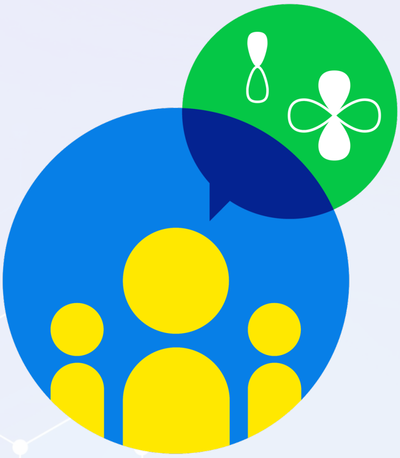

CBOND2024

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24–27 SEPTEMBER 2024

Book of Abstracts

4TH EUROPEAN SYMPOSIUM ON
CHEMICAL BONDING

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Keynote Speakers

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Charge-Shift Bonding: A Unique Class of Chemical Bonding

Sason Shaik,[a]
[a] Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 9190401, Israel
sason.shaik@gmail.com

Charge-shift bonds (CSB) constitute a unique class of bonds different than covalent/polar-covalent and ionic-bonds.[1] Bonding in CSB is not contributed by either the covalent or the ionic structures of the bond, *but rather by the resonance interaction between the structures*. The talk describes the CSB family alongside the traditional covalent and ionic families. **One of the highlights** of the talk is the charge-shift resonance energy of $^3O_2$, which is over 100 kcal/mol, and which constitutes the root cause of the persistence of this diradical in our atmosphere. The sluggish reactivity of $^3O_2$ is an existential manifestation of bonding. **Another highlight** is the potential of quantifying the charge-shift resonance energies of bonds from experimental data.

In summary, CSB is not limited to electron-pair bonds and is found in dative-bonds, coordinative-bonds, hypervalent-bonds, and odd-electron-bonds. *The distinction between covalent-bonds and CSBs is thus fundamental*, with a potential to bring about a Renaissance in the mental-map of the chemical bond, and to contribute to productive chemical diversity.

[1] S, Shaik, D, Danovich, P.C, Hiberty: *J. Chem. Phys.* **2022,** *157*, 090901 (pp. 1-44).

Redox Mysteries of Selenium Catalyzed Reduction of H_2O_2

Laura Orian
Dipartimento di Scienze Chimiche, Università degli Studi di Padova, via Marzolo 1,
35131 Padova, Italy
laura.orian@unipd.it

Selenium catalyzed H_2O_2 reduction is a multidisciplinary challenge.[1]

This process is a key-step in the mechanism of selenoproteins like glutathione peroxidase (GPx),[2] but, notably, after over five decades, the synthesis of efficient GPx mimics has proved to be a failure.[3] The interest on this reaction is not restricted to enzymology and medicinal chemistry. In fact, the emergence of selenium biochemistry coincided with the growing use of selenium in organic chemistry. One of the earliest studies on the catalytic potential of organoselenides dates back to 1973 and involves the activation of H_2O_2 in the form of peroxyseleninic acid.[4] Although this chemistry has been widely used, it is still debated, as recent breakthroughs have shown that Se(VI) (peroxyselenonic acid) rather than Se(IV) (peroxyseleninic acid) is the effective oxidizing agent formed upon H_2O_2 reduction.[5]

Complex and multifaceted, the redox chemistry of selenium remains poorly understood. Quantum chemistry calculations combined with activation strain analysis may indeed fill the lack of mechanistic understanding[6] and guide the design of novel compounds with optimized properties. Selected examples will be presented to illustrate the insight gained through different computational strategies.

[1] L. Orian, L. Flohé *Antioxidants*, **2021**, *10*, 1560.
[2] L. Flohé, S. Toppo, L. Orian *Free Rad. Biol. Med.,* **2022**, 187, 113.
[3] P. A. Nogara, M. Pereira, C. S. Oliveira, L. Orian, J. B. T. Rocha *New J. Chem.*, **2023**, *47*, 9959.
[4] H. J. Reich, I. L. Reich, J. M. Renga *J. Am. Chem. Soc.* **1973**, *95*, 5813.
[5] K. N. Sands, E. Mendoza Rengifo, G. N. George, I. J. Pickering, B. S. Gelfand, T. G. Back, *Angew. Chemie - Int. Ed.* **2020**, *59*, 4283.
[6] F. M. Bickelhaupt, K. N. Houk, *Angew. Chemie - Int. Ed.* **2017**, *56*, 10070.

Nucleophilic addition with computations: From the Felkin-Anh rule to the Grignard reaction

Odile Eisenstein [a,b] and Michele Cascella [b]

[a] ICGM Université de Montpellier, CNRS ENSCM Montpellier France
[b] Department of Chemistry and Hylleraas Center for Quantum Molecular Sciences,
University of Oslo, Norway
Odile.eisenstein@umontpellier.fr

The study of the Grignard reaction is part of our long-standing interest in the study of nucleophilic addition [1]. Many years ago, calculations could be performed using very simplified models of the reagents. These very simplified models of the chemical systems were successful in providing qualitative insights for many reactions [2]. Today, it is possible to model reactions while using realistic representations of the chemical species and methods that represent properly the thermodynamics and kinetics of complex systems. Thus, we have looked at the Grignard reaction in an attempt to provide insight into this reaction, which has remained elusive despite extensive studies since its discovery in 1900. We will present the arguments that lead us to believe that the Grignard reaction can occur via numerous parallel pathways[3,4] We now pursue this topic by trying to understand the role of additives such as LiCl[5].

References

[1] O. Eisenstein *Isr. J. Chem.* **2022**, 62, e202100138
[2] O. Eisenstein *Comptes Rend. Acad. Sciences* **2024,** 27, 5.
[3] R. M. Peltzer, O. Eisenstein, A. Nova, M. Cascella *J. Phys. Chem. B* **2017**, *121*, 4226.
[4] R. M. Peltzer, J. Gauss, O. Eisenstein, M. Cascella *J. Am. Chem. Soc.* **2020**, *142*, 2984.
[5] M. de Giovanetti, S. H. Hopen Eliasson, A. C. Castro, O. Eisenstein, M. Cascella *J. Am. Chem. Soc.* **2023**, *145*, 16305.
[6] M. de Giovanetti, S. H. Hopen Eliasson, S. L. Bore, O. Eisenstein, M. Cascella ChemRixv doi:10.26434/chemrxiv-2024-mxjqn

Quantum Chemistry and Computer Science: A Tightly Connected Parallel Development

Henry F. Schaefer III
University of Georgia, Athens, Georgia, United States
ccq@uga.edu

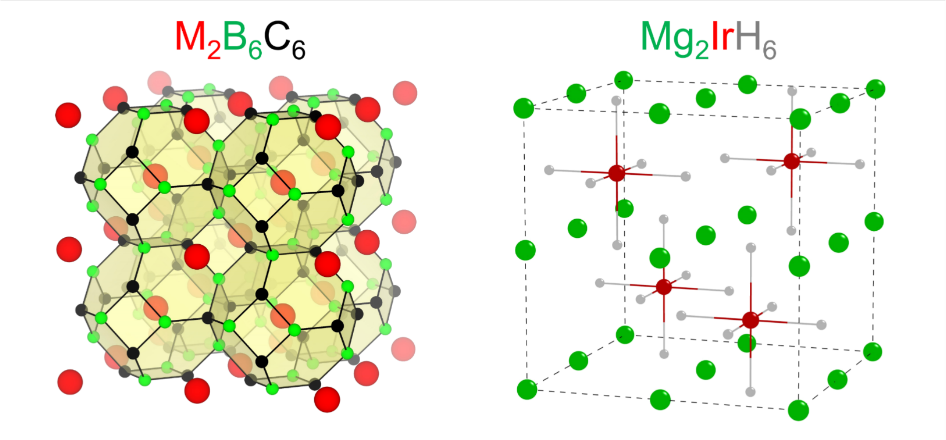
It is not widely recognized that the history of computer science drew very strongly on the development of quantum chemistry.

It will be shown that this symbiotic relationship continues to the present day.

Chemical Bonding in Predicted Superconductors

Eva Zurek[a]
[a] Department of Chemistry, University at Buffalo, State University of New York, Buffalo, USA
ezurek@buffalo.edu

The computational prediction of novel conventional superconductors has successfully unveiled numerous hydrides that have since been synthesized and their (often record-breaking) superconducting critical temperatures, T_cs, have been measured. Unfortunately, these compounds are only stable at pressures that approach those found in Earth's core. Therefore, theoreticians have turned their sights towards the prediction of light-element conventional superconductors that could be metastable at 1 atmosphere. In this talk, we describe the bonding and properties of some of the recently predicted phases from a chemistry perspective. Specifically, we describe binary-guest C-B clathrates, whose structures resemble some of the predicted high-pressure hydrides, and explain trends in their computed properties including Vickers hardness, T_c, and superconducting mechanism [1] (Figure, left). Moreover, we show why Mg_2IrH_6 is predicted to be a high temperature superconductor, but isotypic Ca_2IrH_6 is not [2] (Figure, right).



[1] N. Geng, K. P. Hilleke, L. Zhu, X. Wang, T. A. Strobel, T.A., E. Zurek, *J. Am. Chem. Soc.*, **2023**, *145*, 1696.

[2] X. Wang, W. Pickett, M. Hutcheon, R. Prasankumar, E. Zurek. *arXiv preprint,* **2024** *arXiv:2407.10889*.

Investigation of Chemical Bonding through (Conceptual) Density Functional Theory Based Quantities

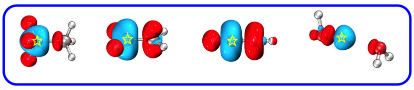
Frank De Proft,[a] Bin Wang,[a] Paul Geerlings,[a] Christian Van Alsenoy,[b] Farnaz Heidar-Zadeh,[c] Paul W. Ayers,[d] Charlotte Titeca,[a,e] and Thomas-C. Jagau[e]

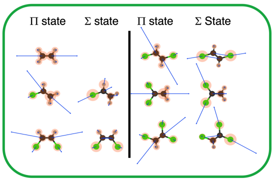
[a] Research Group of General Chemistry (ALGC), Vrije Universiteit Brussel (VUB), Pleinlaan 2, B-1050 Brussels, Belgium.
[b] Chemistry Department, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium.
[c] Department of Chemistry, Queen's University, Kingston, ON, Canada.
[d] Department of Chemistry and Chemical Biology, Mc Master University, Hamilton, ON, Canada.
[e] Division of Quantum Chemistry and Physical Chemistry, KU Leuven, Leuven, Belgium
fdeprof@vub.be

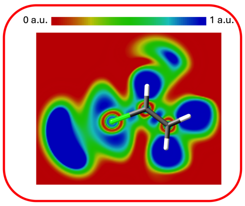
In this lecture, I will discuss some our recent work on the use of electron density based chemical concepts to investigate chemical bonding.

First, attention will be focused on the so-called linear response function,[1,2] the second derivative of the energy of a system with respect to its external potential, introduced within the framework of conceptual DFT[1] and its connection to bonding.[2]

Next, a conceptual study of electronic resonances will be presented, more specifically highlighting dissociative electron attachment (DEA). Central are anionic resonances, which can be investigated through stabilization by adding an artificial potential to the Hamiltonian, enabling a bound-state treatment. In our work, this stabilization is achieved upon scaling the nuclear charges and estimates for the negative electron affinities are obtained through extrapolation. We have extended this method to the study of nuclear forces, electronic and nuclear Fukui functions and electron localization functions (ELF),[3,4] to get insight into the influence of the unbound electron on the molecular bonds. Also, the ELFs are combined with Berlin's binding functions of the neutral compounds. This promising methodology allows for accurate predictions of when and where DEA will happen in the molecules studied and provides more insight into the process.[4]







[1] B. Wang, P. Geerlings, C. Van Alsenoy, F. Heidar-Zadeh, P. W. Ayers, F. De Proft, *J. Chem. Theory Comput.* **2023**, *19*, 3223.
[2] (a) P. Geerlings, F. De Proft, W. Langenaeker, *Chem. Rev.* **2003**, *103*, 1793. (b) S. Liu, *Conceptual Density Functional Theory: Towards a New Chemical Reactivity Theory*; Wiley-VCH, Germany, 2022.
[3] C. Titeca, F. De Proft, T.-C. Jagau, *J. Chem. Phys.* **2022**, *157*, 214106.
[4] C. Titeca, T.-C. Jagau, F. De Proft, *J. Chem. Phys.* **2024**, *160*, 064115.

