Aromaticity 2025

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Talks



Topological Structure of Polyconjugated Molecules and the Design of Open-Shell Systems

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The frontier orbitals of π -conjugated molecules, aside of their aromatic or antiaromatic characters, aside of the shapes and aside of the number of π -electrons in delocalization, are characterized by fractions of non-bonding orbitals. The existence of such non-bonding orbitals is usually paralleled by their disjoint character which makes them ideally suited to minimize electron correlation / repulsion energy, E_{corr} . As a result, the midgap electronic state positions are dominated by orbitals with non-bonding character which separates the chirally symmetric bonding and antibonding orbitals. With these non-bonding orbitals, it is also possible to construct the bonding and antibonding orbitals form which the hybridization energy, E_{hyb} , is deduced. Many of the observed properties of these molecules are dictated by the balance between E_{hyb} and E_{corr} .

Figure 1. Representation on the bonding, anti-bonding and non-bonding states revealing the



topological electronic structure of a chain of CH units, or $(CH)_n$. Also, the frontier molecular orbitals of some molecules such as benzene, naphthalene and azulene are shown.

The Hückel molecular orbital theory (more familiar to chemists) or the tight-binding model (more familiar to physicists) provide the ideal framework to approach the electronic, optical and magnetic properties of many polycyclic organic molecules. In this contribution, all these aspects of the impact of the E_{hyb} and E_{corr} in the formation of polycyclic aromatic compounds in general and also the case of open-shell molecules and the relevance and role of the non-bonding states is discussed.

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Improving the Harmonic Oscillator Model of Aromaticity with Antiaromatic Reference Molecules

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With the goal to realize simple, more accurate and balanced geometry-based probing of aromaticity and antiaromaticity in ground and excited electronic states, I will describe our recent efforts to parameterize the harmonic oscillator model of aromaticity (HOMA) for CC, CN, NN and CO bonds in a state-specific fashion using the actual bond lengths of both aromatic and antiaromatic reference molecules as calculated with a high-level quantum chemical method [1,2]. In particular, I will show that when parameterizations of HOMA developed in this way are applied computationally to a large and variable set of benchmark molecules across the aromatic-antiaromatic spectrum (single-ring, multi-ring, carbocyclic, N,O-heterocyclic), their predictions are much better correlated with magnetic, energetic and π -delocalization-based reference data than are those produced by the standard parameterization of HOMA. This holds true for both ground and excited states, and for each of numerous levels of theory employed for the underlying quantum chemical calculations.

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Close π-Stacking of Antiaromatic Porphyrins Through Four-Electron Multicentered Bonding

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Norcorrole is a ring-contracted antiaromatic porphyrin, which lacks two *meso*-carbons from porphyrin. We previously reported that norcorrole dimer **1** exhibited a closely stacked orientation.¹ The proximity of the two norcorrole units is rationalized by the stacked-ring aromaticity between two antiaromatic systems.²

Recently, we have prepared cyclophane **2**, which exhibited three different solid-state structures.³ Importantly, the aromaticity of **2** is dependent on the twist angle between two norcorrole units. Furthermore, the introduction of electron-withdrawing groups to norcorrole resulted in a shorter stacking distance in 3.⁴ The close stacking originates of **3** from four-electron bonding interactions between two antiaromatic molecules.



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Creation of σ -Delocalization Systems and their Charge Transport Properties

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Creation of new electronic delocalization systems is of importance for the development of fundamental and materials chemistry, and attention has long focused on the extension of π -delocalization by annelation of phenyl rings to form polycyclic aromatic hydrocarbons and by polyenes. However, π -delocalization in non-planar frameworks is generally unfavorable because of less overlapping of π -orbitals.



 $(\sigma + \pi)$ -mixed conjugation

Meanwhile, we have reported on the σ -delocalization on the periphery of a benzene ring composed of lone-pairs interactions between non-bonded selenium atoms,¹ where the σ -delocalized orbitals are perpendicular to the π -orbitals on the central benzene ring. We came up with an idea that the orthogonal geometry of the σ - and π -delocalized systems enabled to create a new electronic delocalization system in a non-planar geometry, and we paid attention to a biphenyl platform, where two aryl groups can be situated perpendicularly with steric congestion. In such a platform, the σ - and π -delocalization systems can interact with each other, and we name the system a (σ + π)-mixed delocalization. In this presentation, we report the creation of (σ + π)-mixed delocalization systems using a biphenyl and a terphenyl platforms and their charge transport properties evaluated by the break junction method.²

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Fine-Tuning Excited States Using Aromaticity

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Aromaticity has been invoked as guiding principle in the design of singlet fission chromophores, but (SF) solid computational assessments are required to unveil the impact of ground- and excited-state aromaticity the on excited-state energies. In this talk, I will focus on innovative inverse design strategies to navigate the combinatorial chemical compound space, aiming to



 $\label{eq:R16} \begin{array}{l} \mathsf{R}_{1\text{-}6} = \mathsf{NMe}_2, \, \mathsf{NH}_2, \, \mathsf{OH}, \, \mathsf{OMe}, \, \mathsf{SH}, \, \mathsf{Me}, \\ \mathsf{SiH}_3, \, \mathsf{H}, \, \mathsf{BH}_2, \, \mathsf{BF}_2, \, \mathsf{F}, \, \mathsf{CI}, \, \mathsf{CF}_3, \, \mathsf{CN}, \, \mathsf{NO}_2 \end{array}$

accelerate the discovery of SF compounds.^[1] These computational strategies can be efficiently used to manipulate the excited state energies of fulvenes, generating a diverse library of systems that fulfil the strict energetic requirements for SF. On the generated database, general design criteria spanning a wider chemical space are devised, including the role of ground- and excited-state aromaticity. Different descriptors to assess ground- and excited-state aromaticity including a meticulous analysis of the magnetically induced currents, which allows for determining the most appropriate combination of ring current circuits in SF materials with complicated fused ring structures.^[2,3] The results highlight how aromaticity and inverse design approaches can reshape the landscape of structures available to SF. Remarkably, the methodological framework is transferable to other molecular design challenges, such as the design of aromaticity-based molecular switches with enhanced optical contrasts.^[4]

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How to stabilize antiaromatic compounds?

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I will report about quantum chemical calculations of formally 4π anti-aromatic molecules, which are stabilized by substituents.



The Journey from the Hückel's 4n+2 Rule to the Wade's 2n+2 Rule

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Looking for molecules that are isoelectronic with already existing ones is a useful strategy to design a new molecule because their electronic structures are known to be stable. For example, molecules with 10 electrons include N₂, CO, CN⁻, NO⁺ and their existence suggest that B_2H_4 could exist, [1] and was made, although in tiny amounts. In contrast, benzene (C_6H_6) is a highly stable molecule that is planar, with a cyclic structure that adheres to Hückel's rule. It contains 6 π -electrons, like the [B₆H₆]⁶⁻ anion, which is also planar when Li counterions are considered. [2] However, its high charge precludes a high stability. To design molecules with improved stability than [B₆H₆]⁶⁻, one possibility is to incorporate neutral atoms. To say by substituting a negative boron atom (B^{-}) by a carbon atom (C). Hence, $[B_6H_6]^{6-}$ is isoelectronic to borabenzene ($[C_5H_5BH]^{-}$), or diborabenzene ($[C_4H_4B_2H_2]^{2-}$)[3] and ultimately with C_6H_6 . Any of the last three will be more stable than $[B_6H_6]^{6-}$. Alternatively, negative charges can be transformed into fragments; for example, 4 electrons (4e-) are isoelectronic to a BH unit. Therefore, $[B_6H_6]^{6-}$ is isoelectronic to $[B_7H_7]^{2-}$, as C_6H_6 is isoelectronic to $[B_7H_7]^{2-}$. These transformations are explained using the Electronically Confined Space Analogy (ECSA). Indeed, π aromaticity and three-dimensional aromaticity are the two sides of the same coin. [4a-d] We have moved from the Hückel's 4n+2 rule to the Wade's 2n+2 rule.

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Navigating the Challenges in Designing Double Aromatic 2D and 3D Molecules

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Inspired by the examples of double σ , π -aromatic hexa-substituted benzene dications [1-3]. we investigate whether similar behavior can be observed in tropylium ion derivatives (2D) and icosahedral boron clusters (3D). For the 2D systems, our motivation is threefold: i) the seven neutral halogen substituents on tropylium cations potentially provide 14 σ -electrons, aligning with the 4n + 2 Hückel number; *ii*) tropylium cations are highly stable and readily generated experimentally; and iii) the distances between substituents in substituted tropylium cations are expected to be shorter than those in substituted benzenes, potentially facilitating stronger σ -aromaticity. Despite these advantages, we encountered significant challenges due to electronic and steric effects, still requiring oxidation to achieve σ -aromaticity. Our findings, which include the tropylium anion and trication in both singlet and triplet states, reveal that there is a need to open a lone pair hole to generate σ -aromaticity [4]. Inspired by the potential for double aromaticity in 2D systems, we also explored this concept in 3D icosahedral boron clusters ($[B_{12}I_{12}]^{0/2+}$). However, our study shows that the σ -delocalization in the I₁₂ shell does not contribute to system stabilization [5]. Overall, our research highlights both the promise and limitations of achieving double aromaticity across different systems, paving the way for future investigations into novel aromatic compounds and their implications in chemical design.

