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# AROMAT CITY 2018

*Riviera Maya, Mexico*

## ABSTRACT BOOK



November 28-December 1, 2018

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## 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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Cinvestav Mérida



## Participants Directory

### **Gabriel Merino**

Centro de Investigación y de Estudios Avanzados. México  
gmerino@cinvestav.mx

### **Jordi Poater**

Universitat de Barcelona. Spain  
jordi.poater@ub.edu

### **Mercedes Alonso**

Vrije Universiteit Brussel. Belgium  
mercedes.alonso.giner@vub.be

### **Hiroyuki Isobe**

University of Tokyo. Japan  
isobe@chem.s.u-tokyo.ac.jp

### **Michael Haley**

University of Oregon. The USA  
haley@uoregon.edu

### **Juan Casado**

Universidad de Málaga. Spain  
casado@uma.es

### **Israel Fernández**

Universidad Complutense de Madrid. Spain  
israel@quim.ucm.es

### **Judy Wu**

University of Houston. The USA  
judyicwu@gmail.com

### **Patrick Bultinck**

Ghent University. Belgium  
patrick.bultinck@ugent.be

### **Fernando Cossío**

Euskal Herriko Unibertsitatea. Spain  
fp.cossio@ehu.es

### **Yoshimitsu Itoh**

University of Tokyo. Japan  
itoh@macro.t.u-tokyo.ac.jp

**Eduard Matito**

Euskal Herriko Unibertsitatea. Spain  
ematito@gmail.com

**Daniel Gryko**

University of Warsaw. Poland  
dtgryko@icho.edu.pl

**Renana Poranne**

ETH Zurich. Switzerland  
renana.poranne@org.chem.ethz.ch

**Anirban Misra**

University of North Bengal. India  
anirbanmisra@nbu.ac.in

**Masaaki Nakamoto**

Hiroshima University. Japan  
mnakamot@hiroshima-u.ac.jp

**Matthias Bickelhaupt**

Vrije Universiteit Amsterdam. The Netherlands  
f.m.bickelhaupt@vu.nl

**Yosadara Ruiz-Morales**

Instituto Mexicano del Petróleo. México  
yruiz@imp.mx

**Yasujiro Murata**

Kyoto University. Japan  
yasujiro@scl.kyoto-u.ac.jp

**Shigeru Yamago**

Kyoto University. Japan  
yamago@scl.kyoto-u.ac.jp

**Roald Hoffmann**

Cornell University. The USA  
rh34@cornell.edu

**J. D. Tovar**

Johns Hopkins University. The USA  
tovar@jhu.edu

**Norihiro Tokitoh**

Kyoto University. Japan  
tokitoh@boc.kuicr.kyoto-u.ac.

**Oscar Jiménez**

Universidad de Guanajuato. México  
jjimenez@ugto.mx

**Aurelio Mateo**

Universidad del País Vasco. Spain  
amateo@polymat.eu

**Peter Karadakov**

University of York. United Kingdom  
peter.karadakov@york.ac.uk

**Fernando Langa**

Universidad de Castilla. Spain  
fernando.langa@uclm.es

**Lechosław Latos-Grażyński**

University of Wrocław. Poland  
lechoslaw.latos-grazynski@chem.uni.wroc.pl

**Marina Petrukhina**

University of Albany. The USA  
mpetrukhina@albany.edu

**Dage Sundholm**

University of Helsinki. Finland  
Dage.Sundholm@helsinki.fi

**Yunlong Zhang**

ExxonMobil Research and Engineering Company. The USA  
yunlong.zhang@exxonmobil.com

**Henrik Ottosson**

Uppsala University. Sweden  
henrik.ottosson@kemi.uu.se

**Laszlo Kürti**

Rice University. The USA  
kurti.laszlo@rice.edu

**Shohei Saito**

Kyoto University. Japan  
s\_saito@kuchem.kyoto-u.ac.jp

**Masaichi Saito**

Saitama University. Japan  
masaichi@chem.saitama-u.ac.jp

**Annon Stanger**

Technion-Israel Institute of Technology. Israel  
stanger@technion.ac.il

**Alvaro Muñoz**

Universidad Autónoma de Chile. Chile  
alvaro.munoz@uautonoma.cl

**Anastassia Alexandrova**

University of California Los Angeles. The USA  
ana@chem.ucla.edu

**Igor Alabugin**

Florida State University. The USA  
alabugin@chem.fsu.edu

**Guglielmo Monaco**

Università degli Studi di Salerno. Italy  
gmonaco@unisa.it

**William Tiznado**

Universidad Andrés Bello. Chile  
wtiznado@unab.cl

**Miquel Solà**

Universitat de Girona. Spain  
miquel.sola@udg.edu

**Minh Nguyen**

KU Leuven. Belgium  
minh.nguyen@kuleuven.be

**Dirk Guldi**

University of Erlangen-Nürnberg. Germany  
dirk.guldi@fau.de

**Arthur Winter**

Iowa State University. The USA  
winter@iastate.edu

**Jonathan Sessler**

The University of Texas Austin. The USA  
sessler@cm.utexas.edu

**Marija Baranac**

University of Belgrade. Serbia  
mbaranac@chem.bg.ac.rs

**Haiping Xia**

Xiamen University. China  
hpxia@xmu.edu.cn

**Jun Zhu**

Xiamen University. China  
jun.zhu@xmu.edu.cn

**Albeiro Restrepo**

Universidad de Antioquia. Colombia  
albeiro@matematicas.udea.edu.co

**Dariusz Szczepanik**

Universitat de Girona. Spain  
dszczpnk@gmail.com

**Mesías Orozco**

Centro de Investigación y de Estudios Avanzados. México  
mesias.orozco@cinvestav.mx

**Daniel Mangel**

University of Texas. The USA  
d\_mangel@utexas.edu

**Sílvia Escayola**

University of Girona. Spain  
silvie7@gmail.com

**Yasminne Esquivel**

Instituto Tecnológico de Toluca. México  
yas\_ema@hotmail.com

**Ricardo Pino**

Universidad de Santiago de Chile. Chile  
ricardo.pino@usach.cl

**Daniel Molina**

Universidad Industrial de Santander. Colombia  
dmolina@uis.edu.co

**Josene Toldo**

Uppsala University. Sweden  
josene.toldo@kemi.uu.se

**Jorge Barroso**

Centro de Investigación y de Estudios Avanzados. México  
jorge.barroso@cinvestav.mx



# AR MAT C TY 2018

*Riviera Maya, Mexico*

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**Gerardo Hernández**

Centro de Investigación y de Estudios Avanzados. México  
gerardo0339@gmail.com

**Maria Beltran**

Universidad Andres Bello. Chile  
m.beltranleiva@uandresbello.edu

**Ricardo Matute**

Universidad Bernardo O'Higgins  
rmatute@caltech.edu

**Lucas Karas**

University of Houston. The USA  
ljkaras@uh.edu

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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 metallabenzenes: 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<sub>zz</sub>

**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  $\pi$ -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<sub>50</sub>: 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 N<sub>2</sub> 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  $\pi$ -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-,  $\sigma$ -, and  $\pi$ -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  $\pi$ -electrons and, in some examples, also in the  $\sigma$ -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  $\pi$ -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.

### References

- G. Merino, T. Heine, G. Seifert, *Chem. Eur. J.* **2004**, *10*, 4367-4371.  
T. Heine, R. Islas, G. Merino, *J. Comput. Chem.* **2007**, *28*, 302-309.  
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## L2. ROLE OF AROMATICITY AND H...H INTERACTIONS IN THE STABILITY OF POLYCYCLIC AROMATIC HYDROCARBONS

J. Poater,<sup>1</sup> G. Merino,<sup>2</sup> C. Fonseca Guerra,<sup>3</sup> F.M. Bickelhaupt,<sup>3</sup> M. Duran,<sup>4</sup> M. Solà<sup>4</sup>

<sup>1</sup>ICREA & Departament de Química Inorgànica i Orgànica & IQTCUB, Universitat de Barcelona, Barcelona, 08028, Catalonia, Spain

<sup>2</sup>Departamento de Física Aplicada, Centro de Investigación y de Estudios Avanzados, Mérida, 97310, México

<sup>3</sup>Department of Theoretical Chemistry & ACMM, Vrije Universiteit Amsterdam, Amsterdam, 1081HV, The Netherlands

<sup>4</sup>Institut de Química Computacional i Catàlisi & Departament de Química, Universitat de Girona, Girona, 17003, Spain

e-mail: jordi.poater@ub.edu

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,<sup>1,2</sup> 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.<sup>3</sup>

### References

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2. J. Poater, R. Visser, M. Solà, F. M. Bickelhaupt, *J. Org. Chem.* **2007**, *72*, 1134.
3. J. Poater, M. Duran, M. Solà, *submitted for publication* **2018**.

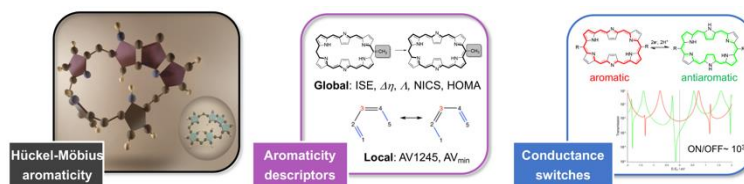
## L3. HOW AND WHY AROMATICITY SHOULD BE QUANTIFIED IN PORPHYRINOIDS?