Excited state (anti)aromaticity in organic molecules

Miquel Solà[a]

[a] *Institute of Computational Chemistry and Catalysis and Department of Chemistry, University of Girona, E-17003 Girona, Catalonia, Spain.*
miquel.sola@udg.edu

From the discovery of benzene in 1825 to the present day, the concept of aromaticity has experienced several revolutions that have fueled the interest of both theoretical and experimental chemists. The discovery of new aromatic compounds is not about to slow down. One of the major breakthroughs of the last decades in the field of aromaticity took place in 2001, when the first all-metal clusters, MAl_4^- (M = Li, Na, or Cu), were characterized. Metals clusters have σ-, π-, and δ-, or even ϕ-aromaticity together with multifold and conflicting aromaticity.[1] Very recently, several works[2] have highlighted the importance of aromaticity in excited states. Aromaticity is essential to understand and predict many photochemical processes. This renaissance of excited state aromaticity represents another important revolution in the field of aromaticity. Although aromaticity is a property usually linked to the ground state of stable molecules, certain excited states are unquestionably aromatic. This is especially the case of organic molecules in their lowest-lying triplet states whose aromaticity follows the $4n$ Baird rule.[3] In this work, we investigate the aromaticity of [*N*]annulenes in their triplet state,[4] we show how Clar's rule can be extended to the lowest-lying triplet excited states of certain polycyclic aromatic molecules,[5] and we briefly analyze the aromaticity of $^{3}n\pi^{*}$ excited states.[6]

Different types of aromaticity have been defined in the last years

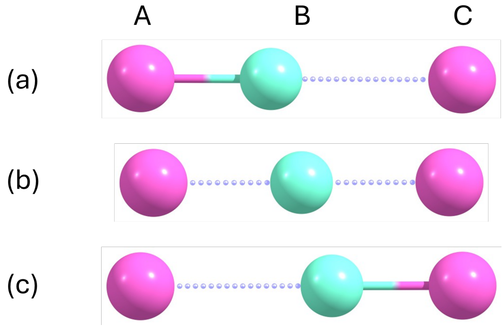
References

[1] A. Boldyrev, L. Wang, *Chem. Rev.* **2005**, *105*, 3716.
[2] (a) H. Ottosson, *Nat. Chem.* **2012**, *4*, 969; (b) M. Rosenberg, C. Dahlstrand, K. Kilså and H. Ottosson, *Chem. Rev.* **2014**, *114*, 5379; (c) J. Yan, T. Slanina, J. Bergman and H. Ottosson, *Chem. Eur. J.* **2023**, *29*, e202203748.
[3] N. C. Baird, *J. Am. Chem. Soc.* **1972**, *94*, 4941; L. J. Karas, J. I. Wu, *Nat. Chem.* **2022**, *14*, 723; M. Solà, *Nat. Chem.* **2022**, *14*, 585.
[4] L. A. M. Van Nyvel, M. Alonso and M. Solà, submitted for publication.
[5] R. Ayub, O. El Bakouri, K. Jorner, M. Solà and H. Ottosson, *J. Org. Chem.* **2017**, *82*, 6327; R. Pino, R. Báez-Grez and M. Solà, *Phys. Chem. Chem. Phys.*, **2021**, *23*, 13574.
[6] N. Proos Vedin, S. Escayola, S. Radenković, M. Solà and H. Ottosson. *J. Phys. Chem. A,* **2024**, *128*, 4493.

Probing the continuum of covalent contributions to noncovalent interactions

Catharine Esterhuysen,[a]
[a] Department of Chemistry and Polymer Science, Stellenbosch University, Private Bag
X1, Matieland, Stellenbosch, 7608, South Africa
ce@sun.ac.za

Although hydrogen and halogen bonds were both originally described as primarily electrostatic in origin, many studies have subsequently shown that there may be a large covalent contribution that aids in stabilising the interactions,[1,2] although this has been contested in the case of hydrogen bonding.[3] The covalency of the interaction may also vary; consider the system shown in the figure below where bond A–B may be regarded as changing from covalent in (a) to noncovalent in (c), with (b) corresponding to an intermediate case where large covalent contributions lead to a strong, symmetric complex. Within this continuum, the nature and properties of the bond/interaction change. In addition, the covalent contribution to the interaction may be influenced by a variety of factors, such as the type of interaction (e.g. halogen vs hydrogen bond), the nature of the donor and acceptor molecules involved and the substituents on both of these that may affect the electronic properties of the interacting atoms. In this presentation, the role of these factors on the covalent nature of a range of different hydrogen and halogen bonds is probed using a variety of computational methods.



[1] S. W. Robinson, C. L. Mustoe, N. G. White, A. Brown, A. L. Thompson, P. Kennepohl, P. D. Beer, *J. Am. Chem. Soc.*, **2015**, *137*, 499.
[2] A. Shahi, E. Arunan, *Phys.Chem.Chem.Phys.*, **2014**, *16*, 22935.
[3] A. J. Stone, *J. Phys. Chem. A*, **2017**, *121*, 1531.

The Basis Electronic Activity of Chemical Systems. A Theory of Bond Reactivity

Alejandro Toro-Labbé, Francisca J. Benítez, Soledad Gutiérrez-Oliva, Bárbara Herrera
Laboratorio de Química Teórica Computacional (QTC), Facultad de Química y de Farmacia,
Pontificia universidad Católica de Chile.
atola@uc.cl

We introduce the Basis Electronic Activity (BEA) of molecular systems, it corresponds to the significant, although non-reactive, vibrationally induced electronic activity that takes place in any molecular system. Although the molecule's BEA is composed by equal number of local contributions as the vibrational degrees of freedom, our results indicate that only stretching modes contribute to it. To account for this electronic activity, a new descriptor, the Bond Electronic Flux (BEF), is introduced. The BEF combined with the force constant of the potential well hosting the electronic activity give rise to the Effective Bond Reactivity index (EBR), that turns out to be the first DFT-based descriptor that simultaneously accounts for structural and electronic effects. Besides quantifying the bond reactivity, EBR provides a basis to compare the reactivities of bonds inserted in different chemical environments and paves the way to exert selective control to enhance or inhibit their reactivities. The new concepts formulated here and the associated computational tools are illustrated with the characterization of the BEA of a set of representative molecules. In all cases the BEFs follow a linear pattern whose slopes indicate the intensity of the electronic activity and quantify the reactivity of chemical bonds.

References

[1] F.J. Benítez, S. Gutiérrez-Oliva, B. Herrera, A. Toro-Labbé: The Basis Electronic Activity of Chemical Systems. A Theory of Bond Reactivity, *J. Phys. Chem. A* 2024, in press. (https://doi.org/10.1021/acs.jpca.4c00359)

Planar Hypercoordinate Atoms

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

It is fascinating to explore and understand the chemical structure of molecules. The chemical structure is determined not only by the elements that make up the molecule but also by how those atoms are connected and arranged in space. Thus, the chemical structure and the connection between atoms—the chemical bond—are intimately related. Any change in the spatial arrangement of the nuclei will alter the nature of the chemical bond, and vice versa. Of course, there are established rules for determining molecular structure, particularly in organic molecules. But ask introductory or even graduate chemistry students to provide an example of a pentacoordinate carbon molecule or a planar tetracoordinate carbon. The likelihood of getting an example is close to zero. However, the chemical literature is full of examples of such non-classical carbon molecules, and this extends to any main group element. In this talk, the structure and bonding of some non-classical carbon (planar tetra- or hexacoordinate carbon), boron (fluxional boron clusters), and other main group element structures with even planar pentadecacoordinate atoms will be discussed.

Invited Speakers

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Understanding and modelling catalytic reactions with valence bond diagrams

Benoît BRAÏDA[a]
[a] Laboratoire de Chimie Théorique, Sorbonne Université, Paris
benoit.braida@sorbonne-universite.fr

Valence Bond diagrams, first introduced in the early 1980's by Sason S. Shaik,[1] is a very powerful conceptual tool to rationalize trends in reactivity. It has been successfully applied along the years to many families of chemical reactions, up to enzymology.[2, 3]

In this contribution, we will show that Valence Bond Diagrams reveal the decisive role for secondary coordination sphere nucleophiles on methane C–H activation. *Ab initio* DFT calculations indicate that nucleophiles can significantly reduce enthalpic barriers to methane C–H bond activation, and following Valence bond diagram analysis suggests the formation of a two-center three electron bond as the origin of the catalytic nucleophile effect. A predictive model for methane activation catalysis follows, leading to the proposition that proteins with hydrophobic active sites, available strong nucleophiles, and hydrogen bond donors can be attractive targets for engineering novel methane functionalizing enzymes.[4] If time remains, a second original application of Valence Bond diagrams on Frustrated Lewis Pairs systems, which have emerged as a new type of metal-free catalysts for reversible H_2 activation, will also be presented.

References

[1] Shaik, S. S., What happens to molecules as they react - a valence bond approach to reactivity. *Journal of the American Chemical Society* **1981,** *103* (13), 3692-3701.

[2] Shaik, S.; Shurki, A., Valence bond diagrams and chemical reactivity. *Angewandte Chemie-International Edition* **1999,** *38* (5), 586-625.

[3] Lai, W.; Li, C.; Chen, H.; Shaik, S., Hydrogen-Abstraction Reactivity Patterns from A to Y: The Valence Bond Way. *Angewandte Chemie-International Edition* **2012,** *51* (23), 5556-5578.

[4] Anderson, M. E.; Braida, B.; Hiberty, P. C.; Cundari, T. R., Revealing a Decisive Role for Secondary Coordination Sphere Nucleophiles on Methane Activation. *Journal of the American Chemical Society* **2020,** *142* (6), 3125-3131.

Ring currents in metal complexes and dyes

Remco W.A. Havenith
[Stratingh Institute for Chemistry and Zernike Institute for Advanced Materials, University of Groningen, 9747 AG Groningen, The Netherlands
[Ghent Quantum Chemistry Group, Department of Chemistry, Ghent University, B-9000 Gent, Belgium
r.w.a.havenith@rug.nl

The induced current density provides insight in the aromaticity and electronic structure of molecules. In this presentation, I shall present situations in which the ring current signature helps in understanding the properties of molecules. One example is in the distinction between (non-)innocent ligands in transition metal complexes (Figure 1) and one is the odd/even effect in cyanine dyes. The observed ring current patterns will be linked to a chemical interpretation using valence bond theory and to reactivity patterns.

