T_1 state structures (planarity) and extent of aromaticity of the dibenzannelated compounds.



Scheme 1: Dibenzannelated 8π -electron compounds investigated in this work.

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P10. ON THE MAGNETIC SIGNATURE OF HELICENES

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The [*n*]helicenes have continuously received considerable attention, not only for their aesthetic helical structure but also for their exceptional properties, giving rise to an exciting class of intrinsic chiral molecules.¹ The characteristic helical structure offers an interesting scenario to explore the possible role of aromaticity in strain-induced helical polyaromatic systems with nonplanar rings. Earlier works from the groups of Solà² and Schulman³ pointed out that a planarity deviation up to 25° does not induce a sizable decrease of electron conjugation, as determined from NICS probes, calculation of energies, structural parameters, magnetic susceptibilities, and chemical shifts. The enhanced NICS values observed in large helicenes may be rationalized in terms of the additive interaction of the magnetic response arising from each stacked aromatic ring. Here, we address the magnetic signature of the helical topology of helicenes, dissected in individual contributions from π -, σ - and core-electron kernels of the [6]- [7]- and [14]helicene, the representative for the cases with zero-, one-, and two- stacked layers of aromatic rings. The results exhibit that both shielding and deshielding regions may interact constructively, showing an enhanced response owing to their particular helicoidal architecture, implying a new addition to the currently known intensified physic-organic properties of such species.

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P11. DOUBLE ($\sigma+\pi$)-AROMATICITY IN CE_5^- (E=AL–TL) CLUSTERS

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One of the most representative systems of these nonclassical molecules is CAI_4^{2-} . Its structure is a perfect Al_4 square with a carbon at the center and its planarity is mainly a consequence of the presence of a four-center peripheral ligand–ligand bonding interaction in the HOMO and the π orbital spread over all five atoms.¹ Herein we extensively explored the Potential Energy Surface of the singlet and the triplet CE_5^- (E=Al, Ga, In, Tl) by means of a heuristic algorithm based on a kick-modified approach.¹ Additionally, we analyzed the hypercoordinated clusters CE_5^- (E = Al–Tl) using different computational tools in conjunction with the induced magnetic field (\mathbf{B}_z^{ind})² to further understand the geometrical preferences in the heavier analogues of CAI_5^- . The results in CE_5^- indicate that, whereas aluminum and gallium clusters have C_{2v} structures with a planar tetracoordinate carbon (ptC), their heavier homologues prefer three-dimensional C_{4v} forms with a pentacoordinate carbon center instead of the ptC one. The reason for such structural differences lies in the ability of the interaction energy between E and the CE_4 fragment to compensate for the high distortion energy. The ptC core in these systems exhibits double aromatic behavior (both σ and π), but the σ contribution dominates.

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P12. INTEGRATED CLASSICAL AND QUANTUM MECHANICAL STUDY OF NDIII COMPLEXES AS ANTICANCER AGENTS: EFFECT OF THE STACKING INTERACTION WITH WELL AND MISMATCHED DNA, SENSITIZATION PATHWAYS AND SPECTROSCOPIC PROPERTIES

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A rigorous study, going from classical to relativistic quantum mechanical methods, has been performed on some phenanthroline derivatives synthesized and characterized herein, *viz.* [Nd(NO₃)₃(H₂O)(dppz - R)] with R= H, NO₂⁻, CN⁻ and its [Nd(NO₃)₃(H₂O)(dpq)] analogue which was modeled computationally. In a first step, MD simulations and MM-GBSA calculations allowed to analyze the binding of these compounds to well and mismatched DNA. The results were in correct agreement with the available experimental data and showed that dppz complexes have higher binding affinities to DNA than dpq ones. Furthermore, no significant differences from an energetic point of view were found between well and mismatched systems. In a second step, the more stable conformations were taken from MM-GBSA calculations and a Morokuma-Ziegler Energy Decomposition Analysis (EDA) analysis was done. The results were in accordance with the main observations obtained in the first part of the work, supporting the idea that these compounds are not selective to mismatch sites. In addition, TDDFT calculations were carried out to study the spectroscopic properties of the isolated and intercalated complexes, and the well-reported hypochromism when the compounds are not bound to DNA was observed. The results also supported a possible sensitization of the neodymium because a ligand-localized absorption was noted. Finally, the SO-CASSCF/NEVPT2 methodology made possible the elucidation of the most probable energy transfer pathways between the dppz, and Nd^{III} and evidenced poor conditions for a good sensitization thus explaining the complications observed experimentally.