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,<sup>1</sup> since they provide congeneric macrocycles with  $[4n+2]$  and  $[4n]$   $\pi$ -electrons and different  $\pi$ -conjugation topologies, including Möbius structures.<sup>2</sup> 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.<sup>1</sup> 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  $\pi$ -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.<sup>3,4</sup> 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  $\pi$ -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.<sup>5</sup> 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.<sup>6</sup>



### References

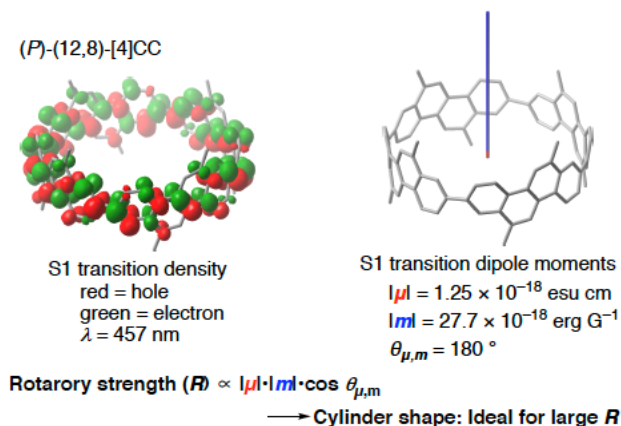
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## L4. RIGID, CYLINDRICAL CYCLOARYLENES: CHIRALITY AND PROPERTIES

Hiroyuki Isobe

Department of Chemistry, University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113-0033, Japan  
ERATO Isobe Degenerate  $\pi$ -Integration Project  
e-mail: isobe@chem.s.u-tokyo.ac.jp

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),<sup>1</sup> flexibility/rigidity and chirality<sup>2</sup> 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.<sup>3</sup>



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

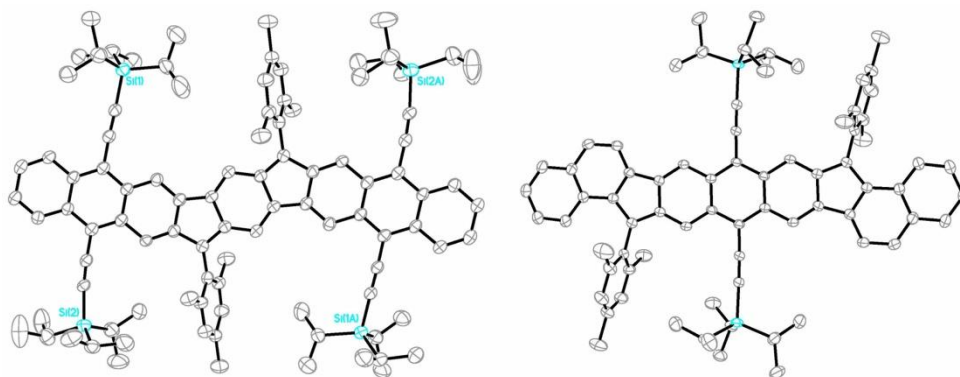
Michael M. Haley

Department of Chemistry & Biochemistry and Materials Science Institute, University of Oregon

1253 Franklin Blvd, Eugene, Oregon 97403-1253, The USA

e-mail: haley@uoregon.edu

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.<sup>1</sup> Access to the fully conjugated, 20  $\pi$ -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.



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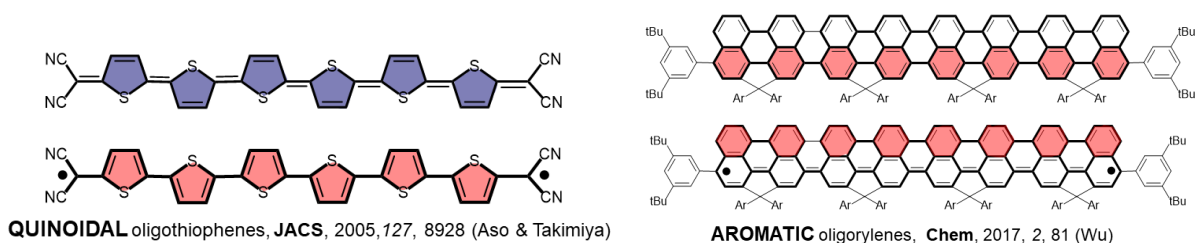
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## L6. DIRADICALS AND THEIR DRIVING FORCES

Juan Casado

Department of Physical Chemistry, University of Málaga, Andalucía Tech,  
Campus de Teatinos, s/n, 29071, Málaga, Spain  
casado@uma.es

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.<sup>1,2,3,4</sup> 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

Departamento de Química Orgánica I, Facultad de Ciencias Químicas,  
Universidad Complutense de Madrid, 28040-Madrid, Spain  
e-mail: israel@quim.ucm.es

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.<sup>1</sup> Only three years later, Roper and co-workers prepared the first metallabenzene, an osmabenzene complex.<sup>2</sup>

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.<sup>3</sup> In addition, the influence of the aromaticity of these species on their Diels-Alder reactivity shall be also discussed.<sup>4</sup>

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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  $4n+2$   $\pi$  electron delocalizations (enhanced aromaticity) in heterocycles are strengthened, while those that decrease (reduced aromaticity) cyclic  $4n+2$   $\pi$  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<sub>zz</sub>

G. Acke,<sup>1</sup> S. Van Damme,<sup>1</sup> R. W. Havenith,<sup>2</sup> P. Bultinck<sup>1</sup>

<sup>1</sup>Department of Chemistry, Ghent University, Krijgslaan 281 S3  
B-9000, Ghent, Belgium

<sup>2</sup>Zernike Institute for Advanced Materials and Stratingh Institute for Chemistry, University of Groningen,  
AG 9747, Groningen, The Netherlands  
e-mail: patrick.bultinck@ugent.be

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  $\sigma$  framework) prompted Schleyer et al. to propose more “refined” indices, such as the  $zz$ -component of the NICS (also called NICS<sub>zz</sub>).<sup>1</sup>

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

The existence of this many-to-one mapping is a consequence of the fact that the NICS<sub>zz</sub> 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<sub>zz</sub> 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<sub>zz</sub>-probe.

As such, our results indicate that any analysis solely based on NICS<sub>zz</sub>-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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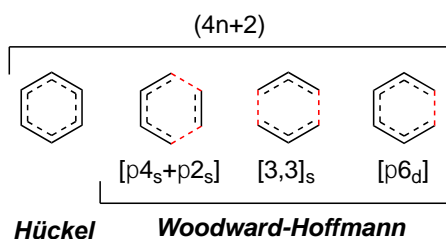
## L10. AROMATIC STABILIZATION IN PERICYCLIC TRANSITION STRUCTURES

F. P. Cossío,<sup>1,2</sup> A. Arrieta,<sup>1</sup> I. Rivilla,<sup>1,2</sup> I. Arrastia<sup>2</sup>

<sup>1</sup>Department of Organic Chemistry I, University of the Basque Country (UPV/EHU),  
Manuel Lardizabal Ibilbidea 3, San Sebastián / Donostia, 20018, Spain

<sup>2</sup>Donostia International Physics Center (DIPC),  
Manuel Lardizabal Ibilbidea 4, San Sebastián / Donostia, 20018, Spain  
e-mail: fp.cossio@ehu.es

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.<sup>1</sup> 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.<sup>2</sup> Magnetic and energetic criteria can be readily extended to transition structures by choosing adequate reference systems.<sup>3</sup> These considerations are especially relevant in pericyclic reactions.<sup>4</sup> 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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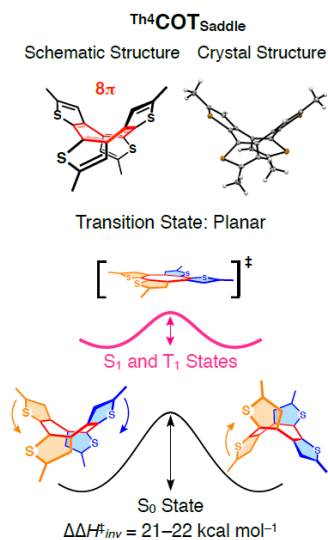
## L11. ENERGETIC IMPACT OF BAIRD AROMATICITY ON MOLECULAR DYNAMICS

Yoshimitsu Itoh

Department of Chemistry and Biotechnology, The University of Tokyo,  
7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-8656, Japan  
e-mail: itoh@macro.t.u-tokyo.ac.jp

Aromaticity is one of the most important concepts in organic chemistry that can explain the stability of planar conformations found in some specific cyclic  $\pi$ -conjugated molecules. In the electronic ground state, such molecules with  $4n+2$   $\pi$ -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.<sup>2</sup> On the other hand, in the electronic excited state, it is known that cyclic  $\pi$ -conjugated molecules with  $4n$   $\pi$ -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 ( $\text{Th}^4\text{COT}_{\text{Saddle}}$ ).<sup>4</sup>  $\text{Th}^4\text{COT}_{\text{Saddle}}$  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

E. Matito,<sup>1,2</sup> I. Casademont-Reig,<sup>1,3</sup> E. Ramos-Cordoba,<sup>1,3</sup> M. Alonso,<sup>4</sup> M. Torrent-Sucarrat,<sup>1,2,5</sup>

<sup>1</sup>Donostia International Physics Center (DIPC), 20018, Donostia, Euskadi (Spain)

<sup>2</sup>IKERBASQUE, Basque Foundation for Science, 48011, Bilbao, Euskadi, (Spain).