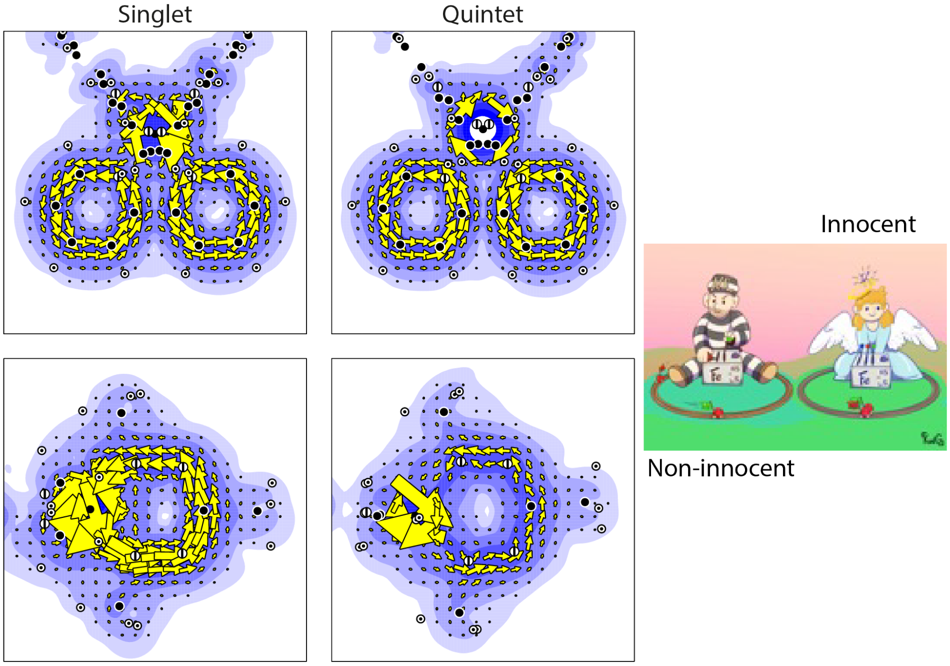
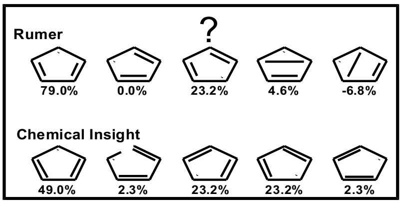


Figure 1. Plots of the induced π current density for different spin states for an innocent and non-innocent ligand.

Improved VB Structures and the ability to better Understand and Design Your Own Molecule?

Avital Shurki,[a] Eden Rubanovich,[a] Sorav Roy[a]
[a] The Institute for Drug Research, The Hebrew University of Jerusalem, Jerusalem, Israel
avital.shurki@mail.huji.ac.il

Valence bond (VB) theory has always been an important conceptual tool for chemists. The distinct abilities of VB stem from the description of the wavefunction as a mixture of well-defined electronic configurations, which are easily interpreted as chemical structures. Still, the choice of the set of structures is an important step and can either hamper or facilitate the overall insight. Classical VB commonly uses Rumer rules to derive a lineally independent set of structures. These rules, however, are restrictive and the resulting sets of structures may sometimes not be optimal for the insight of interest. A newly developed method that constructs linearly independent sets of spin functions with enhanced chemical insight for classical VB will be presented.[1] The method keeps the advantage of the VB structures being meaningful but is also flexible with structure choice and chemical insight that can be controlled and improved. The method imposes fewer restrictions than those imposed by Rumer rules and, hence, overcomes Rumer sets' weaknesses and results in sets which are better chemically adapted to the studied systems.[1]



Furthermore, the VB structures being easily interpreted enable the prediction of their behavior due to external effects such as external electric fields and, as shown in recent years, to control reactivity. The second part of the presentation will extend these ideas and a new concept for molecular design using similar ideas will be presented. Our ability to understand and control different structural, spectral as well as reactivity properties of small molecules will be shown. These include for example the ability to control the stability of certain isomers, blue or red shifts in different spectra as well as proton/electron affinities.

[1] S. Roy and A. Shurki, *J. Chem. Theory Comput.*, **2023**, *19* 3102.

Superconducting Radical Pancakes

Martin Rahm[a], Alvaro Lobato[a], Fernando Izquierdo-Ruiz[a]
[a] Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg, Sweden.

martin.rahm@chalmers.se

This presentation outlines computational crystal structure prediction of stable salts that exhibit an unusual flexibility in terms of oxidation states. Particular attention is given to a phase where charged radicals stack equidistantly in one dimension. Equidistant stacking of radicals is unusual and expected to be unstable due to spontaneous symmetry breaking, Peierls, or Jahn-Teller distortion. This rare configuration facilitates an exceptionally high density of states at the Fermi level, and leads to predictions of extreme metallicity, a potential negative temperature coefficient of resistivity, and the possibility of rare π-band superconductivity under ambient pressure conditions. The multi-centre intermolecular interaction responsible for these properties is reminiscent of so-called pancake bonding and can be explained using molecular orbital theory. Band-engineering strategies are outlined that open for potential design of organic conductors and superconductors.

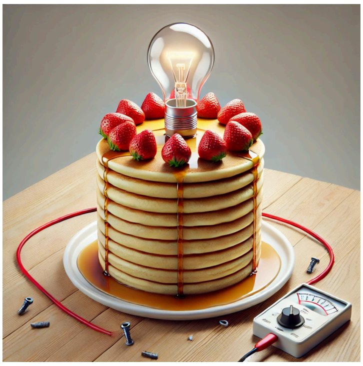


Figure 1. Pancake bonding is one label for the kind of interaction that enables (quasi) one-dimensional stacking of charged radicals in the phases to be presented.

Pushing Quantum Chemistry Accuracy: from Many-body Dispersion Corrected Density Functional Theory to Quantum Computing

Jean-Philip Piquemal[a]

[a] Laboratoire de Chimie Théorique, Sorbonne Université (UMR 7616), Paris, France
jean-philip.piquemal@sorbonne-universite.fr

In the context of the design of datasets for machine learning, pushing the quantum chemistry accuracy is paramount as obtaining the correct bonding patterns across the chemical space is a daunting task. To explore fast strategies for obtaining accurate electronic structure data, we recently extended our proposed Deep Learning-aided many-body dispersion (DNN-MBD) model[1] to quadrupole polarizability (Q) terms using a generalized Random Phase Approximation (RPA) formalism, thus enabling the inclusion of van der Waals contributions beyond dipole.[2] The resulting DNN-MBDQ model only relies on ab initio-derived quantities as the introduced quadrupole polarizabilities are recursively retrieved from dipole ones, in turn modeled via the Tkatchenko–Scheffler method. A transferable and efficient deep-neuronal network (DNN) provides atom-in-molecule volumes, while a single range-separation parameter is used to couple the model to Density Functional Theory (DFT). The DNN-MBQ-corrected functionals reach chemical accuracy while exhibiting lower errors compared to their dipole-only counterparts. In my talk, I will also discuss the advances in quantum computing for chemistry to push further accuracy. Indeed, hybrid quantum-classical Adaptive Variational Quantum Eigensolvers (VQE) hold the potential to outperform classical computing for simulating quantum many-body systems. However, their practical implementation on current quantum processing units (QPUs) faces challenges in measuring a polynomially scaling number of observables during the operator selection so as to optimise a high-dimensional and noisy cost function. In this talk, I will present an extension of the ADAPT-VQE strategy denoted Overlap-ADAPT-VQE.[3] The algorithm iteratively generates a compact quantum approximation of a classical target wave function through a quasi-greedy procedure that maximises, at each iteration, the overlap of the current iterate with the target. Finally, I will present some initial results[4] obtained with our in-house GPU-accelerated quantum emulator to perform full adaptive-VQE simulations at Full-CI accuracy.

[1] P. P. Poier, T. Jaffrelot Inizan, O. Adjoua, L. Lagardère, J.-P. Piquemal, *J. Phys. Chem. Lett.* **2022**, *13*, 4381.
[2] P. P. Poier, L. Lagardère, J.-P. Piquemal, *J. Phys. Chem. Lett.* **2023**, *14*, 1609.
[3] C. Feniou, M. Hassan, D. Traoré, E. Giner, Y. Maday, J.-P. Piquemal, *Commun. Phys.* **2023**, *6*, 192.

Defining the Chemical Bond: A Puzzle in Philosophy of Chemistry and in Chemical Education

Sebastian Kozuch
Ben-Gurion University of the Negev, Beer Sheva, Israel
kozuch@bgu.ac.il

The chemical bond is the biggest paradigm in chemistry. But at the same it is notoriously complex to define it. Under the assumption that knowing what we do not know makes better scientists, I will succinctly describe the three main approaches to define the bond (energetic, structural, and orbital), their advantages and especially their failures. These (rather obvious) definitions, including their theoretical, practical and even philosophical issues, should be taught to advanced undergraduate chemistry students as an essential introduction to the chemical bond module of quantum chemistry courses. It is a controversial topic due to the lack of consensus in the chemical bond community over this heavily disputed topic and the conflicting pedagogical approach; however, and maybe because of this controversy, the teaching, researching, and the philosophical exploration of the definitions of the chemical bond including their open questions and challenges can be positively instructive.[1]

[1] S. Kozuch, **2024**, DOI 10.26434/chemrxiv-2024-jq0dj.

Weak CH...O hydrogen bonds in zeolites – organic structure directing agents: identification and thermal stability

Tzonka Mineva,[a] Karima Ata, Bruno Alonso[a,a]
[a] ICGM, UMR 5253 CNRS-ENSCM-UM, 34293 Montpellier cedex 5, France.

e-mail: tzonka.mineva@umontpellier.fr

The important role of weak hydrogen bonds (HBs) has been well recognized for directing structures and functions in organic chemistry and biology, but is often overlooked in materials studies. Aiming at a better understanding of the intermolecular interactions at the interfaces between inorganic zeolite frameworks (a family of microporous crystals) and organic structure directing agents, OSDA, (often organoammonium cations, used in zeolite syntheses), the formation of weak HBs was recently identified and analyzed (see Figure 1) [1,2].

In this talk we will present a theoretical methodology for identification of these weak HBs, the driving forces that promote their formation and the life time of HBs at room temperatures for a series of zeolites with different OSDAs and zeolite framework types. From the DFT optimized models, we have retrieved various geometrical parameters (H...O and C...O distances, etc.) that demonstrated the directionality of CH..O HBs, which allowed us distinguishing them from the van der Waals interactions. The HBs life-time at room temperature was evaluated from Born-Oppenheimer Molecular Dynamics simulations. The energy contribution of these HBs will be also compared to the known Coulomb electrostatic and van der Waals interactions in OSDA-zeolite assemblies.

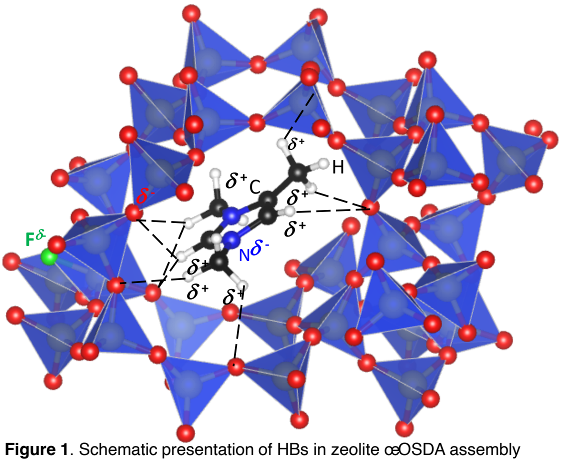


Figure 1. Schematic presentation of HBs in zeolite œOSDA assembly

[1] T. Mineva, E. Dib, A. Gaje, H. Petitjean, J.-L. Bantignies and B. Alonso, *ChemPhysChem*, **2020**, *21*, 149.
[2] S. Al-Nahari, K. Ata, T. Mineva and B. Alonso, *ChemistrySelect*, **2021**, 6, 9728-9734.

Shaping singularities in a high-temperature superconductor

Sebastian Riis Thomsen,[a] Maarten Goesten,[a]
[a] Department of Chemistry, Aarhus, Denmark
maarten.goesten@chem.au.dk

The superconducting critical temperature of H_3S ranks among the highest measured, at 203 K. This impressive value stems from a singularity in the electronic density-of-states, itself induced by a flat-band region that consists of saddle points.[1] The peak sits right at the Fermi level, so that it gives rise to a giant electron-phonon coupling constant. In this work, we show how atomic orbital interactions and space group symmetry work in concert to shape the singularity. The body-centered cubic Brillouin Zone offers a unique 2D hypersurface in reciprocal space: fully connecting squares with two different high-symmetry points at the corners, Γ and H, and a third one in the center, N. Orbital mixing leads to the collapse of fully connected 1D saddle point lines around the square centers, due to a symmetry-enforced s-p energy inversion between Γ and H. The saddle-point states are invariably nonbonding, which explains the unconventionally weak response of the superconductor's critical temperature to pressure. Although H_3S appears to be a unique case, the theory shows how it is possible to engineer flat bands and singularities in 3D lattices through symmetry considerations.