P13. DITHIOPHENO-BRIDGED OCTAPHYRINS: BICYCLOAROMATIC OR EXPANDED POLYCYCLIC AROMATIC HYDROCARBONS?

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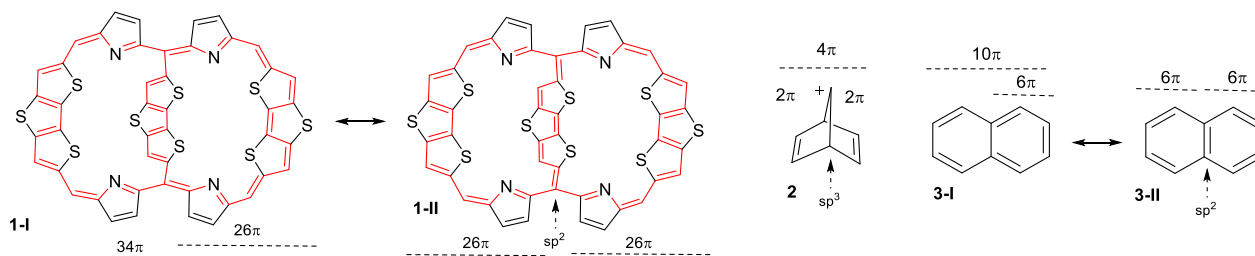
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Bicycloaromaticity has gained recent attention through experimental and computational studies of dithiopheno-bridged octaphyrins (*e.g.*, **1** below) labelled as bicycloaromatic.^{1,2} The concept was coined by Goldstein in 1967,³ and put in a broader context by Goldstein and Hoffmann.⁴ For example, a bicyclic molecule with three separate polyene segments (ribbons) interacting according to so-called longicyclic or laticyclic topologies is bicyclo-aromatic if the total number of π -electrons equals $4n$, illustrated by **2** having two 2π - and one 0π -electron ribbons and a total of four π -electrons. Now, are the dithiopheno-bridged octaphyrins *bicycloaromatic* or bicyclic with two Hückel-aromatic conjugated circuits? Clearly, the total number of π -electrons in **1** is 42, a $4n+2$ instead of a $4n$ number. Thus, octaphyrine **1** does not satisfy the fundamental electron count for bicycloaromaticity. By gradually going from naphthalene (**3**) to **1** we instead argue that **1** is best described as an expanded naphthalene, *i.e.*, a polycyclic aromatic hydrocarbon that can be drawn with several different Hückel-aromatic conjugated circuits (6π - and 10π -electron circuits in **3**).⁵ Depending on the resonance structure, the bridge in **3** has either zero or two π -electrons (**3-I** or **3-II**) while the bridge in **1** has either eight or ten π -electrons (**1-I** or **1-II**). The reason that one 26π -electron circuit in **1** dominates over the other is structural; ring-puckering and a tilted dithiopheno-bridge. In addition to one dominating 26π -electron path, (*cf.*, one 6π -electron cycle in **3**) there is the perimetric 34π -electron path (*cf.*, the 10π -electron path in **3**). Hence, **1** is bicyclic and aromatic similar as naphthalene, but it is not bicycloaromatic.