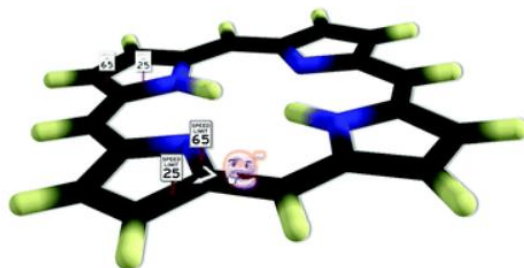
<sup>3</sup>Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU), 20018, Donostia, Euskadi (Spain)

<sup>4</sup>Eenheid Algemene Chemie (ALGC). Vrije Universiteit Brussel (VUB), 1050 Brussels, Belgium

<sup>5</sup>Organic Chem. Dep., Centro de Innovación en Química Avanzada (ORFEO-CINQA), 20018, Donostia, Euskadi (Spain)

e-mail: [ematito@gmail.com](mailto:ematito@gmail.com)

We introduce a new electronic aromaticity measure, AV1245,<sup>1</sup> 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,<sup>2</sup> AV1245 is especially suited to study the conjugation in large circuits such as those occurring in expanded porphyrins or polymeric chains.<sup>3,4</sup> 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

Daniel T. Gryko,<sup>1</sup> Maciej Krzeszewski,<sup>1</sup> Anita Janiga,<sup>1</sup> Mariusz Tasiór,<sup>1</sup> Romal Fasel<sup>2</sup>

<sup>1</sup>Institute of Organic Chemistry, Polish Academy of Sciences

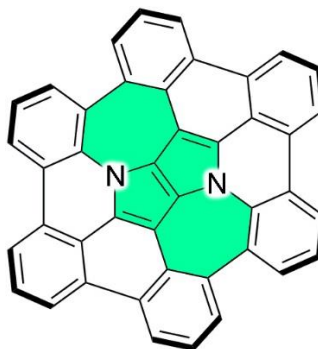
Kasprzaka 44-52, 01-224 Warsaw, Poland

<sup>2</sup>Empa, Swiss Federal Laboratories for Materials Science and Technology

Überlandstrasse 129, 8600 Dübendorf, Switzerland

e-mail: dtgryko@icho.edu.pl

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  $\pi$ -systems. The parent 1,4-dihydro-pyrrolo[3,2-*b*]pyrroles served as building block to construct various  $\pi$ -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 -  $E_{\text{HOMO}}$  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

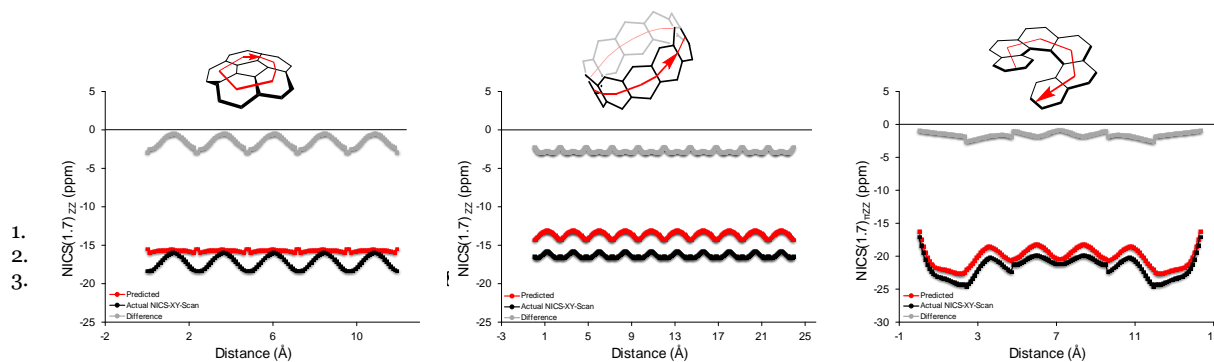
R. Gershoni-Poranne<sup>1</sup> and P. D. Finkelstein<sup>1</sup>

<sup>1</sup>Laboratorium für Organische Chemie, ETH Zürich  
Vladimir-Prelog-Weg 2, Zürich, 8093, Switzerland  
e-mail: renana.poranne@org.chem.ethz.ch

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 manifestation<sup>1</sup> of aromaticity is an additive property. Using NICS-XY-Scans<sup>2</sup> as building blocks within an additivity scheme,<sup>3</sup> 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

Anirban Misra

Department of Chemistry, University of North Bengal, Siliguri, Darjeeling 734013, West Bengal, India

e-mail: anirbanmisra@yahoo.com; anirbanmisra@nbu.ac.in

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'.<sup>1</sup> The aromatic stabilization energy is calculated through a recently developed phenomenological model.<sup>2</sup> 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.<sup>3</sup> Furthermore, we observe that such systems play a key role in stabilizing organic radicals in a unique way.<sup>4</sup>

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**L16. TETRAHEDRANES AND CYCLOBUTADIENES: DIRADICAL CHARACTER OF PARA-PHENYLENE-LINKED CYCLOBUTADIENE**Masaaki Nakamoto,<sup>1</sup> Akira Skiguchi<sup>2</sup><sup>1</sup>Department of Chemistry, Hiroshima University,

1-3-1 Kagamiyama, Higashi-Hiroshima, 739-8526, Japan

<sup>2</sup>The National Institute of Advanced Industrial Science and Technology, AIST Tsukuba Central 5

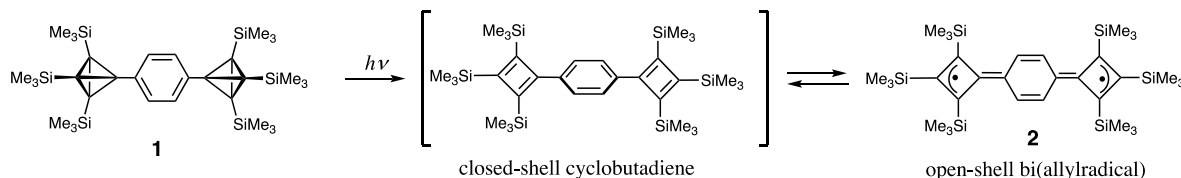
e-1-1 Higashi, Tsukuba, 305-8565, Japan

e-mail: mnakamot@hiroshima-u.ac.jp

Cyclobutadiene is a molecule with four  $\pi$ -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.<sup>1</sup>

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.<sup>2</sup> Recently, we have demonstrated that the photoreaction provides the practical approach to the stable cyclobutadienes because of the excited state aromaticity of four  $\pi$ -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

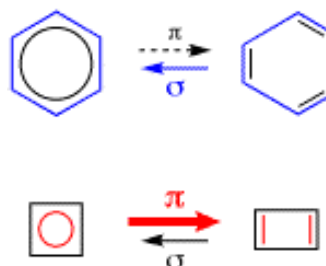
Amsterdam Center for Multiscale Modeling, Vrije Universiteit Amsterdam

De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

e-mail: f.m.bickelhaupt@vu.nl

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  $\pi$  electrons is always, i.e., in both aromatic and antiaromatic molecules, to localize the double bonds, against the delocalizing force of the  $\sigma$  electrons. Interestingly, the  $\pi$  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

Y. Ruiz-Morales

Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas Norte 152, México City 07730, México  
e-mail: yruiz@imp.mx

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  $\pi$ -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  $\pi$ -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  $\pi$ -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  $\pi$ -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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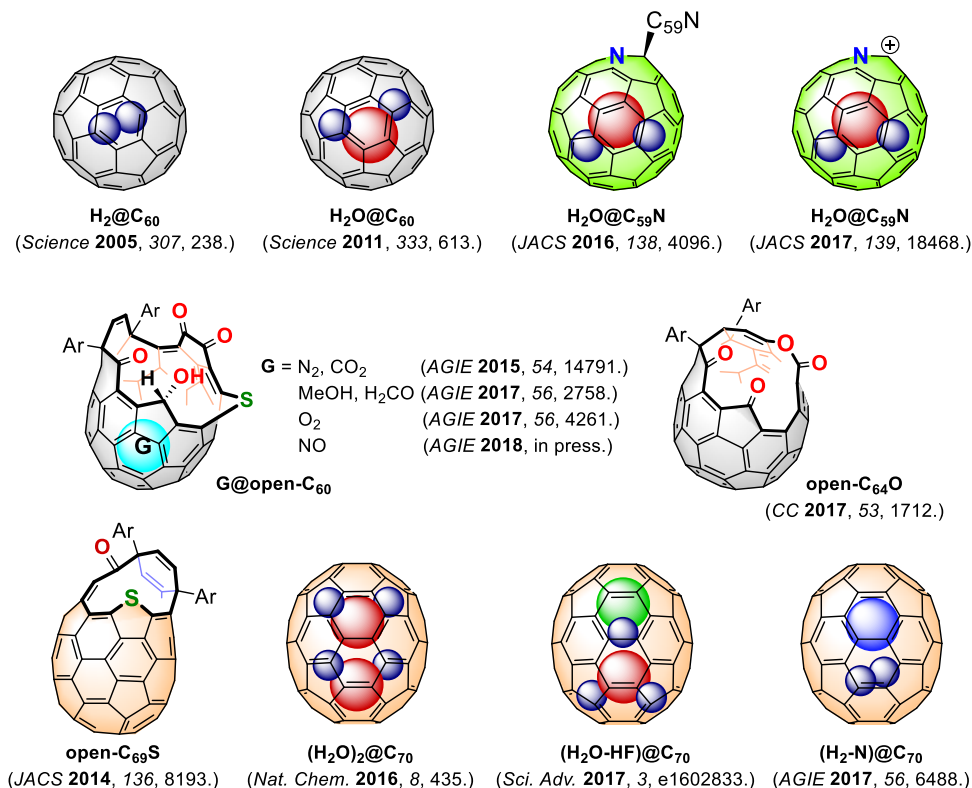
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## L19. OPEN-CAGE FULLERENES TOWARD THE SYNTHESIS OF ENDOFULLERENES AND HETEROFULLERENES

Y. Murata

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan  
e-mail: yasujiro@scl.kyoto-u.ac.jp

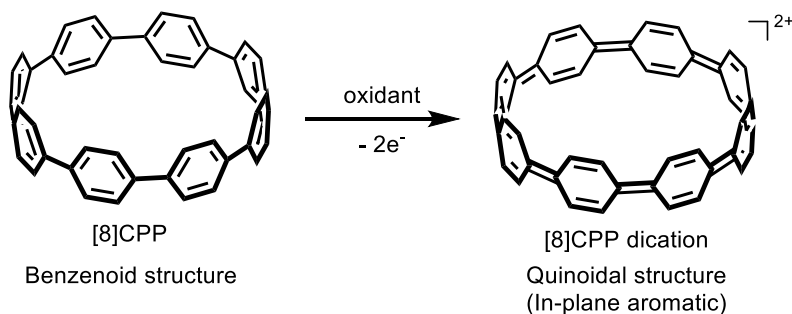
Open-cage fullerene derivatives are synthesized as isomerically pure forms by the reactions starting from pristine  $C_{60}$  and  $C_{70}$ . They are the precursors for heterofullerenes in which one of the carbon atoms is replaced with a hetero atom. Furthermore, in the case that their openings are 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**

Shigeru Yamago  
Institute for Chemical Research, Kyoto University  
Uji 611-0011, Kyoto, Japan  
e-mail: yamago@scl.kyoto-u.ac.jp

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.<sup>1</sup> During the course to clarify their redox properties,<sup>2</sup> 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.<sup>3</sup>



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

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

R. Hoffmann

Dept. of Chemistry and Chemical Biology, Cornell University, Baker Labor. Ithaca NY 14853

rh34@cornell.edu

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.