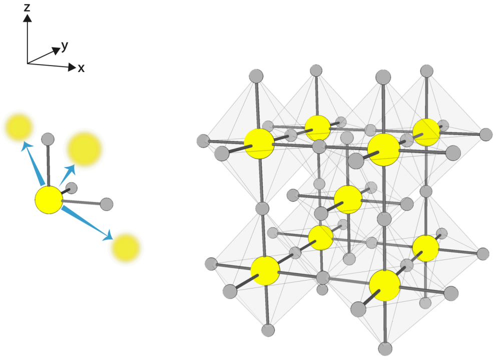


Figure: body-centered cubic (bcc) lattice of high-pressure, high-temperature superconductor H_3S (yellow, S; grey; H).

[1] Bernstein, N et al., *Phys. Rev. B,* **2013**, *91*, 06051

The Best of Two Quantum Worlds: LOBSTER

Richard Dronskowski
RWTH Aachen University, Aachen, Germany
drons@HAL9000.ac.rwth-aachen.de

By fundamental, traditional, and also technical reasons, molecular quantum chemistry (focusing on the wave function, atomic-orbital approach) and computational materials physics & science (focusing on the density, plane-wave approach) have completely diverged from each other, with serious consequences (even damage) to the latter communities, that is, a certain lack of chemical understanding in terms of atoms and bonds. It is possible, however, to bridge the gap and provide molecular quantum-chemical tools to the computational solid-state scientist, namely by an exact (unitary) transformation between the two grossly differing quantum-mechanical representations, technically performed by the LOBSTER package.[1] This strategy will be demonstrated by various molecular and solid-state chemical-bonding problems, in particular using Crystal Orbital Hamilton Populations (COHP),[2] Crystal Orbital Bond Indices (COBI),[3] accurate wave-function-based instead of density-based charges (e.g., Löwdin),[4] automatic fragment-orbital analysis (FMO),[5] etc., all from plane waves. Taken together these tools have allowed to characterize the bonding in Ge-Sb-Te phase-change materials as being electron-rich multicenter-type.[6,7]

[1] S. Maintz, V. L. Deringer, A. L. Tchougréeff, R. Dronskowski, *J. Comput. Chem.* **2016**, *37*, 1030; R. Nelson, C. Ertural, J. George, V. L. Deringer, G. Hautier, R. Dronskowski, *J. Comput. Chem.* **2020**, *41*, 1931.
[2] R. Dronskowski, P. E. Blöchl, *J. Phys. Chem.* **1993**, *97*, 8617.
[3] P. C. Müller, C. Ertural, J. Hempelmann, R. Dronskowski, *J. Phys. Chem. C* **2021**, *125*, 7959.
[4] C. Ertural, S. Steinberg, R. Dronskowski, *RSC Advances* **2019**, *9*, 29821.
[5] P. C. Müller, N. Schmit, L. Sann, S. Steinberg, R. Dronskowski, *Inorg. Chem.*, DOI: 10.1021/acs.inorgchem.4c01024
[6] J. Hempelmann, P. C. Müller, C. Ertural, R. Dronskowski, *Angew. Chem. Int. Ed.* **2022**, e202115778.
[7] P. C. Müller, S. R. Elliott, R. Dronskowski, R. O. Jones, *J. Phys. Cond. Matter* **2024**, *36*, 325706.

Surface-mediated reactivity: chemistry on and with the surface

Ralf Tonner-Zech
Wilhelm-Ostwald Institut für Physikalische und Theoretische Chemie, Leipzig University, Leipzig, Germany, ralf.tonner@uni-leipzig.de

Molecular chemistry usually does not care about surfaces. Surface science often deals with small inorganic molecules (e.g., CO, N_2) targeting catalysis or focuses on chemically unreactive larger adsorbates (e.g., porphyrins). We explored the surface chemistry of organic molecules on semiconductor surfaces in the last decade and discovered many surprising and unexpected reactivity.

Using computational approaches ranging from density functional theory (DFT) over molecular dynamics (AIMD) approaches up to modern bonding analysis approaches using energy decomposition analysis for extended systems (pEDA),[1] we could unveil and quantitatively support the previously proposed concept of the surface as molecular reagent.[2] Nuclear substitution, cycloadditions and dispersion-dominated reactivity have been discovered for organic reactants on silicon surfaces.[3] But the surface can also serve as more or less innocent platform for organic reactivity as in the bottom-up construction of hybrid organic-inorganic interfaces in intense collaboration with experimental UHV-based surface science approaches.[4]

In all investigations, we start from understanding experimental data and thrive to achieve predictive computational results based on quantitative analysis leading to helpful concepts for the challenging and often unintuitive organic chemistry on and with the surface.

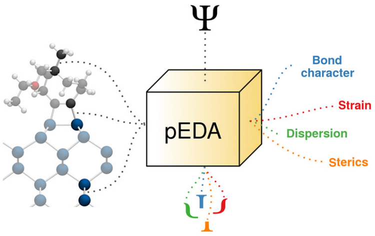


Figure. Quantitative bonding analysis helps disentangle organic reactivity on surfaces.

[1] M. Raupach, R. Tonner, *J. Chem. Phys.* **2015**, *142*, 194105.
[2] M. A. Filler, S. F. Bent, *Prog. Surf. Sci.* **2003**, *73*, 1-56
[3] (a) L. Pecher, R. Tonner, *WIREs Comput. Mol. Sci.* **2019**, *9*, e1401; (b) F. Thiemann, H. Weiske, R. Tonner-Zech, Eur. J. Org. Chem. 2024, DOI: 10.1002/ejoc.202400560.
[4] T. Glaser, J. Meinecke, L. Freund, C. Langer, J. N. Luy, R. Tonner, U. Koert, M. Dürr, *Chem. Eur. J.* **2021**, *27*, 8082-8087.

Computational Modeling of Cooperative Small Molecule Activation by Apolar / Weakly Polar Bonds

P. Belanzoni,[a] D. Sorbelli,[b] and L. Belpassi[c]

[a] *Department of Chemistry, Biology and Biotechnology, University of Perugia, Italy*
[b] *Pritzker School of Molecular Engineering, University of Chicago, USA*
[c] *CNR Institute of Chemical Science and Technologies "Giulio Natta" (CNR-SCITEC), Perugia, Italy*
paola.belanzoni@unipg.it

Activation of small molecules (CO_2, N_2, O_2, H_2, N_2O, SO_2, CH_4, NH_3, H_2O…) is a fundamental topic in chemical research and cooperativity is a valuable strategy for the fine-tuning of its efficiency. In this contribution, recent and remarkable examples in which homogeneous activation processes are mediated by apolar E-E or weakly polar M-M' bonds are illustrated. [1,2] Experimental breakthroughs are analysed from a theoretical perspective, which highlights how a simple yet unbiased computational modeling of cooperative small molecules activation can easily provide a consistent picture of the relationship between bond nature/polarity and reactivity and ultimately lead to experiments driven "by design". Using highly relevant coinage metal-aluminyl M-M' (M = Cu, Ag, Au; M' = Al) compounds as case studies (Figure 1), [3,4] application of computational tools, such as Energy Decomposition Analysis (EDA), Natural Orbitals for Chemical Valence (NOCV), Charge Displacement analysis (CD) and Activation Strain Model (ASM), commonly available in the most popular program packages, is showcased to allow to inductively extract general principles and knowledge on an entire class of processes from single cases, sometimes resulting in unveiling pitfalls in adopting too simple descriptors for monitoring the activation processes.

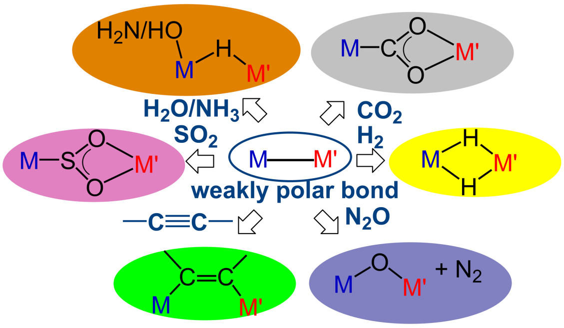


Figure 1 Small molecules reactivity with heterobimetallic M-M' (M = Cu, Ag, Au; M' = Al) compounds featuring a weakly polar bond.

1. J. Hicks, A. Mansikkamäki, P. Vasko, J.M. Goicoechea, S. Aldridge, *Nat. Chem.* **2019**, *11*, 237-241.
2. J. Li, M. Hermann, G. Frenking, C. Jones, *Angew. Chem., Int. Ed.* **2012**, *51*, 8611-8614.
3. D. Sorbelli, L. Belpassi, P. Belanzoni, *J. Am. Chem. Soc.* **2021**, *143*, 14433-14437.
4. D. Sorbelli, L. Belpassi, P. Belanzoni, *Chem. Eur. J.* **2023**, *29*, e202203584.

Many-Electron Probability Density Analysis as Tool for Chemical Bonding Analysis

Arne Lüchow[a]
[a] RWTH Aachen University, Aachen, Germany
luechow@pc.rwth-aachen.de

It is demonstrated that a topological analysis of the many-electron probability density $|\Psi|^2$ (PDA) is possible and useful for the analysis of chemical bonding. The stationary points of the probability density can be visualized in ordinary space. Additionally, basins, or attractor domains, are defined for the maxima of the probability density analogously to the 3D analysis of the electron density in the quantum theory of atoms in molecules (QTAIM). The PDA yields surprisingly comprehensive first-principles insight into chemical bonding and structure. In contrast to the Bader analysis, the maxima of the many-electron probability density yield already substantial insight into chemical bonding as bonding electron pairs or lone pairs are retrieved.[1,2]

The topological analysis of the probability density is based on the efficient sampling of $|\Psi|^2$ with quantum Monte Carlo methods and is possible with arbitrary wave functions. The favorable scaling allows analysis of fairly large molecules. The maximum electron structures and their spin coupling is in close agreement with valence bond results where the VB weights correspond to the weights obtained by integration of the probability density basins.[3] Covalent two-center two-electron bonding is obtained as electron exchange and thus characterized by the corresponding stationary point of the probability density. The analysis of aromaticity,[4] charge shift bonding,[5] and the stabilization of propellane is discussed.

[1] A. Lüchow, *J. Comput. Chem.* **2014**, *35*, 854.
[2] M. A. Heuer, L. Reuter, A. Lüchow, *Molecules* **2021**, *26*, 911.
[3] L. Reuter, A. Lüchow*, Phys. Chem. Chem. Phys.* **2020**, *22*, 25892.
[4] L. Reuter, A. Lüchow, *Nat. Commun.* **2021**, *12*, 4820.
[5] M. V. Heinz, L. Reuter, A. Lüchow, *Chem. Sci.* **2024**, *15*, 8820.

Breaking X-H Bonds via PCET: The Role of Metal-Metal Bonds in Dinuclear Au(II) Complexes

Johannes E. M. N. Klein[a]
[a] Molecular Inorganic Chemistry, Stratingh Institute for Chemistry, Faculty of Science and Engineering, University of Groningen, Nijenborgh 3, 9747 AG Groningen/NL
j.e.m.n.klein@rug.nl

The oxidative homolytic X-H bond cleavage with dinuclear Au(II) complexes featuring O-based ligands will be presented.[1] Such reactivity remains scarce for gold complexes[2] and the role of the Au-Au bond[3] present in these complexes and their involvement in the oxidation process of X-H bonds will be the focus. The mechanistic factors that control PCET for the cleavage of C(sp^3)-H and ArO-H bonds will be compared for both mononuclear[4] and dinuclear gold complexes.[1]

References:

[1] K. M. Hess, I. F. Leach, L. Wijtenhorst, H. Lee, J. E. M. N. Klein, *Angew. Chem. Int. Ed.* **2024**, *63*, e202318916

[2] S. Engbers, J. E. M. N. Klein, *ChemPhysChem* **2022**, e202200475.