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Modulating Paratropicity in Polycyclic Antiaromatic Hydrocarbons

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Polycyclic [4n] antiaromatic hydrocarbons (PAAHs) have attracted significant attention as promising targets for organic electronics, including organic solar cells (OSCs), organic field-effect transistors (OFET), and organic light-emitting diodes (OLED).¹ Their high charge mobilities derive from a narrow HOMO-LUMO energy gap and increased paratropicity of the [4*n*] antiaromatic core. The annelation of heteroarenes to the [4*n*] core provides an effective strategy to modulate the antiaromaticity and optoelectronic properties of PAAHs.^{2,3} However, a structure-property relationship that accounts for the heteroatom's impact on the degree of paratropicity remains a challenge. In this study, we expanded upon Gimarc's topological stabilization (TCS) rule,⁴ which suggests that the best placement of electronegative heteroatoms occurs at positions with the highest charge in an isoelectronic reference compound. Using Extended Hückel theory and DFT calculations, we investigated how heteroarenes stabilize or destabilize the charge density pattern and its correlation with the paratropicity s-indacene, dicyclopenta[b,g]naphthalene degree of in and s-indaceneo[2,1-a]-s-indacene antiaromatic cores. We found that the paratropicity of PAAHs can be modulated using the TCS principles. This work contributes to the rational design of PAAHs with enhanced charge mobilities, advancing in the field of organic electronics.

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Novel Studies on the Aromaticity of Fused Azaheterocycles and Transition Structures

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In this communication, we present and discuss recent results on the aromaticity of diverse fused azaheterocycles containing different aromatic units. These compounds include a novel phenantrene-extended phenazine dication that evades planarity, as well as benzo[*a*]imidazo[5,1,2-*cd*]indolizines, whose photophysical properties permit the bicolor detection of barium cations produced in neutrinoless double-beta decay of Xe-136. Finally, we will extend this discussion to a novel concerted decarboxylative sigmatropic reaction that involves an unusual aromatic transition state.

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Photo-Responsive [4*n*]Annulene Derivatives for Functional Polymers

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For the development of photo-functional polymers, the design of a photo-responsive molecular unit is essentially important. We have been interested in thiophene-fused cyclooctatetraene derivatives for In 2017, we reported the first experimental this purpose. demonstration of the energetics of excited-state aromaticity (Baird aromaticity)¹ using this molecular motif.² This molecule undergoes ring inversion through a planar transition state. Under photo-irradiation, the inversion behavior was significantly enhanced due to the emergence of aromaticity at the [4n]annulene core in the planar transition state. By using this photo-responsive molecular motif, we successfully made the first example of an alternating heterochiral supramolecular polymer.³ This supramolecular polymerization can be initiated by photo-irradiation to the optically



resolved monomer through racemization. Interestingly, this polymerization is "photo-suspendable" due to the rapid fluttering motion of the monomer under photo-irradiation that prevents the monomers from interacting with the growing end of the polymer chain.⁴ In addition, the resultant "racemic" polymer can be made "optically active" by fine-tuning of the reaction conditions.

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Breaking Tropylium Rings in the Ground and Excited States

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The balance between strain relief and aromatic stabilization dictates the form and function of non-planar π -aromatics. Overcrowded systems are known to undergo geometric deformations, but the energetically favorable π -electron delocalization of their aromatic ring(s) is typically preserved. This presentation will discuss the application of (i) steric overcrowding and (ii) photoexcitation to go beyond this balance point, investigating the resulting rearrangements that occur. Increasing the steric bulk around the periphery of π -extended tropylium rings leads them to deviate from planarity to form contorted conformations in which aromatic stabilization and strain are close in energy. Under increasing strain, the aromatic π -electron delocalization of the system is broken, leading to the formation of a non-aromatic, bicyclic analogue referred to as 'Dewar tropylium'. The aromatic and non-aromatic isomers have been found to exist in rapid equilibrium with one another.



Design and Synthesis of Organic Electronic Materials

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Organic semiconductors have garnered significant attention as earth-abundant alternatives to inorganic semiconductors. These materials, consisting of polymers or small molecules with extended π -conjugation, exhibit exceptional electronic, optical, and thermal properties, making them suitable for applications in transistors, solar cells, and light-emitting diodes. However, several challenges must be addressed before developing real-world products.

Our group focuses on designing and synthesizing novel organic semiconductors using low-cost and easily prepared starting materials. Benzobisazoles, our system of choice, possess exceptional electronic, optical, and thermal properties, making them suitable for various organic semiconducting applications. Furthermore, these materials consist of four aryl substituents along the central benzene ring (4,8-(2,6-position/axis)). This arrangement creates spatially segregated frontier molecular orbitals (FMOs), allowing for the nearly independent tuning of the HOMO and LUMO levels through aromatic substitution.

We employ advanced computational tools and machine methods accelerate the discovery learning to and optimization of these materials. By leveraging these techniques, we can efficiently explore vast chemical spaces and predict key properties, significantly enhancing our material design process. We have developed several new based benzobisoxazoles, materials on including wide-bandgap materials for organic light-emitting diodes and narrow-band gap materials for photovoltaic cells.





Core-electron contributions to the magnetic response of molecules with heavy elements

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In this talk, we analyze the magnetic response of core electrons and its influence on the global magnetic response of systems containing heavy elements, employing the removing valence electron (RVE) approximation. We also explore electronic aromaticity indices to understand the potential role of core electrons. The analysis comprises planar and three-dimensional molecular systems, considering the applicability and limitation of the RVE approach. The study reveals that core electrons significantly contribute to the magnetic response, especially to the magnetic shielding, affecting the interpretation of aromaticity. The study emphasizes caution in labeling systems as strongly aromatic based solely on shielding function computations. Thus, the magnetic response of core electrons requires careful consideration, and multiple criteria complement each other for a comprehensive understanding, particularly in systems with heavy elements and intricate structures.



Non-Classical Boron Cluster-Phosphonium Conjugates and other Boron Cage Extensions

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Heteropolycyclic molecular systems, which are essential components in the fields of materials science and pharmacology, are often composed of 2D extended aromatic rings. Here, we introduce a class of 3D aromatic boron cluster-fused heterocyclic phosphoniums by merging a nido-carborane cage with a phosphine and a π -conjugated unit.¹ To achieve this, we developed a new synthetic methodology that encompasses Pd(II)-catalyzed,^{2,3} P(III)-directed B-H activation of nido-carboranes with alkynes. This method facilitates the production of a diverse array of carborane-extended phosphoniums with high yields under mild conditions. The inclusion of the carborane moiety leads to a twisted molecular structure, resulting in increased stability compared to their 2D planar counterparts. Moreover, the fusion between the 3D boron cluster^{4,5} and the novel five-membered borophosphonium heterocycle enables electron delocalization across the structure. This unique feature transforms the inherent photo-inert properties of the carborane cage into high-performance luminogens with a range of emission behaviors, including aggregation-induced emission (AIE), highly efficient tunable color solid-state luminescence, and aggregation-induced circularly polarized luminescence. Consequently, this groundbreaking boron cluster-fused phosphonium framework significantly expands the library of aromatic-based heterocycles and demonstrates considerable promise for applications in functional materials.

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Global and local electron delocalization in Covalent Organic Frameworks (COFs)

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Most Covalent Organic Frameworks (COFs) are porous two-dimensional layered structures composed of fused nano-rings formed from organic building blocks. Some COFs have applications in electronics due to their semiconductor properties, which suggest the presence of electron delocalization—either within the nano-rings, throughout an entire layer, or between layers. However, electron delocalization in existing COFs is rarely studied, and it remains unclear which structural properties are necessary to enhance this delocalization. In our theoretical investigation, we examined the aromaticity of a series of nano-rings derived from the structures of various COFs. Our findings indicate that previously synthesized COFs do not exhibit significant global electron delocalization, even in fully conjugated structures; instead, all delocalization is localized. We also discovered that the electronic current density within each nano-ring is highly dependent on the specific building blocks used as vertices. Additionally, we present a building block that can enhance delocalization within the nano-rings.