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## L22. DISSECTING AROMATICITY WITHIN BOREPIN-BASED POLYCYCLIC AROMATICS

R. E. Messersmith<sup>1</sup> and J. D. Tovar<sup>1</sup>

<sup>1</sup>Department of Chemistry, Johns Hopkins University  
3400 N. Charles St., Baltimore, 21218, The USA  
e-mail: tovar@jhu.edu

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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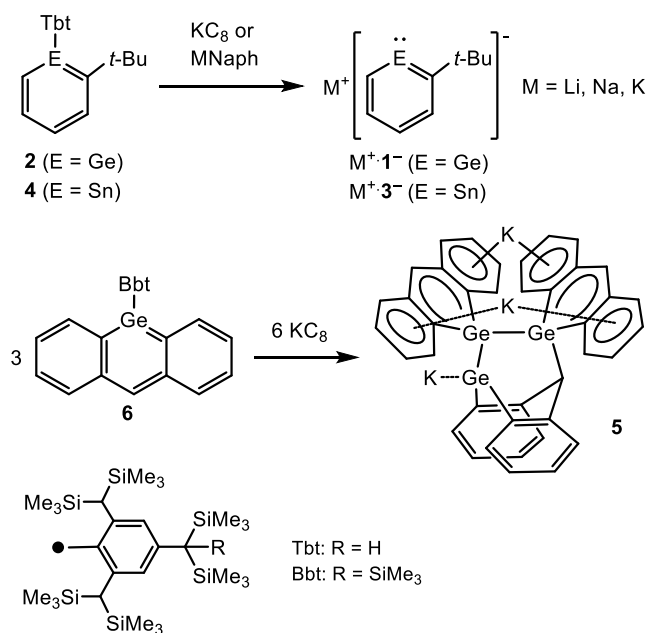
## L23. HEAVIER GROUP 14 ELEMENT ANALOGUES OF ARYL ANIONS

S. Fujimori, Y. Mizuhata, N. Tokitoh,  
 Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan  
 e-mail: tokitoh@boc.kuicr.kyoto-u.ac.jp

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  $KC_8$ .<sup>1</sup> 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.<sup>1</sup>  $Li^+\cdot\mathbf{1}^-$  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.<sup>2</sup>

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-germaantracene **6**, its reaction with  $KC_8$  resulted in the formation of a unique trimer **5** of the initially formed germaantracenyipotassium.<sup>3</sup>



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

J. O. C. Jimenez-Halla,<sup>1</sup> E. Matito,<sup>2</sup> H. Braunschweig<sup>3</sup>

<sup>1</sup>Department of Chemistry, University of Guanajuato, Noria Alta s/n, Guanajuato, 36050, México.

<sup>2</sup>Kimika Fakultatea, Euskal Herriko Unibertsitatea and Donostia International Physics Center, P.K. 1072, 20080 Donostia, Euskadi, SPAIN and IKERBASQUE, Basque Foundation for Science, 48011, Bilbao, Euskadi, Spain.

<sup>3</sup>Institute for Inorganic Chemistry and Institute for Sustainable Chemistry & Catalysis with Boron, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074, Würzburg, Germany.

e-mail: jjimenez@ugto.mx

Boroles are unsaturated, extremely electron-deficient, pentacyclic molecules with four  $\pi$ -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.<sup>1</sup> 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.<sup>2</sup>

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## L25. SYNTHESIS OF GIANT MONODISPERSE N-DOPED NANOGRAPHENES

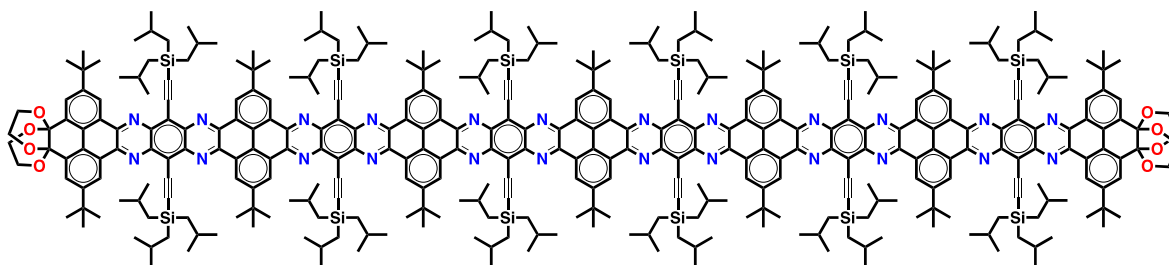
Aurelio Mateo-Alonso<sup>1,2</sup>

<sup>1</sup>POLYMAT, University of the Basque Country UPV/EHU. Avenida de Tolosa 72, E-20018 Donostia-San Sebastián, Spain

<sup>2</sup>Ikerbasque, Basque Foundation for Science. Bilbao, Spain  
e-mail: amateo@polymat.eu

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.<sup>[1]</sup> 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.<sup>[2]</sup>



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

Peter B. Karadakov

Department of Chemistry, University of York, Heslington, York YO10 5DD, The UK  
peter.karadakov@york.ac.uk

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  $\pi$  electrons follows from the extensive resonance between VB structures.

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

F. Langa,<sup>1</sup> P. de la Cruz,<sup>1</sup> V. Cuesta<sup>1</sup>

<sup>1</sup>Department of Chemistry, University of Castilla-la Mancha, Campus de la Fábrica de Armas  
Toledo, 45071, Spain  
e-mail: fernando.langa@uclm.es

Porphyrins are stable  $\pi$ -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%.

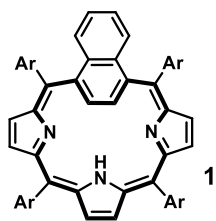
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## L28. AROMATICITY SWITCHING IN PORPHYRINOIDS AND HETEROPORPHYRINOIDS

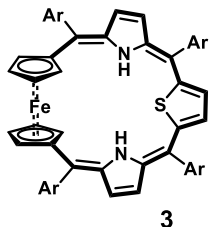
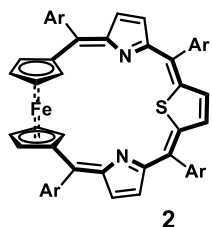
L. Latos-Grażyński

Department of Chemistry, University of Wrocław,  
14 F. Joliot-Curie St., Wrocław, 54 031, Poland  
e-mail: lechoslaw.latos-grazynski@chem.uni.wroc.pl



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  $^1\text{H}$  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  $\pi$ -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  $28\pi$ -electron, aromatic  $26\pi$ - and  $18\pi$ -electron systems was presented for azulene-1,3-diyl-strapped A,D-dithiahexaphyrin. The direct transmission of



metallo-macrocyclic  $\pi$ -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**

Marina A. Petrukhina

Department of Chemistry, University at Albany, State University of New York,  
1400 Washington Avenue, Albany, NY 12222, The USA  
e-mail: mpetrukhina@albany.edu

Curved polycyclic aromatic hydrocarbons such as carbon  $\pi$ -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  $\pi$ -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

Dage Sundholm,<sup>1</sup> Maria Dimitrova,<sup>1</sup> Rashid R. Valiev,<sup>1</sup> Lukas N. Wirz,<sup>1</sup> Heike Fliegl<sup>2</sup>

<sup>1</sup>Department of Chemistry, University of Helsinki,

P.O. Box 55, A.I Virtanens plats 1, FI-00014 Helsinki, Finland

<sup>2</sup>Hylleraas Centre for Quantum Molecular Sciences, Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, NO-0315 Oslo, Norway

e-mail: Dage.Sundholm@helsinki.fi

The basic features of the gauge-including magnetically induced currents (GIMIC) method will be presented.<sup>1</sup> The GIMIC method has been used in studies of current densities of Möbius twisted annulenes,<sup>2</sup> 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.<sup>3,4,5</sup> Calculations on antiaromatic molecules show that closed-shell molecules sustaining a strong paratropic ring current can be paramagnetic.<sup>6</sup>

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

Yunlong Zhang

Corporate Strategic Research, ExxonMobil Research and Engineering Company, Route 22 E., Annandale, NJ 08801  
yunlong.zhang@exxonmobil.com

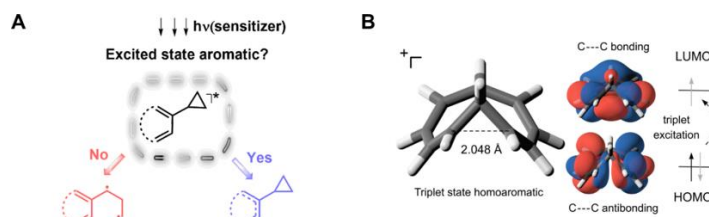
Heavy oils are enriched with aromatic hydrocarbons, but characterization of their chemical structures has been a great challenge due to their tremendous diversity. Recently, with the advent of molecular imaging with non-contact atomic force microscopy (nc-AFM), molecular structures of petroleum have 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