[3] For a representative review on dinuclear gold complexes see: (a) A. A. Mohamed, H. E. Abdou, J. P. Fackler Jr, *Coord. Chem. Rev.* **2010**, *254*, 1253-1259; For representative recent reviews reporting transition metal complexes featuring M-M bonds in catalysis see: (b) K. P. Kornecki, J. F. Berry, D. C. Powers, T. Ritter in Progress in Inorganic Chemistry, Vol. 58 (Ed.: K. D. Karlin), Wiley, Hoboken, 2014, pp. 225– 302; (c) I. G. Powers, C. Uyeda, *ACS Catal.* **2016**, *7*, 936-958; (c) C. M. Farley, C. Uyeda, *Trends in Chemistry* **2019**, *1*, 497-509.

[4] a) S. Engbers, I. F. Leach, R. W. A. Havenith, J. E. M. N. Klein, *Chem. Eur. J.* **2022**, *28*, e202200599; b) M. Lovisari, A. R. McDonald, *Inorg. Chem.* **2020**, *59*, 3659; c) M. Lovisari, R. Gericke, B. Twamley, A. R. McDonald, *Inorg. Chem.* **2021**, *60*, 15610.

Valence bond components and one-electron densities

Stéphane Humbel, [a] Denis Hagebaum Reignier, [a] Julien Racine[a]

[a] iSm2, Aix-Marseille Université, Marseille, France
stephane.humbel@univ-amu.fr

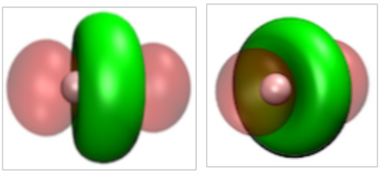


Figure 1: Electronic density difference between a covalent wavefunction and the quasi-classical state. In green the density is larger than in the quasi-classic state.

The components (covalent and Ionics) of the Valence Bond wavefunction of the ground state of 2-electron (single and double) bonds (H_2 and $H_2C=CH_2$) provide a significant and complementary description. Their contributions to the bond are easily shown through their contributions to the energy. But what about their contributions to the one-electron density? And how do they compare to HF and CAS wavefunctions. The one electron density operator will be applied to the components of the VB wavefunction (1), and the density there-obtained will be compared to that of the quasi-classical state that describes the uncoupled electrons of the 2-electron bond (2). Such a quasi-classic state is the non-bonded reference.[1]

$$\Psi_{VBSCF} = C_{cov}(|a\bar{b}| + |b\bar{a}|) + C_{ion}(|a\bar{a}| + |b\bar{b}|) \tag{1}$$

$$\left\langle |a\bar{b}| \middle| \hat{\rho}(r) \middle| |a\bar{b}| \right\rangle = \quad a(r)^2 \; + \; b(r)^2 \tag{2}$$

The electronic density difference (edd) can be plotted with a color code (green for edd >0 vs red for edd <0) (Figure 1) The singlet coupling of the two electron corresponds to an increase of the electron density between the atoms (“bond formation”).

We shall compare as well the ionics, the VB, the HF and the CAS wavefunctions’ densities to that of this quasi-classical unbonded state (2). The presentation will be inspired by our recent paper.[2]

[1] K. Hendrickx, B . Braida, P. Bultinck, P.C. Hiberty, *Comput. Theor. Chem.* **2015,** *1053,* 180.
[2] D. Hagebaum-Reignier, J. Racine, S. Humbel ,J. Chem. Phys., **2022,** *156*, 204310.

X-ray fitted wavefunctions and their information contents

Simon Grabowsky
University of Bern, Department of Chemistry, Biochemistry and Pharmaceutical Sciences, Bern, Switzerland
simon.grabowsky@unibe.ch

Chemical bonding has traditionally been analysed from experimental single-crystal X-ray diffraction data by extracting the total electron-density distribution.[1] However, modern approaches of quantum crystallography go beyond the electron density by fitting molecular orbital coefficients to the experimental structure factors while simultaneously minimising the quantum-mechanical energy of the system.[2] X-ray constrained wavefunction (XCW) fitting is the most widely used of such techniques today.[3] Once an experimentally modified wavefunction is available, the usual set of complementary bonding descriptors can be applied to interpret chemical bonding.[4]

In this presentation, I want to discuss the information contents of such "chimera" wavefunctions, especially with respect to electron correlation, polarization in the crystal field, and relativistic effects.[5] Furthermore, how reliable and reproducible is such information relative to the experimental noise and error that are also included in the fitted wavefunction?[6]

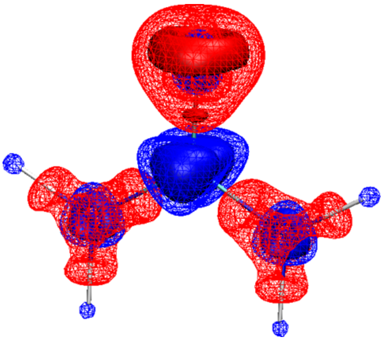


Fig. Difference electron density representing the experimentally reconstructed effect of electron correlation for the urea molecule.

[1] D. Stalke, *Chem. Eur. J.*, **2011**, *17*, 9264.
[2] S. Grabowsky, A. Genoni, H.-B. Bürgi, *Chem. Sci.*, **2017**, *8*, 4159.
[3] M. L. Davidson, S. Grabowsky, D. Jayatilaka, *Acta Cryst. B*, **2022**, *78*, 312.
[4] S. Grabowsky (ed.), Complementary Bonding Analysis, deGruyter STEM, Berlin, **2021**.
[5] E. Hupf, F. Kleemiss, T. Borrmann, R. Pal, J. M. Krzeszczakowska, M. Woińska, D. Jayatilaka, A. Genoni, S. Grabowsky, *J. Chem. Phys.*, **2023**, *158*, 124103.
[6] M. L. Davidson, S. Grabowsky, D. Jayatilaka, *Acta Cryst. B*, **2022**, *78*, 397.

To use or not to use references: that is the question

Ángel Martín Pendás,[a] Evelio Francisco[a]
[a] Universidad de Oviedo, Oviedo, Spain
ampendas@uniovi.es

The use of reference states permeates the theory of chemical bonding. For some researchers, a chemical bond cannot be defined without due consideration of an initial state. For others, chemical bonds are intrinsic features of molecules, and it should be possible to define and characterize them without further reference. We recall that in the standard paradigm of chemical bonds being driven by kinetic energy lowering internal and external reference biases and analyze several other cases. We advocate that the use of real space analyses are as reference-less as possible[1].

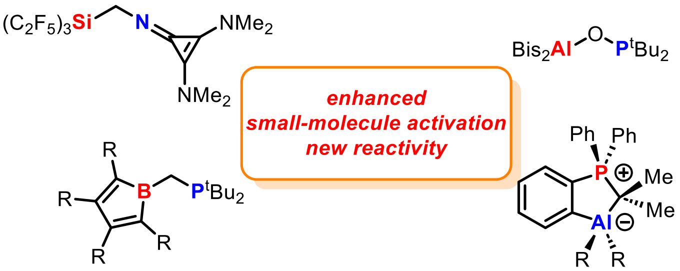
[1] Á. Martín Pendás, E. Francisco, Nat. Commun (2022)13:3327

Understanding and Enhancing the Reactivity of Frustrated Lewis Pairs

Israel Fernández
Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040-Madrid, Spain
israel@quim.ucm.es

Frustrated Lewis pairs (FLPs) are species typically composed of a pair of sterically encumbered Lewis acid and Lewis base, which prevents the formation of a classical donor-acceptor bond between both centers. Due to this particular bonding situation, these compounds exhibit a unique reactivity as a result of the cooperative action of the FLP antagonists. Thus, FLPs have emerged as potential metal-free catalysts able to, among other processes, activate small molecules (H_2, CO, CO_2, SO_2, N_2O, etc.).

Over the last years, we have investigated the factors controlling the cooperative action of the Lewis antagonists by means of state-of-the-art computational methods.[1] Additionally, we aimed to predict new FLPs with enhanced reactivity for the activation of small molecules. In this talk, we will discuss our recent findings on how (anti)aromaticity can enhance the reactivity of geminal FLPs.[2] Furthermore, we will show novel intramolecular systems with improved or new reactivity (such as carbon dioxide reduction, benzidine-like rearrangement, and catalytic ammonia transfer) focusing on the bonding and the ultimate factors governing their reactivity.[3]



[1] For a recent review, see: I. Fernández, I. *Chem. Commun.* **2022**, *58*, 4931.

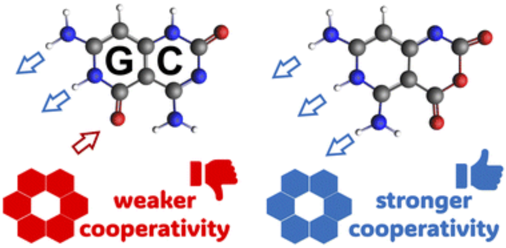
[2] a) J. J. Cabrera-Trujillo, I. Fernández, *Chem. Commun.* **2019**, *55*, 675; b) J. J. Cabrera-Trujillo, I. Fernández, *Chem. Commun.* **2022**, *55*, 6801.

[3] a) L. Wickemeyer, N. Aders, A. Mix, B. Neumann, H. G. Stammler, J. J. Cabrera-Trujillo, I. Fernández, N. W. Mitzel, *Chem. Sci.* **2022**, *13*, 8088; b) L. Wickemeyer, I. Fernández, çB. Neumann, H. G. Stammler, N. W. Mitzel, *Angew. Chem. Int. Ed.* **2023**, *62*, e202216943; c) F. Krämer, J. Paradies, I. Fernández, F. Breher, *Nat. Chem.* **2024**, *16*, 63; d) D. González-Pinardo, F. Krämer, F. Breher, I. Fernández, *ChemistryEurope* **2024**, e202400020.

Strengthened Cooperativity of DNA-based Cyclic Hydrogen-Bonded Macrocycles

Jordi Poater,[a,b] David Almacellas,[a] Pascal Vermeeren,[c] Célia Fonseca Guerra[c]
[a] Universitat de Barcelona, Barcelona, Spain
[b] ICREA, Barcelona, Spain
[c] Vrije Universiteit Amsterdam, Amsterdam, The Netherlands
jordi.poater@ub.edu

Cooperative effects cause extra stabilization of hydrogen-bonded supramolecular systems. In this work we have designed hydrogen-bonded rosettes derived from a guanine–cytosine Janus-type motif with the aim of finding a monomer that enhances the synergy of supramolecular systems.[1] For this, relativistic dispersion-corrected density functional theory computations have been performed. Our proposal involves a monomer with three hydrogen-bonds pointing in the same direction, which translates into shorter bonds, stronger donor–acceptor interactions, and more attractive electrostatic interactions, thus giving rise to rosettes with strengthened cooperativity. This newly designed rosette has triple the cooperativity found for the naturally occurring guanine quadruplex. On the other hand, we have also proven that introducing rigid linear π-conjugated acetylene linkers into a supramolecular building block hampers the cooperative self-assembly of hydrogen-bonded macrocycles.[2,3] This effect originates from the electron abstracting capability of the linker and becomes amplified when the size of the linker increases.



[1] D. Almacellas, C. Fonseca Guerra, J. Poater, *Org. Biomol. Chem.*, **2023**, *21*, 8403.

[2] D. Almacellas, S.C.C. van der Lubbe, A.A. Grosch, I. Tsagri, P. Vermeeren, C. Fonseca Guerra, J. Poater, *Eur. J. Org. Chem.*, **2024**, *27*, e202301164.