Electron delocalization (TVCD) of fully conjugated COF nano-ring



New Insights in the Chemistry of Heavier Aryl Anions

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Recently, we have succeeded in the synthesis and isolation of the first stable heavy aryl anions such as germabenzenyl and stannabenzenyl anions 1^1 and 2^2 by the reductive elimination of the bulky aryl substituent on the corresponding heavy benzenes. Furthermore, it was found that the reaction of germabenzenyl anion 1 with 1,2-dibromodimetallenes resulted in the germanium-nuclear exchange on the germabenzenyl ring to give new heavy benzenes 3 and 4, respectively, accompanying with a novel single germanium atom transfer reaction.³



In this work, we examined the p-extension of the heavy aryl anion system and succeeded in the isolation of the expected 2-germanaphthalenyl anion **5**.⁴ Molecular structure of **5** was successfully established by XRD analysis and its properties were investigated based on the spectroscopic and theoretical studies.



Furthermore, the reactivity of **5** with benzil was compared with that of **1** in order to estimate their germylene character.⁵

In addition, synthetic attempts to generate and isolate the corresponding silabenzenyl anion will also be described.⁶



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(Anti)aromaticity of Cyclo[n]carbons (n = 6 - 24)

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The first association with the term "aromatic" is a stable, cyclic, conjugated molecule that tends to retain its π -electronic structure during a chemical reaction. The perfect example is benzene, whose special properties are attributed to the cyclic, out-of-plane delocalization of its six π -electrons (Figure 1). Hückel's famous π -electron counting rule¹ allows chemists to predict whether an annulene is aromatic (4n + 2) or antiaromatic (4n), the latter being associated with instability due to cyclic delocalization.

Cyclo[n]carbons are a family of carbon allotropes consisting of *sp*-hybridized carbon atoms, which allows them to achieve double π -delocalization, out-of-plane and in-plane,^{2,3} as illustrated for cyclo[18]carbon (Figure 2).



Out-of-plane π delocalization **Figure 1.** Benzene





Out-of-plane π delocalization In-plane π Figure 2. Cyclo[18]carbon

In-plane π delocalization 8]carbon

In this talk, I will analyze (anti)aromaticity of cyclo[n]carbons (n = 6 - 24) in terms of its most important manifestations, such as structure, energy, delocalization and magnetically induced electron currents.

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Y-Rule Aromaticity and Y-Rule Mapping in Oil Asphaltenes. Implications in the Oil Industry

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Reservoir crude oils contain gases, liquids, and asphaltenes, which may be dissolved or nanocolloidally suspended. Asphaltenes are the heaviest, most aromatic, and polar fractions of crude oils and bitumen, posing significant challenges in oil recovery, transportation, and refining. Asphaltenes adversely affect the physical and chemical properties of crude oils, complicating heavy hydrocarbon processing. In addition, they are key components in chemical processes in oil reservoirs, such as emulsion formation, emulsion stability, wettability change, aggregation, and asphaltene precipitation, which can damage the reservoir rock and halt production. Accurate structural characterization of asphaltenes is crucial for understanding chemical processes in oil reservoirs, and to finding correlations between structure, function, and reactivity. These correlations are not only economically important but also of utmost importance for enhanced oil recovery and processing efficiency, which are necessary to mitigate environmental impacts.

Asphaltenes are classified by solubility not by structure. Structurally, they are polycyclic aromatic hydrocarbons, with hexagonal and pentagonal fused aromatic rings, with heteroatoms (N, O, S) and alkyl side chains. The term aromaticity and circle notation, to represent the aromatic π -sextets, are used in structural characterization of asphaltenes. However, the circle notation has been misused, depicting all fused aromatic rings with a circle inside, hindering accurate structural characterization and understanding of asphaltenes' stability and chemical behaviors. The term "aromaticity" is also inaccurately used. It is used to define the percentage of the whole asphaltene molecule that corresponds to the aromatic PAH core.

The misuse of the aromatic π -sextet circle notation, and the word "aromaticity" in asphaltene science stems from a lack of understanding of these terms and their implications by petroleum and geological engineers, and geologists that are starting to work on asphaltene science for reservoir evaluation, but this lack of understanding also extends to the chemical community. Clar's rule helps to construct Clar structures, which contain aromatic π -sextets and localized double bonds, but as PAH size increases so does the number of possible Clar structures with the same number of aromatic π -sextets; therefore, making it impossible to identify the most important Clar structure. The Y-rule, which is a topological rule of aromaticity introduced in 2004, overcomes this limitation by only identifying the most important Clar-type structure, that represents the actual π -electronic distribution. The Y-rule aromaticity is being used to understand the undesired chemical behaviors of asphaltenes, and together with the Y-rule mapping have been used to conclude on the precise nature of heteroatoms in asphaltenes images obtained with atomic force microscopy (AFM) by IBM-Zürich. The Y-rule aromaticity and Y-rule mapping along with their applications in the oil industry will be presented and discussed in the talk.



Finding Ways to Cheat Transition State Theory (Better) in Chemical Reactions

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Not all chemical reactions occur by going over a potential energy barrier. In this talk, I will discuss examples of two scenarios that deviate from the paradigm of a transition state theory. Part 1 of the talk focuses on a classic case of heavy-atom tunneling between benzene oxide and oxpein. Many examples of heavy-atom tunneling involve three membered ring motifs. The effects of geminal hyperconjugation on ring strain are rarely considered, but can have important chemical consequences for controlling heavy-atom tunneling rates. Part 2 of the talk discusses spin-forbidden reactions, such as that involved in the thermal *Z*-*E* isomerization of azoarenes. Azoarenes are popular photoswitches that can undergo *E*-*Z* isomerization by light, and thermally revert to the *E* form. Thermal relaxation involves a crossing between the S₀ and T₁ state, and computations reveal structure-energy relationships pertinent to controlling the energy level of the S₀-T₁-S₀ crossing points. Practical strategies for how to "cheat transition state theory better" are provided. This is a computational chemistry talk for the organic chemist at heart.



Transition State Aromaticity and its Relationship with Chemical Reactivity

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The concept of aromaticity, initially introduced to describe the unique properties of cyclic conjugated hydrocarbons and their ions, has since been extended to include other systems, such as their homoderivatives, saturated cyclic compounds, organometallic and inorganic species, and even excited-state compounds.[1] The application of this concept to transition structures has enormously enhanced our current understanding of molecular reactivity.[2]

In this presentation, we will explore the relationship between transition state aromaticity and reactivity, focusing on how this interplay influences the barrier heights of various representative transformations, primarily (but not exclusively) in pericyclic reactions.^[3]



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Molecular Graphene Nanoribbons

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In the last years, chemists have devoted significant efforts to the synthesis of increasingly larger molecular structures that push boundaries of the molecular world into the nanoscale. Among these structures, molecular nanoribbons have received considerable both as synthetic challenges and as a unique platform to develop new materials because the nanoribbon structure dominates the optical, electronic, electrical, and magnetic properties. In these terms, we have introduced several approaches to prepare molecular graphene nanoribbons and nanographenes that reach up to 36 nm.^[1] The most recent advances in the synthesis of molecular nanoribbons and their properties will be discussed.

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Aromaticity-Active Ligands in Catalysis

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Aromaticity has been known for over a century and is often associated with molecular stability, reactivity, and geometry. However, limited studies connect this phenomenon with thermodynamics and kinetics in the catalysis field. While it is frequently discussed in many catalytic applications, the changes in the aromatic properties of ligands require more attention. Therefore, here we present an aromaticity study of the ligands in catalytic pathways. The metal-centered reactivity (MCR), ligand-centered reactivity (LCR), and the metal-ligand cooperative reactivity (MLCR) were analyzed by means of the aromaticity indexes. In this work, we highlight representative ligand systems and compare Shvo, Ziegler–Natta, Milstein, and Huang catalytic platforms systems with a conceptual insight base. Our work demonstrates that aromatization can provide an additional "*push*" to the reaction driving force and, consequently, a new design tool in catalysis.



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The Glidewell-Lloyd rule: Recent advances and applications

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The Glidewell-Lloyd rule is a lesser-known principle in aromaticity, stating that "the population of π -electrons in conjugated polycyclic systems tends to form the smallest 4n + 2 groups and avoid the formation of the smallest 4n groups".¹ Recent computational studies using modern methods validated and extended this rule by including an exception: when avoiding the smallest 4n groups leads to the formation of larger 4n groups.² This talk will examine our recent work on the explore the rule's effectiveness in predicting the aromatic behavior of compounds with odd-membered and heteroaromatic rings,^{3–5} its impact on electronic structure, and potential applications in molecular design.