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P14. REACTION ELECTRONIC FLUX PERSPECTIVE ON THE EXCITED STATE AROMATICITY OF THE ZIMMERMAN REARRANGEMENT

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The relationship between the reaction electronic flux (REF) and aromaticity on mechanism of the triplet di- π -methane rearrangement has been studied by means of computational methods. The triplet rearrangement is preferred for bicyclic molecules such as dibenzobarrelene (DBB), which leads to dibenzosemibullvalene (SBV) as product.^{1,2} Photoexcitation via singlet S₁ state leads to a different product, a dibenzocyclooctatetraene. Upon triplet sensitization, DBB* can form a 1,4-biradical intermediate (BR-I) that leads to a 1,3-biradical intermediate (BR-II). From BR-II, the intersystem crossing (ISC), leading to the ground state, gives the SBV product. Invoking the Salem's rules for ISC of biradicals, the perpendicular orientation between non-orbitals in BR-II suggests a relatively facile ISC mechanism. Hence, the first transition state (TS-I) on T₁ should be determining in the reaction rate, with ca. 4 kcal/mol above the barrier associated to the second transition state (TS-II). In the mechanism of this [$\pi^2+\sigma^2$] rearrangement, one-step and two-step pathways compete on the triplet surface, since BR-I may bypass in the passive of the alkene triplet to BR-II.^{1,2} Substituent effects can destabilize the radical species on T₁ and eventually BR-II becomes the regioselectivity determining step.³ In a very recent work,⁴ The REF was found to discriminate between electronic flux in π - and σ -bonds, thus providing insights into the key role played by the aromaticity along the reaction coordinate for this aryl-vinyl photorearrangement. Effects arising from triplet antiaromaticity alleviation and the Baird's rule were studied as well.^[4]

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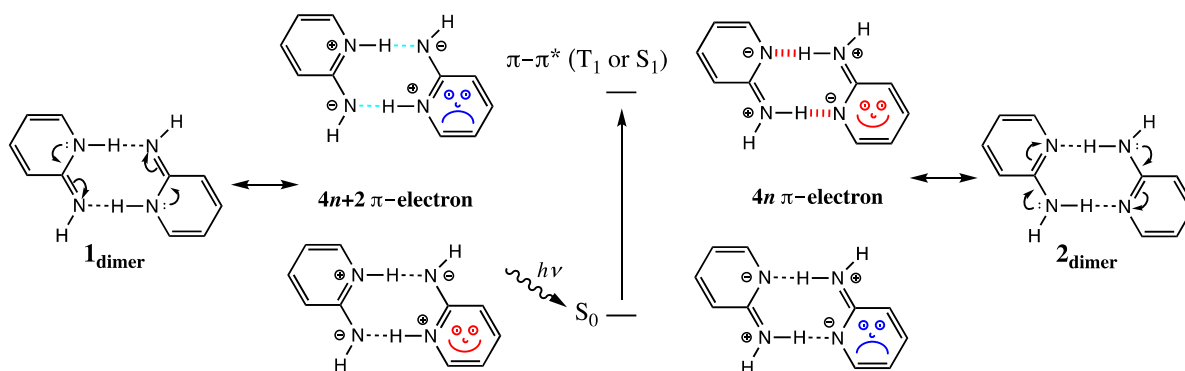
P15. AROMATICITY-MODULATED HYDROGEN BONDING (AMHB) AT THE EXCITED-STATE

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Recent works from our group have shown that hydrogen bonding interactions that increase (or decrease) the cyclic $4n+2$ π -electron delocalization of heterocycles, at their ground states, can be strengthened (or weakened) through Aromaticity-Modulated Hydrogen Bonding (AMHB).^{1,2} Here, we show that such effects reverse at specific π - π^* excited-states, since the (anti)aromatic characters of π -conjugated rings follow a reversed Hückel $4n+2$ π -electron counting rule at those states (i.e., Baird's Rule).³ Quantum-mechanical calculations show that, indeed, hydrogen bonding interactions that polarize π -electrons to enhance cyclic $4n+2$ π -electron delocalization in heterocycles (e.g., **1**_{dimer}) are weakened due to increased excited-state antiaromaticity, while those that reduce $4n+2$ π -electron delocalization (e.g., **2**_{dimer}) are strengthened due to decreased excited-state antiaromaticity (see Scheme 1). We show that the effects of excited-state AMHB have fundamental importance for elucidating photochemical processes, such as excited-state proton transfer mechanisms in DNA nucleobase pairs.



Scheme 1. Schematic illustration of excited-state AMHB.

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