Henrik Ottosson

Department of Chemistry – Ångström Laboratory, Uppsala University, Box 523, 751 20 Uppsala, Sweden.  
e-mail: henrik.ottosson@kemi.uu.se

Aromaticity and antiaromaticity in the lowest  $\pi\pi^*$  excited states of annulenes have received growing attention in the last years.<sup>1</sup> Annulenes with  $4n$   $\pi$ -electrons are aromatic in the first  $\pi\pi^*$  triplet state ( $T_1$ ) while those with  $4n+2$  are antiaromatic (Baird's rule),<sup>2</sup> and this relationship often applies also to the lowest singlet excited state ( $S_1$ ) of small annulenes.<sup>3</sup> 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.<sup>4</sup> 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.<sup>5</sup> 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  $\pi$ -sextets can form in hexagons that are disjoint to the central  $4n\pi$ -electron unit.<sup>6</sup> 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.<sup>7</sup>



**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

L. Kürti,<sup>1</sup> D.H. Ess,<sup>2</sup> G. Li,<sup>1</sup> Q.-L. Xu<sup>1</sup> and H. Gao<sup>1</sup>

<sup>1</sup>Department of Chemistry, Rice University

BioScience Research Collaborative, 6500 Main Street, Houston, TX 77030, The USA

<sup>2</sup>Department of Chemistry and Biochemistry, Brigham Young University

Provo, UT 84602, The USA

e-mail: kurti.laszlo@rice.edu

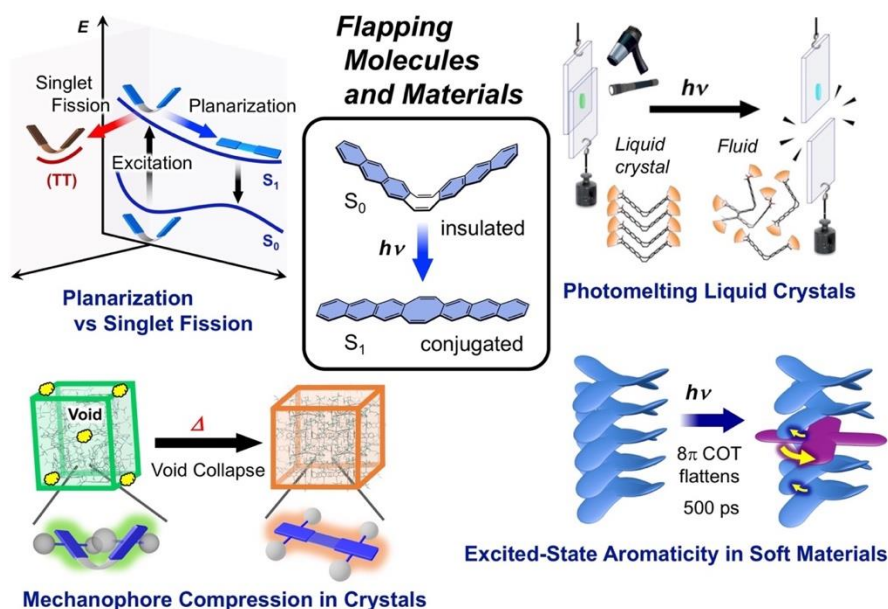
The Kürti lab has been exploring several fundamentally new strategies for the transition-metal-free direct C-H arylation of arenes, in particular the organocatalytic atroposelective synthesis of 1,1'-linked functionalized biaryls. Without exaggeration it can be stated that axially chiral non-racemic 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(sp<sup>2</sup>)-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-C<sub>2</sub>-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

Shohei Saito

Department of Chemistry, Kyoto University  
 Kitashirakawa Oiwake-cho, Sakyo-ku, Kyoto 606-8502 Japan  
 e-mail: s\_saito@kuchem.kyoto-u.ac.jp

Flapping molecules (FLAP) bearing a fused  $8\pi$  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.<sup>1</sup> Along with this line, we have demonstrated the utilities of FLAP as photofunctional materials such as photoresponsive liquid crystals showing excited-state aromaticity,<sup>2</sup> light-melt adhesive,<sup>3</sup> molecular viscosity probes,<sup>4</sup> singlet fission chromophores,<sup>5</sup> and conformationally flexible mechanophores.<sup>6</sup> 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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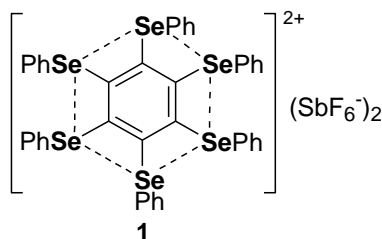
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**L35. CHALLENGE TO EXPAND AROMATICITY—FROM  $\pi$ -AROMATICITY TO  $\sigma+\pi$ -DOUBLE AROMATICITY**

Masaichi Saito

Department of Chemistry, Graduate School of Science and Engineering, Saitama University, Shimo-okubo, Sakuraku, Saitama-city, Saitama, 338-8570, Japan  
e-mail: masaichi@chem.saitama-u.ac.jp

Since the discovery of benzene, aromaticity has been utilized to explain unique properties of benzene and its derivatives. The aromaticity arises from delocalized  $\pi$ -orbitals composed of  $(4n + 2)$   $\pi$ -electrons and is found to be retained even in lead-bearing cyclic compounds.<sup>1,2</sup> 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  $\sigma$ - and  $\pi$ -double aromaticity was reported,<sup>3</sup> experimental evaluation based on bench-stable  $\sigma$ - and  $\pi$ -double aromatic compounds has remained targeted.<sup>4</sup> Inspired by the previous report on the synthesis of a hexaiodobenzene dication,<sup>5</sup> though, which is still controversial,<sup>6</sup> we independently designed a hexaselenylbenzene dication as a possible  $\sigma$ - and  $\pi$ -double aromatic compound, which was predicted by our previous quantum-chemical calculations of a model compound.<sup>7</sup> We herein report the synthesis of dication salt of hexakis(phenylselenyl)benzene and its X-ray characterization.<sup>8</sup> The  $\sigma$ - and  $\pi$ -double aromatic character is also discussed.

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### L36. SOME THOUGHTS ABOUT AROMATICITY

Amnon Stanger

Schulich Department of Chemistry, Technion, Haifa 32000, Israel.

e-mail: stanger@technion.ac.il

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  $\pi$  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 <sub>$\pi$ ,zz</sub> – one of the most popular methods for assessing magnetic aromaticity. A new method that is based on integration of NICS <sub>$\pi$ ,zz</sub> will be presented. The quantitative relations between ASE and magnetic criteria will be discussed.

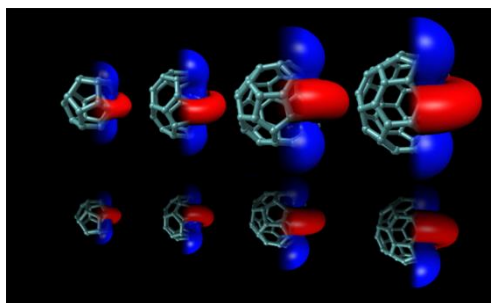


### L37. UNIFYING PLANAR AND SPHERICAL AROMATICS. SHIELDING CONE AS COMMON CHARACTERISTIC

Alvaro Muñoz-Castro

Grupo de Química Inorgánica y Materiales Moleculares, Facultad de Ingeniería, Universidad Autónoma de Chile, El Llano Subercaseaux 2801, Santiago, Chile  
e-mail: alvaro.munoz@uautonoma.cl

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.<sup>1</sup> 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.<sup>2-4</sup> 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).<sup>6,7</sup> 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.

**Acknowledgments:** Authors acknowledge FONDECYT 1180683 for financial support.

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

A. N. Alexandrova,<sup>1,2</sup> E. Jimenez-Izal<sup>1,3</sup>

<sup>1</sup>Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, CA 90095-1569, USA

<sup>2</sup>California NanoSystems Institute, Los Angeles, Los Angeles, CA 90095-1569, The USA

<sup>3</sup>Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU), and Donostia International Physics Center (DIPC), P. K. 1072, 20080 Donostia, Euskadi, Spain  
e-mail: ana@chem.ucla.edu

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  $\pi$ -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**

Gabriel dos Passos Gomes,<sup>1</sup> Kjell Jorner,<sup>2</sup> Henrik Ottosson,<sup>2</sup> Igor V. Alabugin<sup>1</sup>

<sup>1</sup>Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, The USA

<sup>2</sup>Department of Chemistry, Uppsala University, Box 576, 751 23 Uppsala, Sweden

e-mail: [alabugin@chem.fsu.edu](mailto:alabugin@chem.fsu.edu)

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

G. Monaco, R. Zanasi

Department of Chemistry "A. Zambelli", University of Salerno,  
Fisciano, 84084 SA, Italy  
e-mail: gmonaco@unisa.it

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.<sup>1</sup> 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,<sup>2</sup> 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,<sup>3</sup> which we have recently re-defined taking care of its asymmetric character,<sup>4</sup> 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

Tiznado William,<sup>1</sup> Alejandro Vásquez<sup>1</sup>

<sup>1</sup>Departamento de Ciencias Químicas, Facultad de Ciencias Exactas, Universidad Andres Bello, Santiago, Chile.  
e-mail: wtiznado@unab.cl