[3] D. Almacellas, S.C.C. van der Lubbe, A.A. Grosch, I. Tsagri, P. Vermeeren, J. Poater, C. Fonseca Guerra, *ChemistryEurope*, **2024**, *2*, e202300036.

Innovation and Opportunities in Developing Molecules for the Agrochemical and Defense Industries: From Theory to Technology

Teodorico C. Ramalho [a,b]
[a] Chemistry Department. Federal University of Lavras, Lavras, MG, Brazil
[b] Center for Basic and Applied Research, University Hradec Kralove, Hradec Kralove, Czech Republic.
E-mail teo@dqi.ufla.br

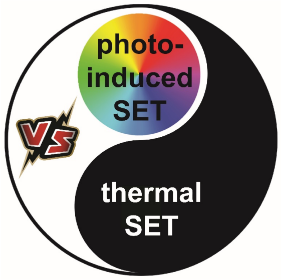
Recently, the growing population has led to the increase of world food production and the intense use of pesticides in agriculture. This current outlook is still aggravated because organophousphorus (OP) compounds, which are potent EPSP synthase inhibitors, are the most widely used pesticides. Accordingly, their persistent overuse worldwide has caused accumulation of their compounds in food, fertile land or waster water runoff [1]. Thus, it is also important to mention that the action of OP compounds, as toxic compounds and acetylcholinesterase (AChE) inhibitors, is well known. In this line, the high frequency of contamination by pesticides suggests the need for more active and selective agrochemicals. To address this, molecular modeling studies employing molecular dynamics simulations and DFT techniques were conducted to understand the interaction and the action mechanism of OP compounds with the both wild type enzyme and Gly96Ala mutant EPSP synthase. Additionally, we investigated the reaction mechanism of the natural substrate. Understanding the reaction mechanism provides valuable insights into how these compounds function within biological systems. In this context, EDA, AIM and NBO analyses were carried out and consistently revealed the presence of a significant interaction along the P-O bond [2]. Our findings highlight key factors for the design of new and more selective agrochemicals. Understanding the nature and occurrence of these interactions is essential for optimizing agents that can prevent the formation of bonds between organophosphorus compounds and AChE. This optimization could significantly enhance the effectiveness of treatments for poisoning by compounds in this category.

[1] J.B.G. Filho, T.C. Ramalho, M.C. Pereira, L.C.A. Oliveira*. Appl. Catal. B.*, **2021**, *285*, 119774.
[2] G.A. Andolpho, T.C. Ramalho. *J. Comput. Chem.* **2024**, *45*, 1303.
[3] L. de Azevedo Santos, T.C. Ramalho, T.A. Hamlin, F.M. Bickelhaupt. *Chem. Eur. J.* **2023**, *29*, e202203791.

A Radical Approach to Main-group Chemistry

J. Chris Slootweg[a]
[a] Affiliation, Amsterdam, the Netherlands
j.c.slootweg@uva.nl

Archetypal phosphine/borane frustrated Lewis pairs are famed for their ability to activate small molecules. The mechanism is generally believed to result from two-electron processes, however, detection of radical intermediates was recently reported indicating that single-electron transfer to generate frustrated radical pairs could also play an important role. These highly reactive radical species lie significantly higher in energy, which prompted our investigation into their formation. In this lecture, I will evidence that the classical phosphine/borane combinations $PMes_3$/BCF and P*t*Bu_3/BCF (BCF = $B(C_6F_5)_3$) both form an electron donor-acceptor (charge-transfer) complex, which undergoes visible light induced single-electron transfer (SET) to form the corresponding highly reactive radical ion pairs.[1,2] This study has resulted, for the first time, in the EPR detection of both radicals in the radical ion pairs. Subsequently, I will illustrate that by tuning the properties of the Lewis acid and base pair, the energy required for SET can be reduced to be thermally accessible.[3,4] These findings provide important insight for understanding and controlling the generation of highly reactive radical pairs by photoinduced or thermal single-electron transfer, which we are currently applying to the design of new radical ion pairs tuned for exploiting radical reactivity.[5]



[1] F. Holtrop, A. R. Jupp, N. P. van Leest, M. Paradiz Dominguez, R. M. Williams, A. M. Brouwer, B. de Bruin, A. W. Ehlers, J. C. Slootweg, *Chem. Eur. J.* **2020**, *26*, 9005

[2] F. Holtrop, A. R. Jupp, B. J. Kooij, N. P. van Leest, B. de Bruin, J. C. Slootweg, *Angew. Chem. Int. Ed.* **2020**, *59*, 22210

[3] L. J. C. van der Zee, S. Pahar, E. Richards, R. Melen, J. C. Slootweg, *Chem. Rev.* **2023**, *123*, 9653

[4] L. J. C. van der Zee, J. Hofman, J. M. van Gaalen, J. C. Slootweg, *Chem. Soc. Rev.* **2024**, *53*, 4862

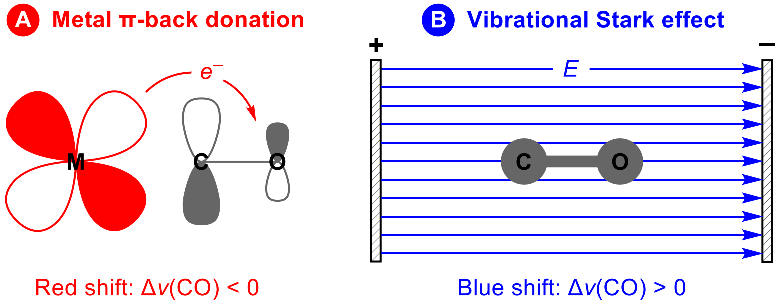
[5] C. Helling, L. J. C. van der Zee, J. Hofman, S. Mathew, M. Nieger, J. C. Slootweg, *Angew. Chem. Int. Ed.* **2023**, e202313397

Deconvoluting the role of electrostatics in metal carbonyl bonding

Mercedes Alonso,[a] Ruben Van Lommel,[a] Nil Roig,[a,b] Adrian B. Chaplin[b]
[a] Algemene Chemie (ALGC), Vrije Universiteit Brussel (VUB), Brussels, Belgium
[b] Department of Chemistry, University of Warwick, Coventry, United Kingdom
mercedes.alonso.giner@vub.be

An unexpected blue shift in the carbonyl stretching was recently observed across a homologous series of metal pybox carbonyl compounds. This shift was attributed to conformational changes in the tridentate ligands, which modify the magnitude of the local external electric field projected along the M–CO bond.[1] This phenomenon, known as the internal Stark effect, plays a significant role in metal-carbonyl interactions but is frequently overlooked in conventional descriptions.

To broadly assess the role of electrostatics in metal carbonyl bonding, we investigated a comprehensive dataset of 66 pincer carbonyl metal complexes using density functional theory methods. We propose a conceptual model that explains the observed trends in carbonyl stretching frequencies by combining the extent of π-backbonding, as determined through energy decomposition analysis with natural orbitals for chemical valence, and the dipole moment of the pincer–metal fragment, which serves as a proxy for the local electric field projected onto the ligand.



[1] G. L. Parker, R. Van Lommel, N. Roig, M. Alonso, A. B. Chaplin, *Chem. Eur. J.*, **2022**, *28*, e202202283.
[2] N. Roig, R. Van Lommel, M. Alonso, A. B. Chaplin, *Organometallics*, submitted.

Contributed Talks

CBOND2024
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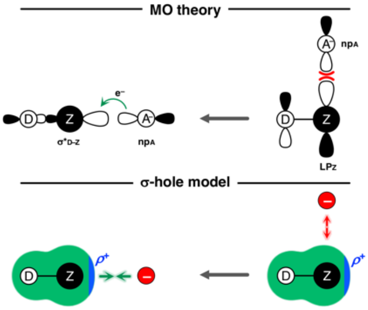
Intermolecular Covalent Interactions

Lucas de Azevedo Santos,[a] F. Matthias Bickelhaupt[a]
[a] Vrije Universiteit Amsterdam, Amsterdam, The Netherlands
l.deazevedosantos@vu.nl

Pnictogen (PnB), chalcogen (ChB), halogen (XB), and hydrogen (HB) bonds are intermolecular interactions of the type $D_mZ\cdots A$, where Z = Pn, Ch, X, H.[1,2] Typically, the σ-hole model is invoked to rationalize the unexpected attraction between two partially negatively charged atoms and the geometry of these intermolecular interactions.[3] This model posits that the $D_mZ\cdots A$ complexes are bound and linear due to a Coulombic attraction between a positive electrostatic potential on the molecular surface of the bond donor (D_mZ) and the negative, point charge-like bond acceptor (A). We show how this treatment of atoms and molecules is oversimplified and unphysical.[4] Not the Coulombic interactions, but the steric Pauli repulsion is the driving force preventing the bending of the bond acceptor away from $D–Z\cdots A$ linearity. In fact, the Coulombic interactions favor (not oppose) bending. The cohesion in these interactions furthermore receives a major contribution from covalent, donor–acceptor interactions, which are responsible for the well-known redshift in the D–Z bond stretching frequency.[5]

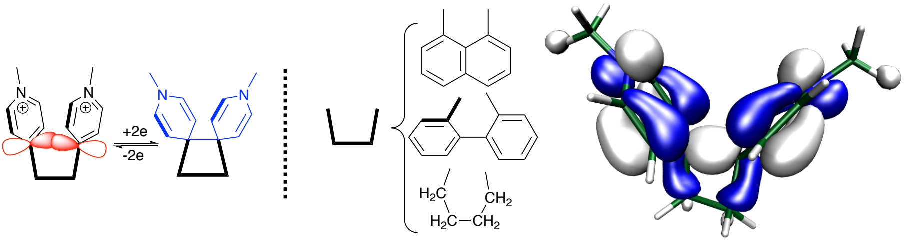


[1] L. de Azevedo Santos, T. A. Hamlin, T. C. Ramalho, F. M. Bickelhaupt, *Phys. Chem. Chem. Phys.*, **2021**, *23*,13842.
[2] L. de Azevedo Santos, S. C. C. van der Lubbe, T. A. Hamlin, T. C. Ramalho, F.M. Bickelhaupt, *ChemistryOpen*, **2021**, *10*, 391.
[3] J. S. Murray, P. Politzer, *ChemPhysChem*, **2021**, *22*, 1201.
[4] L. de Azevedo Santos, T. C. Ramalho, T. A. Hamlin, F. M. Bickelhaupt, *Chem. Eur. J.*, **2023**, *29*, e202203791.
[5] L. de Azevedo Santos, P. Vermeeren, F. M. Bickelhaupt, C. Fonseca Guerra, *J. Am. Chem. Soc.*, **2024**, *accepted*.