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Multiple Aromatic Units within a Single Molecular Structure. Overall Aromaticity in Local Aromatic Aggregates.

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Pursuing a rational design and synthesis of functional materials, the building-up approach is an attractive strategy based on the controlled aggregation of multiple cluster building blocks. Spherical aromatic species as an extension to planar aromatics,^{1,2} sustaining related magnetic properties, enabling an induced shielding cone behavior given from any orientation of the applied field,³ contrasting to planar species, which sustain such character under a parallel oriented external field.⁴ Here, we discuss the resulting aromatic characteristics for oligomers involving several building cluster units, encouraged by the understanding of how multiple spherical aromatic units behave together in the birth of extended linear arrays, highlighting the use of descriptors to locate spherical aromatic states and their related magnetic anisotropy, favoring the understanding of how multiple spherical aromatic units behave together towards in molecularly conceived materials.

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Helicenes as Attractive Building Blocks for Complex Chiral Nanocarbons

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Inherently chiral helicenes¹ have attracted considerable interest in recent years because of their distinctive electronic structure, properties, and potential applications in diverse areas of chemistry, including enantioselective catalysis, molecular recognition, self-assembly, surface science and chiral materials.

Significant advances in helicene synthesis now make it possible to use these unique aromatic systems as building blocks for the construction of complex molecular architectures that are π -conjugated and chiral. After a brief introduction to the modular synthesis of helicenes by intramolecular [2+2+2] cycloisomerisation of the corresponding aromatic triynes, attention will be paid to the preparation of π -conjugated macrocycles based on helicenes.² Suitable synthetic strategies will be discussed. The properties of these large chiral nanocarbons will be highlighted with a focus on their local *vs.* global aromaticity, emission and redox behaviour.



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Mission ImPASsible: Deep Learning Decodes Aromatic Systems

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Polycyclic aromatic systems (PASs) present a seemingly insurmountable challenge: vast chemical spaces, complex electronic structures, and elusive aromatic properties. Our mission, should we choose to accept it, is to harness the power of deep learning to decode these molecular mysteries.

In this talk, we embark on a journey through this complex chemical space, combining traditional computational methods with cutting-edge artificial intelligence tools. We demonstrate how neural networks can be trained to predict aromatic character, electronic properties, and molecular behavior with unprecedented speed and accuracy. More importantly, we show how they can be used interpretably to extract chemical insight.

By analyzing thousands of PAS structures, our AI agents have uncovered hidden patterns and structure-property relationships that traditional methods might have missed. From small benzenoid systems to extended graphene-like structures, we show how deep learning can navigate this complex chemical landscape, offering new insights into molecular design and property prediction. This talk will not self-destruct in five seconds, but it will revolutionize how we think about combining artificial intelligence with molecular science.



Deciphering the astrophotochemical inertness of H₃⁺ at the molecular level

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The trihydrogen cation, H_3^+ , is unique in the Universe.¹ It serves as the primary proton reservoir, driving essential astrochemical reactions,² and functions as a thermostat for giant gas planets.³ H_3^+ has also a remarkably low photodissociation rate, explained by its exceptionally high first electronic excitation energy (19.3 eV).⁴ We now reveal the key factors behind this high energy: (*i*) aromatic stabilization in its electronic ground state, (*ii*) antiaromatic destabilization in its first excited state, and (*iii*) a high nuclear-to-electronic charge ratio (+3 *versus* -2).⁵ Through comparisons with analogous π -conjugated carbocations, we find that ground state aromatic stabilization plus excited state antiaromatic destabilization energy of H_3^+ by 4.8 - 6.0 eV. Only with this increase can it fulfil its unique functions in space. Although our study focuses on H_3^+ , it unravels that excited state antiaromaticity also impacts on the excited state properties other species of astrochemical importance, *e.g.*, the cyclopropenium cation.⁶



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Localization vs. Delocalization: Geometric and Electronic Structure Evolution of Group 13 Hydrides

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The term "electron deficiency" is traditionally employed to describe compounds which do not have enough valence electrons to form localized two-center two-electron (2c-2e) bonds joining all atoms. Diborane, B₂H₆, is a classical example of such species, where two 3c-2e B-H-B bonds are necessary to distribute 12 valence electrons over 8 B-H contacts.^{1,2} An electron-deficient nature of B gives rise to electron delocalization which may involve more than three centers, as previously demonstrated by various exotic gas-phase clusters exhibiting multicenter bonding.³ In turn, electron delocalization may invoke aromatic properties, correlating with the extra stability and decreased reactivity of such compounds. While over 100 individual B hydrides are known,⁴ the hydride chemistry of the heavier congeners (AI, Ga, In, TI) remains more cryptic, which is primarily attributed to their lower thermal stability.⁵ As the orbitals become more diffuse down the group from B to TI, the properties of these hydrides begin to change qualitatively, revealing a dichotomy in their structures and electron distributions depending on the number of H atoms. In my talk, I will describe the evolution of the changes in the geometric and electronic structures of Group 13 hydrides as a function of H saturation. Specifically, I will identify their global minimum structures, assess thermodynamic stability towards hydrogen dissociation and compare the degree of electron delocalization and aromatic properties from B to TI in Z_2H_x and Z_3H_y (Z = B-TI; x=0-6; v=0-9).⁶⁻⁸

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The Aromaticity and the Relative Stability of the n,π* States of Heteroaromatic Compounds

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The photochemistry of heteroaromatic compounds depends on the character of their lowest electronically excited states, which are of either n,π^* or π,π^* type. For species with 4n+2 π -electrons, the n,π^* type of states have an odd number of π -electrons leading to an unclear character, spanning from aromatic to antiaromatic. We analyze here the n,π^* excited states of $(4n+2)\pi$ -electron heteroaromatics with in-plane lone-pairs $(n_{\sigma}, herein n)$ applying Mandado's 2n+1 rule for aromaticity of separate spins [1]. After excitation of an electron from n to π^* , a $(4n+2)\pi$ -electron species has $2n+2\pi_{\alpha}$ -electrons and $2n+1\pi_{\beta}$ -electrons (or *vice versa*), and becomes π_{α} -antiaromatic and π_{β} -aromatic. Yet, the antiaromatic π_{α} - and aromatic π_{β} -components seldom cancel, leading to residuals with aromatic or antiaromatic character. Having (anti)aromatic residuals influence the relative stability of the n,π^* states. We discuss which factors determine which type of vertical excited state (n,π^* or π,π^*) is the lowest in energy for various heteroaromatics [2].



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A Stable Silapyramidane from Silyl Cyclobutadiene and a Single Silicon Atom

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This study presents the first successful synthesis of stable silapyramidane, starting from cyclobutadiene and a stable silylene derivative, achieved through a silylene addition-reductive elimination of a ligand via a cyclobutene intermediate. Previously, various low-valent silicon compounds, including silicon π -complexes, have been explored. Still, this work provides new insights into the structures and reactivity of silicon analogues of highly strained 3D cluster molecules. Unlike pyramidane studies on heavier group 14 elements like Ge, Sn, and Pb, this research mainly focuses on silicon. The reactivity of silapyramidane was examined, revealing its ability to form a fluorescent spirobis(silole) and an iron complex with silapyramidane as a ligand. This study progress our understanding of the relationship between the antiaromaticity of planar molecules and the stability of three-dimensional cluster structures.





Advancements in the Calculation of the Magnetic Response and Applications in the Realm of Magnetic Aromaticity

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Several decades of research have allowed reliable computations of the magnetic response, which, at first order has its core in the current density tensor. Nowadays this tensor can be computed by several codes, among which there is also SYSMOIC [1]. Despite its long history, the topic continues to be enriched by new approaches for the computation of the current density and its manipulation. As for new computational approaches, it has been recently shown how is it possible to obtain a divergence-free current density with a finite basis set, something unaffordable until present [2]. As for new manipulations of the tensor, it has been shown that the Isotropically Averaged Lorentz force density $<\mathbf{F}$, a scalar field obtained from it, can be a useful tool for the characterization of the molecular electronic structure [3,4]. In particular, $\nabla \cdot <\mathbf{F}$, the Divergence of the Isotropically Averaged Lorentz force density CIAL) is a scalar field which gives an indication of the local magnetic character: a positive DIAL means local paramagnetism, and a negative DIAL means local diamagnetism. The IAL field reveals the chemical structure, such as the different C-C bond types, and can distinguish aromatic and antiaromatic molecules on the magnetic criterion [3,4].

These new features enrich the tools for the computation of the magnetically induced current density, which is ever more encountered in literature, especially for the characterization of the magnetic response in the realm of magnetic aromaticity. We will discuss some of our most recent applications, focusing on cycloporphyrin nanorings [5], clarenes [6], and cyclopenta-ring-fused oligo-(m-phenylenes) [7]. The results, sometimes in contrast with previous reports, highlight a lively contribution of new computations and methods for the characterization of magnetic aromaticity.