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 Si<sub>6</sub> 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 Li<sub>12</sub>Si<sub>7</sub>, which is made up of planar Si<sub>5</sub> rings (stacked in one-dimensional columns) and trigonal planar Si<sub>4</sub> stars (located in the planes between the Si<sub>5</sub> rings). Each pentagonal silicon-ring is rationalized as a negatively charged Si<sub>5</sub><sup>6-</sup> species, which is  $\pi$ -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<sub>7-x</sub>Si<sub>5</sub><sup>1-x</sup> (x = 0, 1, 2) clusters, which consist in a Si<sub>5</sub><sup>6-</sup> pentagonal ring interacting with the corresponding Li<sup>+</sup> cations. More recently, after exploring their potential energy surface, our high-level quantum chemical computations strikingly show that the lowest energy structures of the (Li<sub>6</sub>Si<sub>5</sub>)<sub>2-5</sub> systems are comprised of 2-5 Si<sub>5</sub><sup>6-</sup> aromatic units and surrounded by Li<sup>+</sup> 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 Li<sub>6</sub>Si<sub>5</sub> 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 Si<sub>6</sub> 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

Miquel Solà

Institut de Química Computacional i Catàlisi and Departament de Química, Universitat de Girona, C/ Maria Aurèlia Capmany, 69, 17003 Girona, Catalonia, Spain  
e-mail: miquel.sola@udg.edu

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,<sup>1-4</sup> the lowest-lying triplet excited state Baird's rule,<sup>5,6</sup> or the  $4n$  rule followed by monocyclic conjugated hydrocarbons in a Möbius-type conformation.<sup>7,8</sup> These rules of (anti)aromaticity are nicely connected in the Ottosson's cube.<sup>9</sup> 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  $\pi$ -sextet rule.<sup>10</sup> 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,<sup>11,12</sup> and to the extension of Hirsch's rule<sup>13</sup> and the Jellium model<sup>14</sup> to open-shell systems.

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**L43. THE QUASI-PLANAR BORON CLUSTER B<sub>50</sub>: LEAP-FROG FORMATION AND DISK AROMATICITY**

Minh Tho Nguyen

Department of Chemistry, KU Leuven, B-3001 Leuven, Belgium

Email: minh.nguyen@kuleuven.be

The pure B<sub>50</sub> 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) B<sub>50</sub> is formed from a leap-frog operation starting from B<sub>10</sub>, and ii) its 32  $\pi$  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.

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

Dirk M. Guldi

Department of Chemistry and Pharmacy & Interdisciplinary Center of Molecular Materials, Engineering of Advanced Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstrasse 3, 91058 Erlangen, Germany  
e-mail: dirk.guldi@fau.de

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.

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## L45. ROLE OF ANTIAROMATICITY IN GROUND STATE DIRADICAL CARBOCATIONS

A. Winter

Department of Chemistry, Iowa State University, Ames, IA, 50010, The USA

e-mail: winter@iastate.edu

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.



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## L46. EXPLORING AROMATICITY WITH EXPANDED PORPHYRINS

Jonathan L. Sessler<sup>1,2</sup>

<sup>1</sup>Department of Chemistry, The University of Texas at Austin  
105 E 24th St - A5300, Austin, TX 78712-1224, The USA

<sup>2</sup>Center for Supramolecular Chemistry and Catalysis  
Shanghai University, Shanghai 200444, China  
e-mail: sessler@cm.utexas.edu

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  $[4n + 1]$   $\pi$ -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**

M. Baranac-Stojanović,<sup>1</sup> M. Stojanović<sup>2</sup>

<sup>1</sup>University of Belgrade – Faculty of Chemistry, Studentski trg 12-16  
11000, Belgrade, Serbia

<sup>2</sup>Institut of Chemistry, Technology and Metallurgy, Center for Chemistry, University of Belgrade, Njegoševa 12,  
11000, Belgrade, Serbia  
e-mail: mbaranac@chem.bg.ac.rs

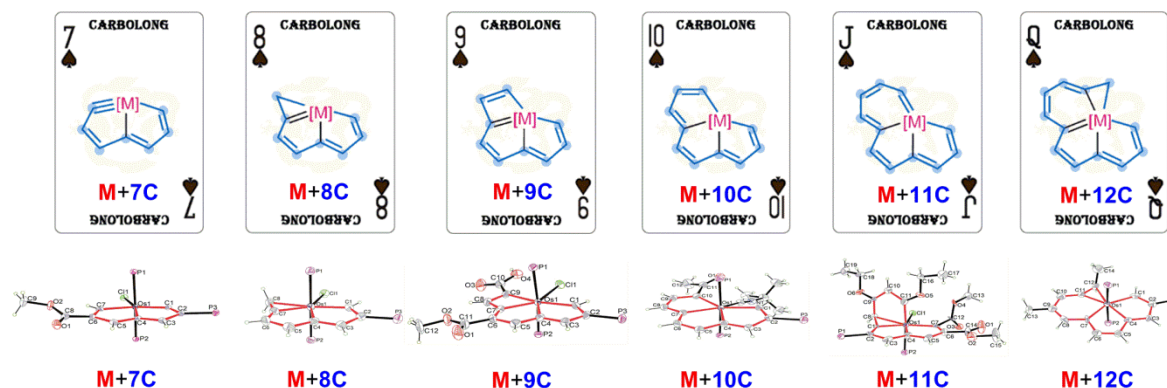
Aromaticity is an important concept in chemistry associated with enhanced thermodynamic stability of cyclic conjugated molecules, relative to acyclic structural analogues, and their special chemical reactivity (substitution instead of addition reaction) which retain the cyclic conjugation. Commonly, 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

Haiping Xia

Department of Chemistry, Xiamen University  
 No. 422, Siming South Road, Xiamen, 361005, China  
 e-mail: hpxia@xmu.edu.cn

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.<sup>1</sup> In particular, these complexes exhibit remarkable aromaticity. For example, **M+7C** displays unprecedented Craig Möbius aromaticity,<sup>2</sup> while **M+8C** demonstrates dominant  $\sigma$ -aromaticity.<sup>3</sup> 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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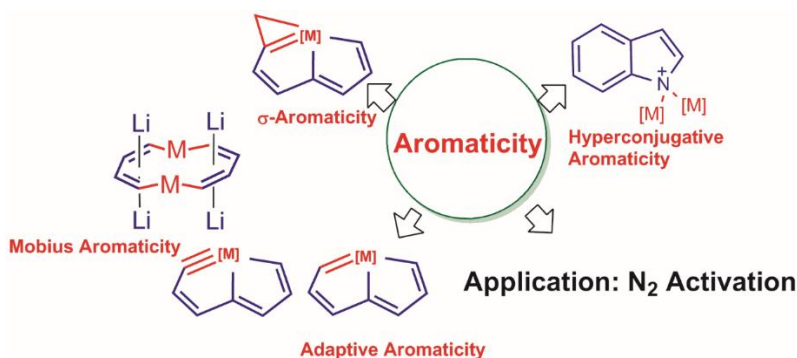
## L49. AROMATICITY IN ORGANOMETALLICS AND ITS APPLICATION IN N<sub>2</sub> ACTIVATION

Jun Zhu

Department of Chemistry, Xiamen University, Xiamen, P.R. China, 361005

e-mail: jun.zhu@xmu.edu.cn

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,  $\sigma$ -aromaticity dominating in an unsaturated ring, hyperconjugative aromaticity and adaptive aromaticity are achieved due to an introduction of transition metals.<sup>1-5</sup> In addition, the application of aromaticity in N<sub>2</sub> activation will be also discussed.



**Figure 1.** Schematic illustration of some unconventional aromaticity and its application in N<sub>2</sub> activation.

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## P1. MOLECULAR HELMHOLTZ COILS

M. Orozco-Ic,<sup>1</sup> A. Restrepo,<sup>2</sup> A. Muñoz-Castro,<sup>3</sup> G. Merino<sup>1</sup>

<sup>1</sup>Departamento de Física Aplicada, Centro de Investigación y de Estudios Avanzados, Unidad Mérida. Km 6 Antigua Carretera Progreso. Apdo. Postal 73, Cordemex, 97310, Mérida, Yuc., México.

<sup>2</sup>Instituto de Química, Universidad de Antioquia UdeA, Calle 70 No. 52-21, Medellín, Colombia

<sup>3</sup>Laboratorio de Química Inorgánica y Materiales Moleculares, Facultad de Ingeniería, Universidad Autónoma de Chile, Llano Subercaseaux 2801, San Miguel, Santiago, Chile.

e-mail: gmerino@cinvestav.mx

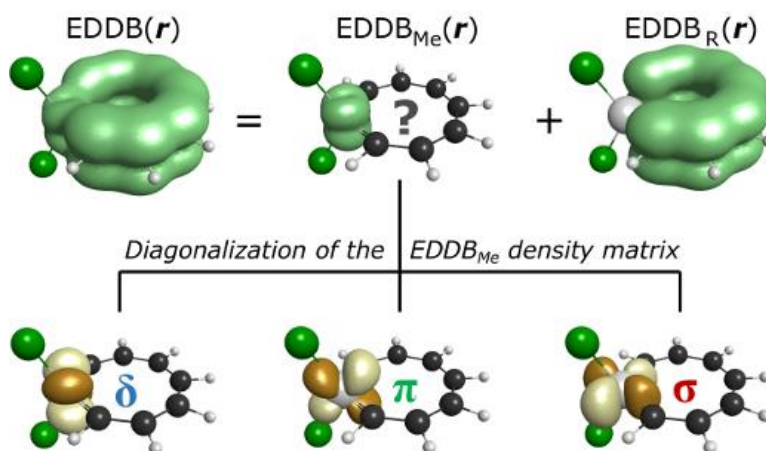
How to build a molecular Helmholtz coil? To evaluate the nature of feasible homogeneity as classical electrodynamics predicts in an ideal case, the induced magnetic field is computed in systems comprised by two stacked  $\pi$ - $\pi$  hydrocarbon rings in such a way that they satisfy the condition of 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  $\pi$ -magnetic responses for dimers with  $n = 8-10$ , independently of the induced field intensity. Conversely,  $\sigma$ -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?