Electron Chemistry

Philippe P Lainé,[a] Éric Brémond,[a] Magdaléna Hromadová,[b]
[a] Université Paris Cité, CNRS, ITODYS, 15 rue J-A de Baïf, F-75013, Paris, France
[b] J. Heyrovský Institute of Physical Chemistry of the Czech Academy of Sciences,
Dolejškova 3, 182 23 Prague, Czech Republic
Philippe.laine@u-paris.fr

It's about using an electron flow as the sole reagent of a CC bond formation, with the substrate being a binding empty molecular orbital such as the LUMO of a host assembly. In fact, this LUMO results here from the sigma-type overlap of $2p_z$ atomic orbitals associated with vicinal electrophilic centers C(γ) of pyridiniums in close van der Waals contact ($d(C\gamma\text{-}C\gamma) < 3.40$ Å; Figure). Upon two-electron acceptance, the LUMO transforms into an emerging elongated carbon-carbon covalent bond (HOMO), which is an integral new part of the thus reduced host assembly. We have therefore called this host a "structronic"[1,2] entity, based on a neologism derived from "structure" and "electronics", and the electrochemically formed bond is regarded as a "two-electron reservoir", insofar as reoxidation of the loaded assembly leads to specific cleavage of this reservoir bond (localized electro-chemistry). Due to the fact that this LUMO strides over the redox-innocent scaffold that positions the pyridiniums (through-space interaction; see Figure), whether the framework is rigid,[1] semi-rigid[3] or even flexible,[4] it is referred to as a supra-molecular orbital (supra-MO). The structronic paradigm is characterized by a two-way inversion of standard potentials (one-step two-electron processes).[1]



[1] A. Gosset, L. Wilbraham, Š. Nováková Lachmanová, R. Sokolová, G. Dupeyre, F. Tuyèras, P. Ochsenbein, C. Perruchot, H.-P. Jacquot de Rouville, H. Randriamahazaka, L. Pospíšil, I. Ciofini, M. Hromadová, P. P. Lainé. *J. Am. Chem. Soc.*, **2020**, *142*, 5162.
[2] M. Hromadová, P. P. Lainé. *Curr. Opin. Electrochem.*, **2022**, *34*, 100996.
[3] A. Gosset, Š. Nováková Lachmanová, S. Cherraben, G. Bertho, J. Forté, C. Perruchot, H.-P. Jacquot de Rouville, L. Pospíšil, M. Hromadová, É. Brémond, P. P. Lainé. *Chem. Eur. J.*, **2021**, *27*, 17889.
[4] E. Vaněčková, M. Dahmane, J. Forté, S. Cherraben, X.-Q. Pham, R. Sokolová, É. Brémond, M. Hromadová, P. P. Lainé. *Angew. Chem. Int. Ed.* **2024**, e202406299.

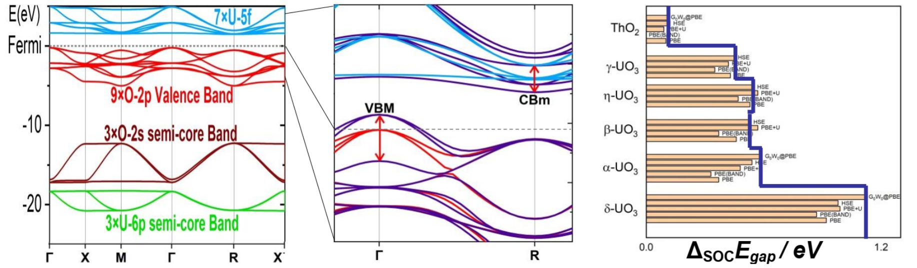
Bonding in δ-[UO_3]: Huge O-2p Spin-Orbit Splitting Observed

('Pushing from below' by the U-6p^6-pseudo-core)

W.H.Eugen SCHWARZ,[a,b] Shi-ru WEI,[b] Jun LI[b,c]

[a] Chemistry Dept., University, Siegen, Germany; [b] Chemistry Dept., Tsinghua University, Beijing, China; [c] Chemistry Dept., SUSTech, Shenzhen, China
eugen.schwarz@uni-siegen.de; wsr20@mails.tsinghua.edu.cn; junli@tsinghua.edu.cn

U forms many oxidic phases. [UO_3] is a major industrial product. Most [UO_3] phases contain chains of short-bonded 'axial' (O≡U≡) uranyl groups, connected by 4 to 7 longer 'equatorial' coordination bonds, while the δ-phase has 6 equivalent U($\dot{-}$O)$_6$ bonds at octahedral symmetry.[1,2] A common assumption is that relativistic effects, at least spin-orbit coupling (SOC), need NOT be considered concerning the band structure around the Fermi level, since the valence band is of non-relativistic O-2p character, and the 'small' SOC of the U-5f6d valence shell is even partially quenched by the asymmetric ligand field. The estimated band gaps of the different UO_3 phases in the literature deviate more or less from the observations.[1-3] We found unexpected SOC effects of up to 1 eV on the gap above the O-2p band of δ-[UO_3], where O_h symmetry at U allows for particularly strong U-6p mixing into the O-2p valence band, causing an observable effect at Γ and R points. Our findings for [UO_3] solids match Autschbach's finding[4] for U-complexes, where multi-center bonding, the inverse trans influence, and the pushing from below (PFB) by valence-active core-shells couple synergically. Here is the band structure of δ-[UO_3]:



U-6p interacts with O-2s & O-2p. **O-2p valence is pushed up, even higher by U-6p SOC.** **From DFT to Green-Function: reliably large SOC for O-2p !**

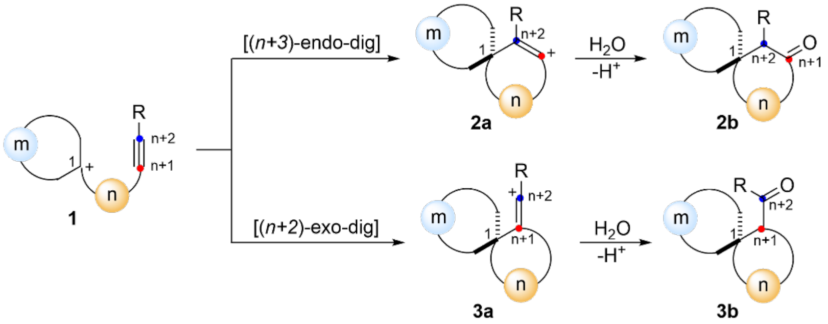
[1] N A Brincat, S C Parker, M Molinari, G C Allen, M T Storr, Inorg Chem, 2014, 53, 12253.
[2] J J Ma, C B Zhang, R Qiu, P Zhang, B Ao, B T Wang, Phys Rev B, 2021, 104, 174103.
[3] H He, D A Anderson, D D Allred, K D Rector, J Phys Chem C, 2013, 117, 16540.
[4] L C Motta, J Autschbach, Nat Commun, 2023, 14, 4307.

Selectivity and solvent effects in alkyne cationic cyclizations

Abel de Cózar,[a,b]* Ana Arrieta,[a] Fernando P. Cossío[a]*
[a] Departamento de Química Orgánica I, University of the Basque Country (UPV/EHU)
and Donostia International Physics Center (DIPC), P. Manuel Lardizabal 3, Donostia/
San Sebastián, Spain.
[b] IKERBASQUE, Basque Foundation for Science, E-48013, Bilbao, Spain
abel.decozar@ehu.eus

The electrophylic cyclization between alkynes and transient carbocations has emerged as an efficient tool for the selective synthesis of bicomplex structures such as steroids.[1] However, it has been reported that the regiochemistry of this reaction depends on the terminal or internal position of the triple bond: reactants possessing terminal alkynyl groups lead to six-membered rings, whereas internal alkynes yield five-membered rings through 6-endo-dig and 5-exo-dig electrophilic cyclizations, respectively (Scheme 1).

In this communication we will present our computational analysis performed in order to find the driving forces that dominate the cyclization through cationic intermediates in model and polycyclic systems.[2] Additionally, the relevance of solvent molecules in the reactivity of alkyne cations towards cyclization or elimination reactions has been also analyzed.[3]



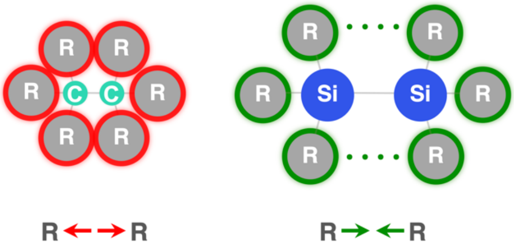
Scheme 1

[1] O. García-Pedrero, F. Rodriguez, *Chem. Commun.*, **2022**, *58*, 1089.
[2] A. de Cózar, A. Arrieta, F. P. Cossío, *Chem. Eur. J.*, **2023**, *29*, e202204028.
[3] A. de Cózar, A. Arrieta, F. P. Cossío, *Eur. J. Org. Chem.,* submittted**.**

Nature and Strength of Group-14 A–A' Bonds

Daniela Rodrigues Silva,[a] Eva Blokker,[a] Trevor A. Hamlin,[a] F. Matthias Bickelhaupt[a]
[a] Department of Chemistry and Pharmaceutical Sciences, Vrije Universiteit Amsterdam
d.rodriguessilva@vu.nl

We have quantum chemically investigated the nature and stability of C–C and Si–Si bonds in $R_3A–AR_3$ (A = C, Si; R_3 = H_3, Me_3, Me_2Ph, $MePh_2$, Ph_3, *t*-Bu_3) within the framework of Kohn-Sham molecular orbital (KS-MO) theory. We address the questions of why the $H_3Si–SiH_3$ bond is intrinsically longer and weaker than the $H_3C–CH_3$ bond as well as why the systematic increase of steric bulk of the substituents R strengths the $R_3Si–SiR_3$ bond whereas weakens the $R_3C–CR_3$ bond. Our bonding analyses show that the H3Si–SiH3 bond is weaker than the $H_3C–CH_3$ bond due to the increase in effective atom size of Si compared to C and, thus, the increase in Pauli repulsion. Furthermore, the different behaviour upon increasing the steric bulk of the substituents stems from the interplay of (Pauli) repulsive and (dispersion) attractive steric mechanisms (see below). Further increasing the size of the group-14 atoms from C–C and Si–Si to Ge–Ge, Sn–Sn, and Pb–Pb leads to a further decrease in the sensitivity of the bond strength with respect to the substituents' bulkiness. Our findings can be used as design principles for tuning A–A and A–A' bond strengths.



[1] D. Rodrigues Silva, E. Blokker, J. M. van der Schuur, T. A. Hamlin, F. M. Bickelhaupt, *Chem. Sci.* **2024**, *15*, 1648.

Electron density of delocalized bonds (EDDB) – a powerful tool for studying electron delocalization

Paweł Wieczorkiewicz[a, b], Dariusz Szczepanik[a], Halina Szatylowicz[b]
[a] Jagiellonian University, Cracow, Poland
[b] Warsaw University of Technology, Warsaw, Poland
pawel.wieczorkiewicz.dokt@pw.edu.pl

Recently proposed electron density partitioning method rooted in the chemical information theory, EDDB (electron density of delocalized bonds), allows to quantify and visualize electron localization and delocalization directly from single-determinant wavefunctions in an intuitive way[1,2]. Moreover, cyclic and noncyclic contributions to delocalization and various symmetric orbital contributions (σ, π, δ,…) can be separated. Because the output from EDDB partitioning scheme are the densities of various electrons, it is possible to subtract one from another, even between different molecules sharing a common structural fragment. This provides a plethora of possibilities for analyzing how the electron delocalization changes due to various factors – substitution, deformation, excitation, intermolecular interaction, etc. In this presentation, we will introduce the EDDB method and showcase some of its capabilities on the examples of our recent studies[3,4].

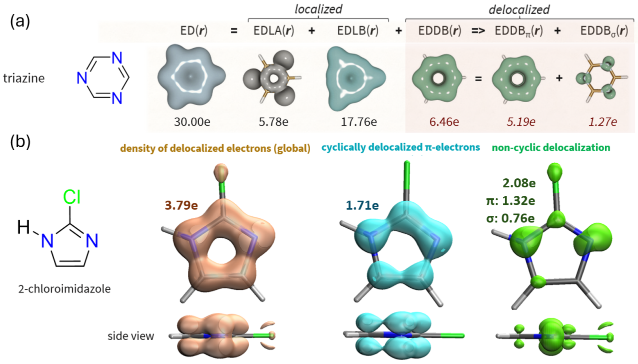


Figure 1. (a) Electron density (ED) partitioning scheme – EDs localized at atoms (LA), bonds (LB) and delocalized; (b) electron delocalization in 2-chloroimidazole.