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Magnetic Carbon

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It is generally accepted that carbon is the most versatile element of the periodic table, and it offers a plethora of compounds ranging from biology to materials science. While the list of fascinating properties carbon materials offer is long, they are not yet famous for magnetism. Indeed, most carbon materials are diamagnetic. Defects, dopants and dangling bonds can introduce paramagnetic centers without the potential to generate magnetic ordering. Recently reported magic-angle twisted bilayer graphene may become ferromagnetic due to a half-filled flat band at the fermi level and spin-orbit coupling [1]. A spectacular early report on magnetic carbon in pressurized fullerenes [2] was found to be caused by defects and the paper has been retracted five years later.

We propose an alternative concept to generate carbon materials with strongly coupled magnetic centers. Our materials are based on molecular triangulene and its derivatives, aromatic molecules intrinsically carrying one or two unpaired electrons. Using covalent linkages that preserve electron conjugation, we construct two-dimensional polymers with honeycomb-kagome lattice. The magnetic coupling between the monomers is facilitated by the linker groups. This has been examined in detail for the dimers [3]. When extending this concept to 2D polymers, we predict magnetic carbon materials with intriguing electronic structure that includes orbital ferromagnetism, while it maintains the Dirac and flat bands which are characteristic for the honeycomb-kagome lattice of the underlying 2D polymer.

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On the relationship between stacked-ring aromaticity and Baird's rule

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We have theoretically examined the mechanism of reduction in antiaromatic characters in closely stacked cofacial $\pi\text{-dimers}$ of $4n\pi$ antiaromatic molecules, often called stacked-ring aromaticity.¹ We performed high-precision quantum chemical calculations based on the multi-configurational wavefunction treatment. Then, we transformed the wavefunctions into the diabatic basis representation using monomer-localized orbitals, which enabled us to analyze the ground state wavefunction of the dimers in terms of the electron configurations provided in Fig. **1**.² revealed that double-triplet electron We have



Fig. 1. Examples of electron configurations in the diabatic basis representation.

configurations (**TT**) mix substantially in the ground state wavefunctions of several π -dimer models at small stacking distance (*d*). The calculation results indicate that each monomer in the π -dimers tends to have a T₁-like electronic structure at small *d*. Thus, we can interpret several experimental and theoretical results of aromaticity indices for such π -dimer systems based on Baird's rule. The unpaired electrons derived from the T₁-like electronic structure of each monomer are used to form intermolecular covalent-like bondings,³ owing to the coupling between **TT** and one-electron charge-transfer (**CT**) configurations. However, the stabilization energy gained by this bonding interaction is considered insufficient for achieving self-aggregation of the π -dimers at *d* ~3 Å, suggesting additional mechanisms for achieving substantial stabilization energy in actual π -dimers.

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Revolutionizing (Bio)Materials: The Experimental Breakthrough of 3D Aromaticity

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Aromatic organic compounds that play important roles in chemistry find numerous applications from drug delivery to nanotechnology or biological markers. We met a major achievement demonstrating experimentally/theoretically that carboranes, as well as anionic boranes and metallabis(dicarboranes), display global aromaticity.[1] Based on the relationship between stability-aromaticity, we have opened new applications of boron clusters as key components in the field of new (bio)materials.[2] Significant advancements have been achieved by incorporating metallacarboranes into COP and NPs,[3] directly linked to their unique chemical nature and 3D aromaticity.[3] Their interactions with biomolecules, such as amino acids, proteins, lipids, and *ds*-DNA-driven by this 3D aromaticity-have been experimentally and theoretically reported,[4] and these findings will be presented.

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Unusual conjugation topologies and their impact on delocalization within pi-electron materials

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The palate used to create high performance organic electronic materials is rich in aromatic building blocks, including numerous variations of benzene, thiophene and pyrrole rings. Although these materials can be photoexcited leading to subsequent exciton migration or subjected to redox processes to inject charge carriers, they all are formed from "static" ground electronic states. This presentation will highlight two new avenues in conjugated material design. The first entails the use of photoswitchable structural units that undergo electrocyclizations leading to subtle but electronically dramatic alterations of pi-electron conjugation topology. This is achieved through the photochemical creation and disruption of local aromatic substructures along the polymer backbone as a way to externally attenuate electronic properties thus providing a way to toggle between two distinct electronic ground states. The second will introduce prospects for radial topologies and their impact on linear conjugated polymer electronics. Our understanding of cyclic conjugation remains far behind the much more studied linear pi electron delocalization, especially in exotic systems maintaining both cyclic and linear conjugation pathways. we describe the synthesis and electronic properties of small-molecule and polymeric cycloparaphenylenes (CPPs) as part of extended linearly pi-conjugated frameworks, showing the unique nature of hybrid radial and linear pi electron delocalization operative in these new conjugation pathways.

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Anti-aromaticity and electronic structure: From cyclocarbons to 2D materials

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In this talk, we will explore the relationship between (anti-)aromaticity and electronic structure, using cyclocarbons (~10 atoms), porphyrin nanorings (~100 atoms), and porphene (>1000 atoms) as examples.

Cyclo[n]carbons (Fig. 1a) are monocyclic rings of n carbon atoms. We will illustrate the relationship between electronic structure, geometry, and anti-aromaticity in these unusual molecular carbon allotropes.^{1,2}

Conjugated porphyrin nanostructures (Fig. 1b,c) display remarkable properties such as quantum interference and length-independent conductance, which make them excellent candidates for molecular electronics.³ These properties stem from the coherent delocalisation of the wavefunction through the whole molecule, which becomes weaker as the molecule become larger. We will estimate the maximum size at which edge-fused porphyrin nanorings (Fig. 1b) can still be expected to exhibit quantum behaviour.⁴

Porphene (Fig 1c) is a recently characterised 2D material composed of fully fused porphyrins.⁵ We will show how the electronic properties of porphene arise from a balance between its aromatic and anti-aromatic fragments, and discuss potential applications.⁶



Fig. 1. (a) Cyclo[16]carbon. (b) Edge-fused porphyrin nanoring. (c) Porphene.

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Formation of quasi-plannar boron clusters applying topological path to smaller boron clusters

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The lowest-lying isomers of the B_{50} and B_{56} boron clusters are confirmed to have a quasi-planar shape. An extensive global energy minimum search for the B₅₀ and B₅₆ system, carried out using the Mexican Enhanced Genetic Algorithm (MEGA) in conjunction with density functional theory computations, confirms quasi-planar structures as their energetically most stable isomer. By applying a topological (leap-frog) dual operation followed by boron capping, we demonstrated that such quasi-planar structures come from B_{10}^{2-} and B_{12} , respectively. The high thermodynamic stability of B_{50} and B_{56} can be explained by the disk aromaticity model in which the delocalization of its π orbitals can be assigned to the levels of a particle in a circular box with the $[(1\sigma)^2(1\pi)^4(1\delta)^4(1\phi)^4(2\sigma)^2...]$ electronic configuration. Other delocalization indices confirm this π delocalization. While the B₅₆ has a similar electron delocalization to that of the quasi-planar B₅₀, they have opposite magnetic ring current properties because of the symmetry selection rules of their HOMO-LUMO electronic transitions. A strong diatropic magnetic current flow further supports the aromatic character of the quasi-planar B50. The sudden appearance of a quasi-planar B₅₀ again points out that the growth pattern of pure boron clusters is still far from being completely understood. The π delocalization in the boron clusters is larger at long distances than in carbon clusters at similar sizes, but such a trend is reversed at shorter distances.



Li₆E₅Li₆: Tetrel Sandwich Complex with 10-π-Electrons

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A single planar ring containing (4n+2) π -electrons is conventionally deemed to exhibit aromatic characteristics. In accordance with Hückel's rule, systems that possess ten π electrons are expected to exhibit aromatic characteristics. Herein we report a series of D_{5h} $Li_6E_5Li_6$ sandwich structures, representing the first global minima featuring ten π electrons E_5^{10-} ring (E = Si-Pb). However, the π -electrons localize as five π -lone pairs rather than delocalized orbitals. The high symmetry structure achieved is a direct consequence of σ -aromaticity, which is particularly favored in elements from Si to Pb. This results in a pronounced diatropic ring current flow that contributes to the enhanced stability of these systems.