D. W. Szczepanik, M. Solà

Institut de Química Computacional i Catàlisi, Universitat de Girona,  
C/ Maria Aurèlia Capmany, 69, 17003 Girona, Catalonia, Spain.  
e-mail: dszczpnk@gmail.com

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.<sup>1,2</sup> 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.<sup>3,4</sup> 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),<sup>5</sup> and relies on decomposition of the total EDDB( $r$ ) density into two fragments representing metal and carbon ring,  $\text{EDDB}_{\text{Me}}(r)$  and  $\text{EDDB}_{\text{R}}(r)$  respectively, followed by diagonalization of the  $\text{EDDB}_{\text{Me}}$  density matrix to get the corresponding  $d$ -orbital contributions to the aromatic stabilization. We use our method to study selected metallacycles with  $8\pi$ -electrons and different bonding topologies.



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### P3. INDUCED MAGNETIC FLUX ANALYSIS IN PLANAR CYCLIC MOLECULES

Mesías Orozco-Ic,<sup>1</sup> Sudip Pan,<sup>1</sup> José Luis Cabellos,<sup>1</sup> Gabriel Merino<sup>1</sup>

<sup>1</sup>Departamento de Física Aplicada, Centro de Investigación y de Estudios Avanzados, Unidad Mérida, Km. 6, Antigua Carretera a Progreso, A. P. 73, Cordemex, Mérida 97310; México

e-mail: mesias.orozco@cinvestav.mx

Fundamental concepts as the chemical bond, electronegativity or electron delocalization (ED) have not a simple definition and always are immersed in controversy.<sup>1</sup> 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 NICS<sup>2</sup> or the induced magnetic field<sup>3</sup> ( $\mathbf{B}^{\text{ind}}$ ). The systems with delocalized electrons (aromatic) are sensible to external magnetic fields, they respond with an induced current density that produces the  $\mathbf{B}^{\text{ind}}$ . In this sense, we can compute the magnetic flux associated with the induced field ( $\Phi^{\text{ind}}$ ). 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” ( $\Phi^{\text{ind}}/A$ ). Thus,  $\Phi^{\text{ind}}/A$  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  $\mathbf{B}^{\text{ind}}$  as well as for  $\Phi^{\text{ind}}$ . Our calculations show that the valence contributions to the magnetic flux ( $\Phi^{\text{ind}}$ ) describe correctly electron delocalization of the systems, even better than NICS and  $\mathbf{B}^{\text{ind}}$  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  $\Phi^{\text{ind}}/A$  in ppm for monocyclic molecules.

	$\Phi_{\text{core}}^{\text{ind}}/A$	$\Phi_{\sigma}^{\text{ind}}/A$	$\Phi_{\pi}^{\text{ind}}/A$	$\Phi^{\text{ind}}/A$
Benzene	-14.73	3.00	-32.18	-43.90
Al <sub>4</sub> <sup>2-</sup>	-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

D. Mangel, J. Brewster, X. Ke, G. Anguera, J. Sessler

Department of Chemistry, University of Texas, 105 East 24th Street, Stop A5300, Austin, 78712-1224,  
The USA

d\_mangel@utexas.edu

Since the first report of sapphyrin by Woodward in 1966, significant efforts have been made in developing and characterizing expanded porphyrins.<sup>1,2</sup> 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  $\pi$ -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  $[4n]$   $\pi$ -electron species to the corresponding  $[4n+1]$   $\pi$ -electron radical species. Similar treatment with HI produced a fully aromatic  $[4n+2]$   $\pi$ -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<sub>3</sub>) 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<sub>2</sub>[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>) 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  $\pi$ -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 $\pi$ -SYSTEM LENGTH ON THE ELECTRONIC STRUCTURE OF CHICHIBABIN DIRADICALOIDS

Sílvia Escayola,<sup>1</sup> Marc Callís,<sup>1</sup> Albert Poater,<sup>1</sup> Miquel Solà<sup>1</sup>

<sup>1</sup>Institut de Química Computacional i Catàlisi (IQCC) and Department of Chemistry, University of Girona, Maria Aurèlia Capmany 69, Girona, 17003, Spain  
e-mail: silvieg7@gmail.com

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.<sup>1</sup> 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  $\pi$ -system and the exocyclic substituents.<sup>2</sup> 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,  $I_{\text{ring}}$ , and MCI aromaticity indices. Our results show that the shortest  $\pi$ -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

Yasminne Esquivel and Juan Pacheco

Instituto Tecnológico de Toluca, División de Estudios de Posgrado e Investigación, Toluca, Estado de México, México

C.P.52149.Avenida Tecnológico 100, La Virgen, Metepec, México  
e-mail: yas\_ema@hotmai.com, jpachecos@toluca.tecnm.mx.

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 *DMol<sup>3</sup>* 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  $\pi$ , 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 *DMol<sup>3</sup>* 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

R. Pino-Rios,<sup>1</sup> W. Tiznado,<sup>2</sup> G. Cárdenas-Jirón<sup>1</sup>

<sup>1</sup>Departamento de ciencias del Ambiente, Universidad de Santiago de Chile, Av. Libertador Bernardo O'Higgins 3363, Región Metropolitana, Chile.

<sup>2</sup>Departamento de Química, Universidad Andrés Bello, Av. República 275, Santiago, Región Metropolitana, Chile.

e-mail: ricardo.pino@usach.cl; ricardopinor@gmail.com

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 ( $B_{zz}^{ind}$ ).<sup>1</sup> 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.<sup>2</sup>

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,<sup>3</sup> 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

Daniel Molina V.,<sup>1</sup> Tania Chanagá,<sup>2</sup> Hector Picón<sup>2</sup>

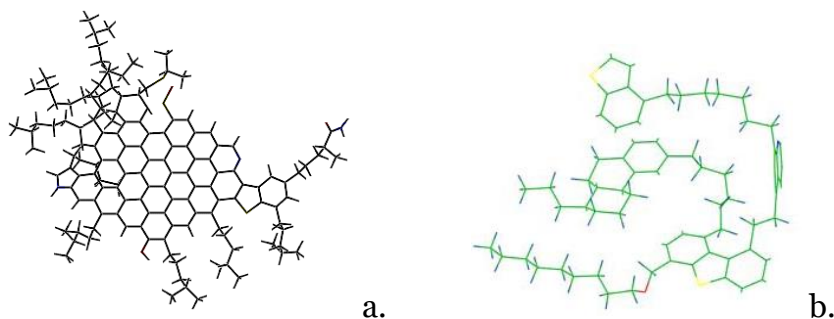
<sup>1</sup>Laboratorio de Resonancia Magnética Nuclear, Universidad Industrial de Santander, Bucaramanga, Colombia.

<sup>2</sup>Instituto Colombiano del Petróleo, ECOPEPETROL S.A. Piedecuesta, Colombia

e-mail: dmolina@uis.edu.co

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.<sup>1</sup> 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 $8\pi$ -ELECTRON HETEROCYCLIC COMPOUNDS

Josene Toldo,<sup>1</sup> Ouissam El Bakouri,<sup>1</sup> Ferran Feixas,<sup>2</sup> Miquel Solà,<sup>2</sup> Per-Ola Norrby,<sup>3</sup> and Henrik Ottosson<sup>1</sup>

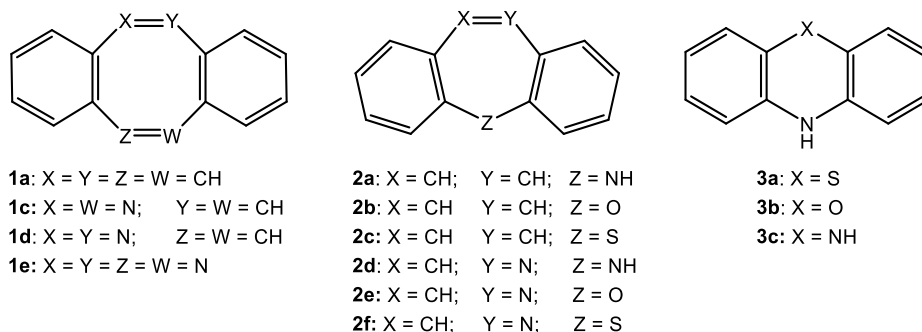
<sup>1</sup> Department of Chemistry - Ångström Laboratory, Uppsala University, 751 20 Uppsala, Sweden

<sup>2</sup> Department of Chemistry, Facultat de Ciències, University of Girona, Girona, 17003, Spain

<sup>3</sup> Early Product Development, Pharmaceutical Sciences, IMED Biotech Unit, AstraZeneca, Gothenburg, Sweden

e-mail: josene.toldo@kemi.uu.se

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.<sup>5</sup> Dibenzannelated molecules with central  $8\pi$ -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).<sup>6</sup> 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.<sup>7</sup> We now report on a quantum chemical study focused on how the position, type, and number of heteroatoms in the central  $8\pi$ -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  $8\pi$ -electron compounds investigated in this work.