Challenges and Opportunities in the On-Surface Synthesis of Carbon-Based Aromatic Nanostructures

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In recent years, the synthesis of new carbon-based nanostructures has advanced significantly by the integration of cutting-edge microscopies like ultrahigh-resolution atomic force microscopy (AFM) and scanning tunneling microscopy (STM) in molecular synthesis, alongside the impressive development of on-surface synthesis. This interdisciplinary approach presents several key advantages for molecular sciences: (i) characterization at the single-molecule level,¹ (ii) exploration of novel reactivity profiles,² and (iii) stabilization of highly reactive species.³ In this contribution, I will present a selection of examples from our group related with relevant aromatic nanostructures.



Figure 1. Triangulene-based macrocycle on Au(111).^{3a}

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Synthesis, Antiaromatic Character, and Coordination Behavior of Highly Antiaromatic Thiophene-Fused Pentalenes

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Antiaromatic π -conjugated systems have attracted continuous attention from the viewpoint of both fundamental and material science because of their characteristic properties such as an narrow HOMO-LUMO gap, multiple redox properties, a low-lying triplet state, and capability to exhibit through-space aromaticity, all of which are hardly achieved conventional aromatic by hydrocarbons. However, а major challenge in pursuing intramolecular



interactions of antiaromatic compounds and their application to electronic materials has been how to stabilize them without the use of bulky substituents, while retaining antiaromaticity. Although the condensation of benzene rings has been widely recognized as a powerful approach for thermodynamic stabilization of antiaromatic systems without bulky substituents, the pronounced aromaticity of fused benzene rings plays a dominant role in canonical structures, diminishing the antiaromatic character of the resulting π -electron systems. To address the above-mentioned issues, we have been focusing on the molecular design based on the introduction of less-aromatic heteroarenes such as phenanthrene and thiophene on the $4n\pi$ electron scaffold in a ring-fused manner.^[1–4] In this presentation, I will describe the overview and some of our recent studies based on this strategy.

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Aroma 2.0

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About a decade ago, we introduced Aroma 1.0 and put it on our website. It is a python 2 program for automating NICS-scan procedures for Gaussian 09 and NBO6, in order to get better concepts of magnetic aromaticity. It has been downloaded well over 250 times and is cited frequently although never published as a formal paper.

The developments in computer programing and in computational chemistry called for serious updates of Aroma. In this paper, Aroma 2.0 is introduced. It contains several features resulting from the changes mentioned above and the experience of working with Aroma 1.0.

The main changes are:

Aroma 2.0 is written in Python3.

It is compatible with Gaussian 09, Gaussian 16, NBO6 and NBO7, ORCA 5 and ORCA 6. It includes all the methods that Aroma 1.0 has and two new NICS-scan procedures. It has an option to produce only the input files, changing them, running as regular (Gaussian or ORCA) jobs and analyze the output files. Control of the σ -only multiplicity.

The details and examples will be presented.

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Cyclizations and Cycloaromatizations: Interplay Between Aromaticity and Antiaromaticity

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Is aromaticity a property of only cyclic molecules? What if the cycle is in the process of its formation? Can we still use this concept for the molecular design and control reactivity? And (if we have time for that discussion and if we define aromaticity as "symmetry-enforced delocalization"), can we talk about aromaticity if there is no cycle at all?



Calculating orbital contributions to the magnetically induced current density using gauge-including atomic orbitals

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We have developed a method to calculate orbital contributions to magnetically induced current density (MICD) susceptibilities in molecules using gauge-including atomic orbitals (GIAO). It has been implemented in the GIMIC program. Orbital contributions to magnetically induced ring-current (MIRC) strengths and molecular magnetic properties are analyzed and visualized. We have studied the orbital contributions to the MIRC strengths of free-base porphyrin (H₂P), benzene (C₆H₆), cyclopropenium cation (C₃H₃⁺), C₂N₂B₂H₆, borazine $(B_3N_3H_6)$, 1,4-cyclohexadiene (C_6H_8) , planar (D_{4b}) and bent (D_{2d}) cyclooctatetraene (C_8H_8) , cyclobutadiene (C_4H_4), hexadehydro[12]annulene (HD[12]A) and isophlorin (ISO). Five of the molecules are aromatic, four are antiaromatic, and one is nonaromatic. The orbital contributions to magnetic properties of benzene agree well with those previouslycalculated with the ipsocentric method. The largest contribution to the ring-current strength of antiaromatic molecules originates from the highest occupied molecular orbital (HOMO), whereas aromatic molecules have significant contributions from many orbitals. The σ contribution is significant for molecules with a strained molecular structure. The charge conservation of the MICD is fulfilled for each irreducible representation of the molecular structure in the presence of the external magnetic field.



Orbital contributions to the MIRC strength of benzene for each irreducible representation of the C_{6h} point group as a function on the angle of the integration plane.

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Efficient Assessment of Aromaticity through Electron-Delocalization Metrics

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Electronic aromaticity indices focus on electron delocalization as the primal signature of aromaticity and are among the most reliable measures for assessing it [1]. They depend on how we define an atomic partition, *i.e.*, on how we define an *atom-in-the-molecule* (AIM). Real-space atomic partitions are often preferred for their accuracy, however, they come with two significant drawbacks: high computational cost and an increase in numerical errors as the size of the ring grows [2]. Consequently, indices link I_{ring} or MCI are restricted to medium-sized molecules and relatively small rings (up to 12-14 atoms). This limitation significantly impedes the study of aromaticity in large conjugated systems, such as porphyrins and nanorings, which prompted us to develop indices more robust to numerical errors [2-4].

In this talk, we explore the use of AIMs based on Hilbert-space partitions and introduce three *robust* Hilbert-space partitions—meta-Löwdin, Natural Atomic Orbitals (NAO), and Intrinsic Atomic Orbitals (IAO)—that combine the reliability of real-space partitions without their associated disadvantages [5]. These partitions are devoid of numerical errors and are capable of effectively replacing the quantum theory of atoms in molecules (QTAIM) partition [6] to evaluate the aromatic character of molecules. We also introduce ESIpy, an open-source code to compute aromaticity indices from Hilbert-space partitions [7]. Finally, we analyze the performance of various electron-delocalization measures for assessing aromaticity.

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POSTERS



Exploration of Local, Semi-local, and Global Aromaticity in Three Dimensional Systems: The Case of Ge₂₄⁴⁻

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In 1931, Erich Hückel formulated what is now known as Hückel's rule,¹ providing a foundational criterion for identifying aromaticity in monocyclic compounds in their ground state. For planar polycyclic aromatic hydrocarbons (PAHs), Clar's rules have been widely applied to describe the distribution of aromatic π -sextets.² However, while these rules offer essential qualitative insights, precisely quantifying aromaticity in more complex systems requires complementary approaches. Ring current analysis is a key method for distinguishing between local, semi-local, and global aromaticity, as reflected in the corresponding ring current strengths (RCS), particularly in polycyclic and complex molecular systems.³ This study extends the concept of multiple aromaticity (local, semi-local, and global) to three-dimensional systems composed of three-dimensional molecular building blocks. Local, semi-local, and global ring currents in these systems are investigated. The GIMIC (Gauge-Including Magnetically Induced Current) method, originally developed by Sundholm and Berger.^{4,5} is applied to analyze the magnetically induced current density and, through their profiles, identify the ring current circuits that emerge in the Ge₂₄⁴⁻ system.⁶ Using established computational protocols,⁷ the results reveal a local distribution of ring currents within the Ge₈–Ge₈–Ge₈ fragments, with ring current strengths (RCS) of 41.4 and 42.6 nA/T for the two Ge₉ moieties, and an RCS of 20.8 nA/T for the central Ge₆ unit. The system also exhibits a global current of 104.8 nA/T. These findings demonstrate the presence of a predominant global ring current, while local and semi-local currents are present but weaker. This work extends the concepts of local, semi-local, and global aromaticity through corresponding ring currents in three-dimensional systems, offering new perspectives for their study and evaluation in metal clusters and other complex systems.

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Aromaticity-Driven Electron Transport in Linear-, Broken-, and Cross-Conjugated Polycyclic Architectures

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Molecular electronics aims to create nanoscale devices using individual molecules for electronic components, with potential to surpass the capabilities of traditional silicon-based technologies.¹ Recent advancements have led to innovative experimental techniques for manipulating electron transport, as well as theoretical methods for predicting molecular properties.² Notably, quantum effects like destructive quantum interference offer opportunities to control charge transport in a single molecule through structural modifications. Despite significant progress, the role of the aromaticity in these quantum interference remains ambiguous, with literature presenting conflicting conclusions. In this contribution we have shed light on the relationship between the aromaticity and electron transmission values in a set of polycyclic compounds possessing linear-, broken-, and cross-conjugation pathways. Using delocalization indices and distinct aromaticity descriptors rooted in structural, electronic and magnetic criteria we have shown a positive relationship between the electron transmission properties and aromaticity for a given connectivity.³



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Reactivity and Redox Properties of Amtiaromatic Indenofluorenes

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Antiaromatic molecules are generally unstable and are known to rapidly undergo reactions, such as structural rearrangements or electron transfer, in their hurry to relieve their antiaromaticity [1]. We propose to harness the tendency of antiaromatic molecules to transfer electrons for the design of redox-active ligands for organometallic catalysts based on earth-abundant metals.

To this end, we investigated a series of indenofluorene derivatives and their resulting Ni-complexes, which have shown promise as redox-active ligands. Using the antiaromatic indeno[2,1-c]fluorene (IF) [2] as a novel ligand scaffold, we systematically replaced the flanking benzene rings with heterocycles containing nitrogen, oxygen, and sulfur (Figure 1). These structural modifications modulate the complex's electronic, aromatic, and geometric properties, leading to unexpected reactivity in nickel complexes.

Through this study, we established a series of structure-property relationships and design principles, demonstrating how various structural features affect reactivity and molecular behavior. This advances the rational design of effective redox-active ligands with potential catalytic applications.



Fig.1. Ligand (a), complex of IF with Ni (b) and dimer with Ni investigated in this work

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Toward helicene-based π -electron macrocycles

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Shape-persistent π -electron macrocycles are becoming of increased interest to researchers as they present a synthetic challenge and may be attractive for materials chemistry. Moreover, some of them can spontaneously aggregate and form supramolecular assemblies. An inner cavity of a certain size can be used for a variety of purposes. Research on this type of compounds has resulted in reports on their organization to porous molecular crystals, liquid crystals, guest binding abilities, organization in solution, condensed phase or a solid surface, and their self-association in solution. Fully π -conjugated macrocycles with a well-defined diameter show interesting electronic and optical properties.

The main objective of this work is to explore synthetic methodologies for the preparation of new chiral helicene-based π -electron macrocycles containing phenylene butadiynylene linkers. Macrocyclization reactions have been studied using Eglinton coupling under high dilution conditions (Figure 1). The synthesis of appropriate building blocks and their combination to macrocycles will be discussed.



Figure 1



Transition-Metal-Free C-H Functionalization of Pentafulvenes Using 1-Haloacetylenes and 1-Halopolyynes

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Pentafulvenes are a peculiar group of five-membered ring cross-conjugated hydrocarbons. They are classified at the borderline between aromatic rings and cyclic olefins. Fulvenes exhibit a lot



of interesting properties making them applicable in charge transfer or biologically active systems. For decades, they were employed in research focused both on the theoretical and experimental studies that supported their versatility. In regard to the synthetic aspect, attention was focused mostly on cycloaddition reactions, rather than as ligands for organometallic sandwich complexes. Since the first synthesis of fulvene by Thiele in 1900 to this day only two methods that could be defined as C-H functionalization were described – glioxylation of pentafulvenes catalysed by ytterbium or aluminium compounds and palladium catalysed arylation of fulvenes. The aim of this study was to develop and optimise a novel method of C-H functionalization of pentafulvenes leading to derivatives containing acetylene and polyyne moiety. Both mechanochemical, solvent-free activation as well as catalyst-free approaches in solution were tested. The results of the aforementioned study provided the procedure that gives monosubstituted alkynyl derivatives of pentafulvenes which have been characterised by NMR, IR and Raman spectroscopy, as well as HRMS and in some cases X-ray single crystal diffraction.

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Use of Lawesson and Woollins reagent to synthesize indolizines

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Indolizines, planar bicyclic aromatic compounds with fused five- and six-membered rings featuring nitrogen at the ring junction, are valued in medicinal chemistry, optoelectronics, and material sciences. Their electron-rich structure and distinct aromaticity make them versatile for functionalization. Lawesson's reagent (LR) and Woollins' reagent (WR), widely utilized for thionation and selenation of carbonyls, respectively,¹ remain underexplored in the context of indolizine synthesis and elimination reactions.^{2,3} This study investigates the mechanism of a reaction employing LR for the direct synthesis of indolizines and proposes a predictive framework for using WR in similar transformations. These findings could pave the way for novel indolizine-based applications.



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Evaluation of Electronic Delocalization in Iminobora-Benzene and Iminobora-Cyclobutadiene Isomers

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Carbomers, proposed by Chauvin, are extended molecules formed by inserting acetylene into each bond, preserving symmetry and delocalization.¹ Replacing acetylene with isoelectronic boron-nitrogen analogues (iminobore) led to iminobore-benzene and iminobore-cyclobutadiene as inorganic analogues of carbo-benzene and carbo-cyclobutadiene.³ The main objective of the study is to analyze how the orientation of the nitrogen and boron atoms in iminobore, within the iminobore-benzene and imino-cyclobutadiene isomers, influence electronic delocalization and reactivity (Figure 1). The difference in electronegativity between nitrogen and boron atoms is critical in determining the electronic behavior of these compounds.



Figure 1. Structural association of the carbo-benzene (left) and carbo cyclobutadiene (right) isomers.

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1,2,3-Triarylazulenes as precursors of azulene-embedded PAHs

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Recently, there has been increasing interest in non-alternant PAHs (polycyclic aromatic hydrocarbons) for organic materials.¹ Among non-alternant compounds, azulene-containing π -scaffolds are particularly important molecules.² PAHs containing azulene moiety show properties like biradical character³ or NIR absorption.⁴ However, general synthetic methodologies leading to such molecules are still limited and there is a need of development in this area.

Here we show studies on the Scholl-type oxidation of a series of precursors aiming for synthesis of fully conjugated azulene-embedded PAHs (Scheme 1).⁵ Surprisingly, we discovered that 1,2,3-triphenyl precursors undergo migration a phenyl group under oxidizing conditions leading to azulen-1(8a*H*)-ones (I). However, the gradual replacement of phenyl groups to 2-pyrenyl groups gives partially (II) or fully conjugated PAHs (III). In out opinion, this work significantly contribute to the design of synthetic routes leading to azulene-embedded PAHs.



Scheme 1. Examples of Scholl-type oxidation of azulene-containing precursors.

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1,3-Azulenylen-butadiynylene macrocycles

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Organic molecules with azulene-containing π -scaffolds might possess interesting redox and photochemical properties due to their ability to stabilize both negative and positive charges.[1] While azulene-containing polyaromatic hvdrocarbons have been intensively studied in recent years,[1,2] shape-persistent macrocycles with azulene structures embedded in conjugated unexplored. The π-systems remain self-assembly potential of acetylene-based macrocycles[3] suggests that their azulene analogues could exhibit intriguing properties e.g. due to non-covalent π -interactions between adjacent molecules. Here, we present the synthesis, characterization,



photochemical, and electrochemical studies of a series of 1,3-azulenylen-butadiynylen macrocycles. These compounds were obtained according to previously published method involving Eglinton homocoupling of a diethynyl precursor under pseudo-high dilution conditions.[4]

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Doubly σ - and π -Aromatic Planar Pentacoordinate Boron Polyanions

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Planar hypercoordinate systems continue to challenge traditional bonding paradigms, with planar pentacoordinate boron (ppB) structures representing a particularly intriguing class. In this study, we report ten novel ppB systems stabilized within pentagonal frameworks composed of triels, pnictogens, or their combinations. These systems exhibit double aromaticity $(\sigma \text{ and } \pi)$, adhering to Hückel's $4n+2 \text{ rule}^2$, a hallmark of aromatic stability. The aromatic character is confirmed through computed diatropic ring currents under an applied magnetic field, indicating significant electron delocalization. To support experimental viability, we analyze the stability of these polyanions under solvation effects (PCM) and counterion interactions, revealing their persistence as global minima on the potential energy surface. These findings expand the understanding of planar hypercoordinate boron systems, highlighting their potential for practical realization and further advancing the design principles of hypercoordinate species stabilized by aromaticity.

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η^{5} -C₅H₅Fe(η^{5} -Li₅B₅H₅): A Novel Sandwich Complex with an Aromatic Boron Ring

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Certain small, naked boron clusters are connected to aromatic arenes as their π -electron delocalization patterns resemble those observed in traditional aromatic systems. However, their ability to form sandwich complexes with metals—a hallmark feature of arenes such as the cyclopentadienyl anion (C₅H₅⁻) and benzene (C₆H₆)—is significantly constrained. To date, only a single global minimum of such a complex, B₇Be₆B₇,¹ has been reported in the scientific literature. This limitation arises from the strong B-B bonds in boron clusters, which make the formation of sandwich structures energetically unfavorable.²

This study presents the first example of a cluster containing boron rings in a sandwich structure that is fully analogous to ferrocene. This complex, the global minimum on its potential energy surface, features an iron atom sandwiched between the pentagonal rings C5H5 and Li5B5H5 and exhibits Cs symmetry. A detailed chemical bonding analysis reveals that the complex can be described as $[C_5H_5]$ – $[Fe]^{2+}$ – $[Li_5B_5H_5]$ –, emphasizing its strong aromatic character derived from the local contributions of the C_5H_5 and $Li_5B_5H_5$ rings.