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## P10. ON THE MAGNETIC SIGNATURE OF HELICENES

Mesías Orozco-Ic,<sup>1</sup> Jorge Barroso,<sup>1</sup> Gabriel Merino,<sup>1\*</sup> Alvaro Muñoz-Castro,<sup>2,\*</sup>

<sup>1</sup>Departamento de Física Aplicada, Centro de Investigación y de Estudios Avanzados, Unidad Mérida. Km 6 Antigua Carretera a Progreso. Apdo. Postal 73, Cordemex, C.P. 97310, Mérida, Yucatán, México

<sup>2</sup>Lab. De Química Inorgánica y Materiales Moleculares, Universidad Autónoma de Chile, Llano Subercaceaux 2801, San Miguel, 8910060, Santiago, Chile  
e-mail: jorge.barroso@cinvestav.mx

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.<sup>1</sup> 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 Solà<sup>2</sup> and Schulman<sup>3</sup> 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  $\pi$ -,  $\sigma$ - 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**

G. Hernández-Juárez,<sup>1</sup> Estefanía Ravell,<sup>1</sup> J. Barroso,<sup>1</sup> Mesías Orozco-Ic,<sup>1</sup> G. Merino.<sup>1</sup>

<sup>1</sup>Departamento de Física Aplicada, Centro de Investigación y de Estudios Avanzados Unidad Mérida km 6 Antigua carretera a Progreso. Apdo. Postal 73, Cordemex 97310 Mérida, Yuc. México  
e-mail: gerardo0339@gmail.com

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  $\pi$  orbital spread over all five atoms.<sup>1</sup> 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.<sup>1</sup> Additionally, we analyzed the hypercoordinated clusters  $CE_5^-$  (E = Al–Tl) using different computational tools in conjunction with the induced magnetic field ( $\mathbf{B}_z^{ind}$ )<sup>2</sup> 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  $\sigma$  and  $\pi$ ), but the  $\sigma$  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**

María J. Beltrán-Leiva,<sup>1</sup> Isabel Fuenzalida-Valdivia,<sup>2</sup> Plinio Cantero-López,<sup>1,3</sup> Ana Bulhoes-Figueira,<sup>4</sup> Jans Alzate-Morales,<sup>5</sup> Dayán Páez-Hernández,<sup>1,3</sup> and Ramiro Arratia-Pérez<sup>1,3</sup>

<sup>1</sup>Relativistic Molecular Physics Group, Universidad Andrés Bello, República 275, Santiago, Chile.

<sup>2</sup>Facultad de Ciencias Biológicas, Centro de Biotecnología Vegetal, Santiago 8370146, Universidad Andrés Bello, Santiago, Chile.

<sup>3</sup>Center for Applied Nanosciences (CANS), Facultad de Ciencias Exactas, Universidad Andrés Bello, Av. República 275, Santiago, 8370146, Chile.

<sup>4</sup>Centro de Bioinformática y Simulación Molecular (CBSM), Facultad de Ingeniería, Universidad de Talca, 1 Poniente 1141, Talca, Chile

<sup>5</sup>Centro Universitário Estácio de Ribeirao Preto, Rua Abrahao Issa Halach, 980 Ribeirania, Ribeirao Preto, Sao Paulo 14096-160, Brazil

e-mail: m.beltranleiva@uandresbello.edu

A rigorous study, going from classical to relativistic quantum mechanical methods, has been performed on some phenanthroline derivatives synthesized and characterized herein, *viz.* [Nd(NO<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)(dppz - R)] with R= H, NO<sub>2</sub><sup>-</sup>, CN<sup>-</sup> and its [Nd(NO<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)(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<sup>III</sup> and evidenced poor conditions for a good sensitization thus explaining the complications observed experimentally.



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

Ouissam El Bakouri,<sup>1</sup> Rabia Ayub,<sup>1</sup> Kjell Jorner,<sup>1</sup> Patrick Bultinck,<sup>2</sup> Miquel Solà,<sup>3</sup> Henrik Ottosson<sup>1</sup>

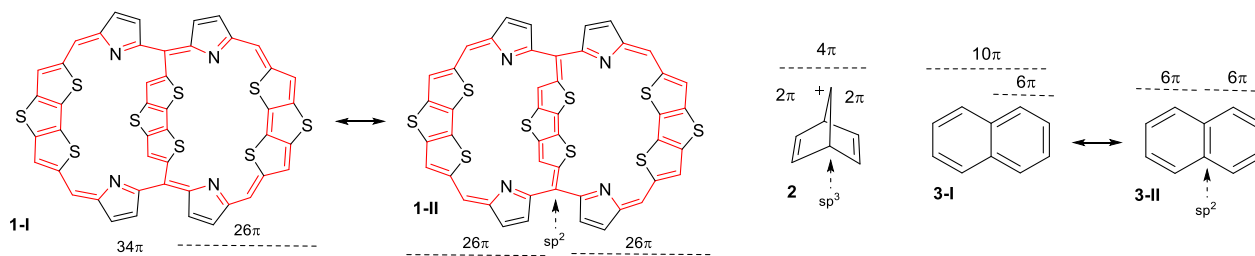
<sup>1</sup> Department of Chemistry – Ångström Laboratory, Uppsala University, Box 523, 751 20 Uppsala, Sweden.

<sup>2</sup> Department of Inorganic and Physical Chemistry, Ghent University, 9000 Ghent, Belgium

<sup>3</sup> Institut de Química Computacional i Catàlisi (IQCC), Universitat de Girona, 17003 Girona, Spain

Patrick.Bultinck@UGent.be, miquel.sola@udg.edu, henrik.ottosson@kemi.uu.se

Bicycloaromaticity has gained recent attention through experimental and computational studies of dithiopheno-bridged octaphyrins (*e.g.*, **1** below) labelled as bicycloaromatic.<sup>1,2</sup> The concept was coined by Goldstein in 1967,<sup>3</sup> and put in a broader context by Goldstein and Hoffmann.<sup>4</sup> 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  $\pi$ -electrons equals  $4n$ , illustrated by **2** having two  $2\pi$ - and one  $0\pi$ -electron ribbons and a total of four  $\pi$ -electrons. Now, are the dithiopheno-bridged octaphyrins *bicycloaromatic* or bicyclic with two Hückel-aromatic conjugated circuits? Clearly, the total number of  $\pi$ -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 ( $6\pi$ - and  $10\pi$ -electron circuits in **3**).<sup>5</sup> Depending on the resonance structure, the bridge in **3** has either zero or two  $\pi$ -electrons (**3-I** or **3-II**) while the bridge in **1** has either eight or ten  $\pi$ -electrons (**1-I** or **1-II**). The reason that one  $26\pi$ -electron circuit in **1** dominates over the other is structural; ring-puckering and a tilted dithiopheno-bridge. In addition to one dominating  $26\pi$ -electron path, (*cf.*, one  $6\pi$ -electron cycle in **3**) there is the perimetric  $34\pi$ -electron path (*cf.*, the  $10\pi$ -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

R. A. Matute<sup>1,2</sup>

<sup>1</sup>Centro Integrativo de Biología y Química Aplicada (CIBQA), Universidad Bernardo O Higgins, Santiago 8370854, Chile

<sup>2</sup>Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA

e-mail: rmatute@caltech.edu

The relationship between the reaction electronic flux (REF) and aromaticity on mechanism of the triplet di- $\pi$ -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.<sup>1,2</sup> Photoexcitation via singlet S<sub>1</sub> 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 T<sub>1</sub> 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.<sup>1,2</sup> Substituent effects can destabilize the radical species on T<sub>1</sub> and eventually BR-II becomes the regioselectivity determining step.<sup>3</sup> In a very recent work,<sup>4</sup> The REF was found to discriminate between electronic flux in  $\pi$ - and  $\sigma$ -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.<sup>[4]</sup>

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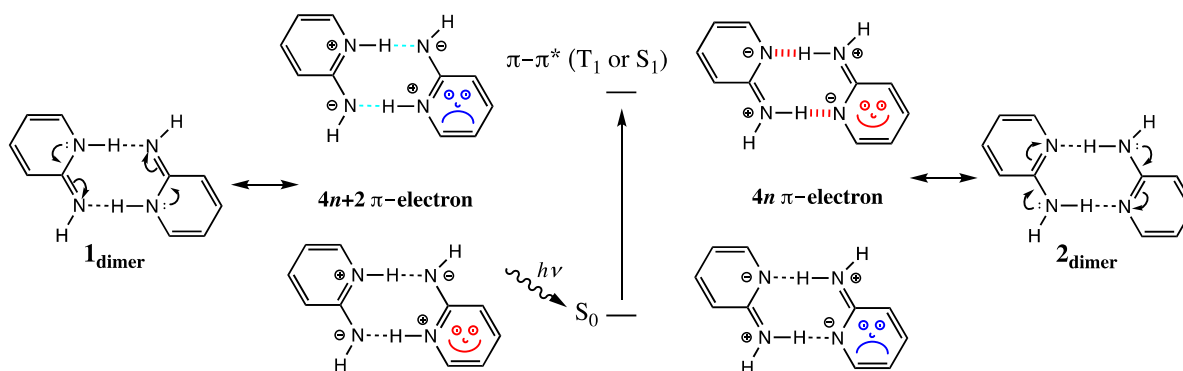
## P15. AROMATICITY-MODULATED HYDROGEN BONDING (AMHB) AT THE EXCITED-STATE

Lucas J. Karas, Chia-Hua Wu, Judy I. Wu

Department of Chemistry, University of Houston, Houston, Texas 77204, The USA

e-mail: ljkaras@uh.edu

Recent works from our group have shown that hydrogen bonding interactions that increase (or decrease) the cyclic  $4n+2$   $\pi$ -electron delocalization of heterocycles, at their ground states, can be strengthened (or weakened) through Aromaticity-Modulated Hydrogen Bonding (AMHB).<sup>1,2</sup> Here, we show that such effects reverse at specific  $\pi$ - $\pi^*$  excited-states, since the (anti)aromatic characters of  $\pi$ -conjugated rings follow a reversed Hückel  $4n+2$   $\pi$ -electron counting rule at those states (i.e., Baird's Rule).<sup>3</sup> Quantum-mechanical calculations show that, indeed, hydrogen bonding interactions that polarize  $\pi$ -electrons to enhance cyclic  $4n+2$   $\pi$ -electron delocalization in heterocycles (e.g., **1**<sub>dimer</sub>) are weakened due to increased excited-state antiaromaticity, while those that reduce  $4n+2$   $\pi$ -electron delocalization (e.g., **2**<sub>dimer</sub>) 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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