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Understanding the Kinetic Persistence of Ethynyl TIPS Substituted Azaheptacenes: Spin Delocalization Effects on Dimerization Energies

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Azaheptacenes are highly conjugated π -systems with desirable charge transport properties but can easily dimerize, which limits their application as optoelectronic materials. Steric protection (e.g., by installing ethynyl TIPS groups) is one way to prevent dimerization;¹ however, how the positions of ethynyl TIPS groups relate to the kinetic persistence of azaheptacenes remains poorly understood. In a recent work, Bunz et al. reported half-lives ($\tau_{1/2}$) of 6 h to 7 d for azaheptacene derivatives with ethynyl TIPS groups at varying positions.² We hypothesize that, besides steric effects, the positions of ethynyl TIPS groups also alter the degree of diradicaloid character and spin delocalization in the π -system, which can in turn affect dimerization energies. Computational investigations of model systems based on 2,4-, 2,5-, and 2,6-dimethylnaphthalenes suggest that increased spin delocalization can lead to stronger dimerization interactions by forming double "pancake bonds." These findings are applied to understand variations in the kinetic persistence of ethynyl TIPS-substituted azaheptacenes.

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PyClar, a software for the exhaustive generation of Clar structures of polycyclic aromatic compounds

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Clar structures are a model used to describe polycyclic aromatic systems, such as polycyclic aromatic hydrocarbons (PAHs).¹ These structures are particularly useful for understanding and visualizing electronic delocalization in molecules that satisfy the π -sextet rule. Clar structures allow predicting the relative stability of different PAHs as a function of the number and distribution of π -sextets.¹ Calculating the maximum number of independent π -sextets (aromatic rings) that can be distributed in a polycyclic molecule is a problem of the NP-Hard class for 2-connected planar graphs.²

In this work, we present PyClar, software to identify aromatic rings in polycyclic systems and generate viable Clar structures efficiently. Our work's originality lies in developing and applying a new set of transformations to molecular graphs to construct Clar structures as induced graphs. These graphs help distinguish equivalent Clar structures, guaranteeing the construction of unique structures.

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Global Minima Found in Gradually B,N-Substituted 6π-e[−] Benzene Isosteres

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Aromaticity is a fundamental concept in understanding the stability and electronic structure of cyclic compounds, playing a crucial role in fields ranging from organic chemistry to materials science. In this work, we explore how the substitution of carbon atoms in benzene and cyclopentadiene with boron and nitrogen, performed isoelectronically, influences aromaticity at the ω B97X-D/def2-TZVPP level. We analyzed both 4π - and 6π -electron systems in singlet and triplet states conducting a thorough conformational study using GLOMOS.¹ We calculated HOMA, NICS and MCI aromaticity indices² at the B3LYP/def2-TZVPP level using previously optimized geometries. As expected, aromaticity decreases from benzene to borazine and the same for other ring systems. However, we found that for 6-membered 6π -e⁻ rings, these structures correspond each to the global minima whereas this is not the case in other rings that even show imaginary frequencies. Our results emphasize the importance of strain effects in aromatic species.



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RATE CONSTANT CALCULATION FOR UNIMOLECULAR REACTIONS IN *EYRINGPY* BASED ON RRKM THEORY

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Evringpy¹ is a program that calculates rate constants in the gas phase and in solution, based on electronic structure. In systems where pressure plays a role, the unimolecular constant determined the rate can be usina Rice-Ramsperger-Kassel-Marcus (RRKM)² theory, which has not yet been developed in *Eyringpy*. This work implements a code to calculate the microcanonical rate constant in *Eyringpy*. To achieve this, the energy-dependent rate constant k(E)must be computed by summing the states of the transition complex and evaluating the density of states at a specific energy. This calculation is performed using the Stein-Rabinovitch direct counting method.

The validation was performed by comparing the results with the *Multiwell* program. The density of states of three compounds Ge_2H_6 , Coronene, and C_{60} was analyzed, evaluating the algorithm's efficiency as the degrees of freedom increased. Additionally, the thermal decomposition reaction of Ge_2H_6 was validated, obtaining the *k*(*E*) curve. The validations demonstrated consistency in trends and magnitude, highlighting the precision and reliability of the implemented algorithm.

The method was applied to the unimolecular decomposition of the perdeuterated benzene cation ($C_6D_6^+$) and indene, showing agreement between experimental and theoretical rate constants. This enabled the determination of energy thresholds for different reaction channels and highlighted the relevance of RRKM in studying complex aromatic compounds, which are significant in both chemical and astrophysical contexts³.

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Unveiling the Stability and Aromaticity of Pyrene and Its Polycyclic Isomers

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Pyrene, a well-known molecule for its diverse applications, including its use in dye manufacture, as a fluorescent probe, as an environmental pollution marker, and in biomedical research. Although it does not follow Hückel's rule, this compound exhibits remarkable stability due to its classification as a polycyclic aromatic hydrocarbon (PAH) that adheres to Clar's rule. The objective of this study was to determine the stability of pyrene in a restricted isomeric search, considering the large number of potential isomers. To this end, the restriction criteria were rings with 5, 6, or 7 atoms, no branching, sp² hybridization in all atoms and all structures were generated using SmilX and optimized via a DFT method with Gaussian16, employing the ω B97XD functional and the def2svp basis set. Under the restricted conditions, a total of 1,426 isomers were identified, of which 97.3% successfully converged. Among these, 95.9% represented distinct PAH systems. After the calculations, five isomers were found to be below 35 kcal/mol in relative energy. The most stable systems were pyrene, fluoranthene, acephenanthrylene, aceanthrylene, and cyclopenta[<code>ɑ]phenalene</code>. Pyrene exhibited the highest stability, which can be

attributed to its high molecular symmetry (D_{2h} point group), resulting in a null dipole moment and reduced electronic repulsion. In contrast, other isomers displayed lower stability due to less symmetrical geometries, such as C_{2v} , C_s , and C_1 , which led to uneven charge distributions and increased dipole moments. This study highlights the exceptional stability of pyrene compared to other PAH isomers, which stems from its symmetrical structure and adherence to Clar's rule. These findings underscore the importance of symmetry and aromaticity in determining the stability of polycyclic aromatic systems.



C₂H₇NO isomers in the interstellar space: A quantum theoretical study

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The discovery and identification of Complex organic molecules (COMs) in the interstellar medium (ISM) is an ongoing research area aimed at understanding the chemical processes that might relate to the origin of life on early Earth. N-bearing and O-bearing COMs have been pursued in the ISM; their relevance is related to their possible role as intermediates in the formation of the building blocks of life, such as the amino acids[1]. Ethanolamine, with a molecular formula C₂H₇NO is the only isomer of this family detected in the ISM[2]. By far, ethanolamine is the most complex amine detected in the ISM and is considered a precursor of phospholipids[3]. Herein, we explored the potential energy surface of the structural isomers of the C₂H₇NO system, employing a code based on the SMILES representation to identify all the structural isomers. We optimized the structures at MP2/aug-cc-pVTZ basis Subsequently, the the set. CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ level of theory was implemented to refine the energy.

We identified 1-aminoethanol as the most stable isomer in this family, which is a chiral molecule with seven different conformers in an energy range of 5 kcal/mol. The most stable conformer holds a dipole moment of 1.6 D, which makes it suitable for detection through rotational spectroscopy. This suggests that 1-aminoethanol is indeed waiting for its discovery in the ISM.

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Evaluation of magnetic resilience in deformed benzenes

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Aromatic systems, such as benzene, exhibit distinctive magnetic properties that allow their aromatic behavior to be evaluated under significant structural deformations. In this study, six distorted benzene structures, previously analyzed by Feixas *et al.*,¹ were studied, including in-plane and out-of-plane deformations. Magnetic properties were calculated at the DFT level using the PBE0 functional and def2-TZVP basis. The pseudo- π model² was applied to assess π contributions, while *Gaussian 09*,³ *GIMIC*,⁴ and *Aromagnetic*⁵ were used to obtain magnetic data. Visualizations of induced magnetic fields and currents were performed with *VisIt* and *ParaView*. The results confirm that, despite deformations, the structures retain their aromaticity. However, in the clamping and pyramid systems, changes in aromaticity were observed despite the carbon ring topology remaining intact. Induced magnetic currents also highlighted the resilience of aromatic behavior under extreme distortions.

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