[1] D.W. Szczepanik, *Comput. Theor. Chem.*, **2016**, *1080*, 33.
[2] D.W. Szczepanik, M. Andrzejak, J. Dominikowska, B. Pawełek, T. M. Krygowski, H. Szatylowicz, M. Solà, *Phys. Chem. Chem. Phys.* **2017**, *19*, 28970.
[3] P. Wieczorkiewicz, M. Shahamirian, T. Kupka, N. Makieieva, T. M. Krygowski, H. Szatylowicz, *Chem. Eur. J.* **2024**, *30*, e202303207.
[4] P. Wieczorkiewicz, T. M. Krygowski, H. Szatylowicz, *Phys. Chem. Chem. Phys.* **2024**, *10.1039.D4CP01709A*

Electrides and Core-Electrons Bonding. When Alkali Metals Feel the Pressure

Stefano Racioppi,[a] Eva Zurek[a]
[a] State University of New York at Buffalo, Buffalo, United States
sraciopp@buffalo.edu

Under extreme pressures, elements often undergo a reorganization of their energy levels to counteract the influence of Pauli exclusion, Coulomb repulsion, and core orthogonality. This phenomenon is particularly noteworthy in alkali and alkaline earth metals, as well as various other elements, leading to the potential formation of high-pressure electrides (HPEs).[1] These compounds exhibit a unique characteristic wherein valence electrons seemingly localize within interstitial voids. Additionally, in certain compounds like alkali halides, it has been theorized that, under significant compression and/or oxidation, the inner shells of metals may even participate in the formation of chemical bonds.

The emergence of HPE and the activation of core-electrons in chemical interactions under compression are intricately governed by the principles of quantum mechanics.[2,3] Crafting intuitive models that comprehensively incorporate quantum effects in multi-electron interactions, enabling a deeper understanding and prediction of these exotic phenomena, proves to be a nontrivial challenge. Nonetheless, striking the right balance between rigorous quantum computations and more intuitive concepts, such as chemical bonding, is feasible, offering a pathway to unravel and anticipate the complexities arising in these high-pressure scenarios.

Guided by density functional theory (DFT) calculations, we will delve into the nuanced chemistry and electronic structures of alkali metals at non-ambient conditions. On one hand, we will highlight the key role of electronic transitions and orbital hybridization in the formation of HPE. [4] On the other hand, we will demonstrate that the core-electrons of the heavier alkali elements, *i.e.*, K, Rb and Cs, do not need extreme conditions (either pressure or oxidation) to be activated. In the appropriate chemical environment, these core-electrons could potentially engage in chemical bonds even at near ambient conditions.

[1] Y. Ma, M. Eremets, A. R. Oganov, Y. Xie, I. Trojan, S. Medvedev, A. O. Lyakhov, M. Valle, V. Prakapenka, *Nature* **2009**, *458*, 182–185.

[2] M. Miao, Y. Sun, E. Zurek, H. Lin, *Nat. Rev. Chem.* **2020**, *4*, 508–527.

[3] C. S. Yoo, *Matter Radiat. Extrem.* **2020**, *5*, 018202.

[4] S. Racioppi, C. V. Storm, M. I. McMahon, E. Zurek, *Angew. Chem. Int. Ed.* **2023**, *27*, e202310802.

Chiral Electron Clouds: Investigating Aromatic Character in Azulene-derived Helical Structures

Yannick Carissan,[a] Fatim Ndeye Ndiaye[a], Albert Artigas[b], Yoann Coquerel[a], Denis Hagebaum-Reignier[a]
[a] Aix Marseille Univ, CNRS, Centrale Med, ISM2, Marseille, France
[b] Institut de Química Computacional i Catàlisi (IQCC) and Departament de Química, Universitat de Girona (UdG), Girona 17003 Catalunya, Spain
yannick.carissan@univ-amu.fr

The intersection of chirality and azulene's unique photophysical properties presents a promising avenue for developing novel materials with diverse applications, including chiroptical probes and sensors, spin filters, and chiroptical switches. Recent advancements have led to the successful synthesis of modified azulene helical systems. Concurrently, theoretical studies have illuminated how azulene-containing compounds can modulate excited state properties. However, our understanding of how the integration of five- and seven-membered rings influences these properties remains limited.

This study aims to provide a comprehensive theoretical comparative analysis of aromaticity in azulene-based helicenes and their classical benzenoid helicene analogues. We focus on both ground and excited states to elucidate the unique characteristics imparted by the azulene moiety.

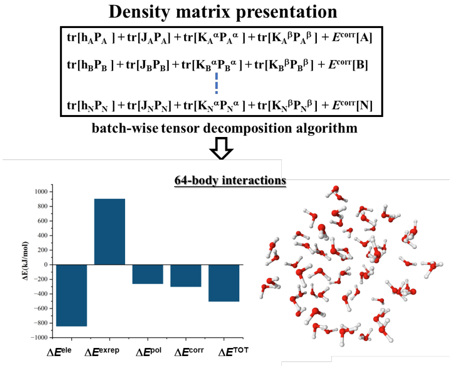
We demonstrate distinct aromatic behaviors in pure azulene-unit helicenes (n-azu) compared to hybrid benzenoid-azulene helicenes (n-hel-azu). Notably, in 6- and 8-cycle azulene-based helicenes, we observe, a closer energetic proximity between singlet and triplet states and enhanced propensity for aromaticity in the triplet state compared to isoelectronic analogues

These findings contribute to our fundamental understanding of azulene-based helicenes and may guide the design of novel materials with tailored electronic and optical properties for advanced applications.

Energy decomposition analysis for intermolecular interactions and chemical bonds in complex systems

Peifeng Su[a]
[a] College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, China
E-mail supi@xmu.edu.cn

Intermolecular interactions and chemical bonds in complex systems, which are related to variable spin states, excited states, and environment effects, are important but challenging. In this talk, first, I will present a brief review of our energy decomposition analysis (EDA) methods for complex systems, which were developed based on KS-DFT (GKS-EDA),[1,2,3] tight-binding DFT (DFTB-EDA),[4] and valence bond theory (VB-EDA). [5] Secondly, I will introduce a density matrix strategy-based EDA method, called DM-EDA, [6] for n-body intermolecular interactions. Different from traditional EDA methods, instead of intermediate state wave function, the EDA terms in DM-EDA are expressed in the forms of density matrix. New insights would be provided when the results of different density matrices are compared. Density matrix-based reformulation and the batch wise algorithm ensure that DM-EDA can be used for interactions involving a large number of monomers.

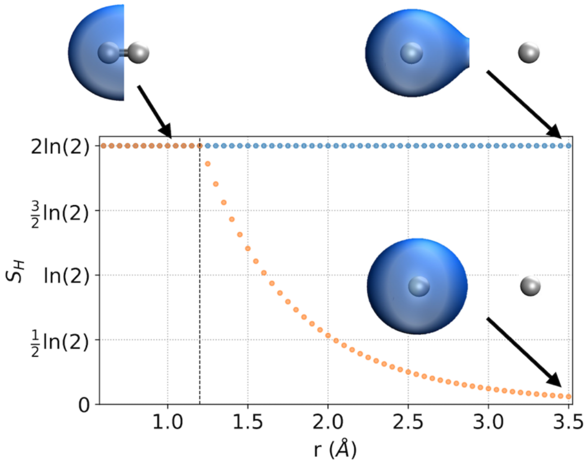


[1] Su. P; Jiang. Z; Chen. H; Wu. W. Phys. Chem. A **2014**, 118, 2531
[2] Tang. Z; Jiang. Z; Chen. H; Su. P; Wu, W. J. Chem. Phys. **2019,** 151, 244106
[3] Tang. Z; Shao, B.; Wu. W; Su. P. Phys. Chem. Chem. Phys. **2023**, 25, 18139
[4] Xu. Y; Zhang. S; Lindahl. E; Friedman, R; Wu, W; Su, P. J. Chem. Phys. **2022**, 157, 034104
[5] Zhang. Y; Wu. X; Su. P; Wu, W. J. Phys.: Condens. Matter **2022**, 34, 294004
[6] Zhang. Y; Yan. L; Wu. W; Su. P. J. Chem. Phys. In revision

Quantum Information Patterns Between Atoms in a Molecule

Patrick Bultinck,[a] Daria Van Hende[a], Ruben Van der Stichelen[a], Guillaume Acke[a]
[a] Ghent University, Department of Chemistry, Gent, Belgium
Patrick.Bultinck@UGent.be

Quantum information theory provides a toolbox of descriptors that characterize many-electron systems based on quantum information patterns between open quantum systems. Despite the insights gained in the condensed matter community, the use of these descriptors to study interactions between atoms in a molecule remains limited. We present a framework that characterizes the quantum information patterns between quantum atoms as defined in the Quantum Theory of Atoms in Molecules. This framework harnesses the interpretative power of orbital-based entanglement diagrams together with the atoms-in-molecules approach. We show that the quantum information patterns capture key properties of quantum atoms and how they interact with their molecular environment, which further aids in building a much-needed bridge between quantum information theory and quantum chemistry [1].

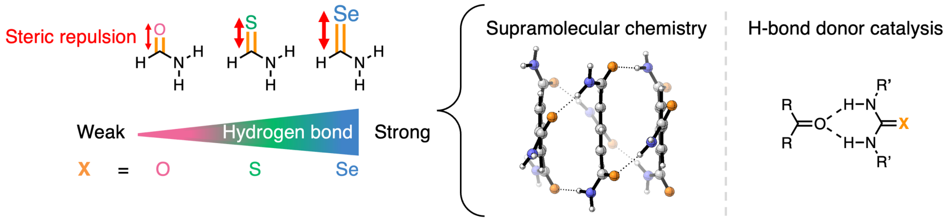


[1] D. Van Hende, R. Van der Stichelen, P. Bultinck, G. Acke, *Chemistry Eur. J.*, **2024**, *In press*. https://doi.org/10.1002/chem.202400819

Chalcogen Atom Size:
A Key Parameter in Tuning Amide Hydrogen Bonding

Celine Nieuwland,[a] Célia Fonseca Guerra[a]
[a] Department of Chemistry and Pharmaceutical Sciences, Vrije Universiteit Amsterdam
c.nieuwland@vu.nl

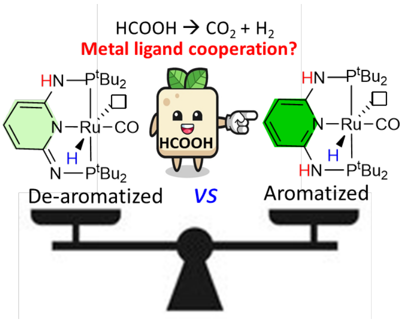
The hydrogen-bond donor strength of amides $H_2NC(=X)R$ increases when X descends in Group 16 (chalcogens) of the Periodic Table. This trend may seem counterintuitive because a reduced electronegativity of X down the group suggests, erroneously, a reduced C=X group electronegativity and, thus, a reduced hydrogen-bond donor strength. Our quantum-chemical bonding analyses have revealed that it is the steric size of the chalcogen atom, not its electronegativity, that is at the origin of this experimentally observed phenomenon.[1] Thus, a larger atom X pushes the C=X bond to a longer distance at which the $\pi^*_{C=X}$ molecular orbital drops in energy and becomes a better electron acceptor. This makes the C=X group effectively more electronegative in the sense that it accommodates more charge of the lone pair on the NH_2 group which becomes more positive and thus a better hydrogen-bond donor. In this talk, I show that this phenomenon and the steric mechanism behind it is not exclusive to Group 16 but can be generalized to varying X in the amide C=X moiety down Groups 14 and 15 of the periodic table.[2] Finally, the application of the chalcogen atom size as a key parameter to aid the design of hydrogen-bond donor catalysts and self-assembled polymers will be demonstrated.[3–5]



[1] C. Nieuwland, C. Fonseca Guerra, *Chem. Eur. J.* **2022**, *28*, e202200755.
[2] C. Nieuwland, R. Verdijk, C. Fonseca Guerra, F. M. Bickelhaupt, *Chem. Eur. J.* **2024**, *30*, e202304161.
[3] C. Nieuwland, S. Lekanne Deprez, C. de Vries, C. Fonseca Guerra, *Chem. Eur. J.* **2023**, *29*, e202300850.
[4] C. Nieuwland, A. N. van Dam, F. M. Bickelhaupt, C. Fonseca Guerra, *submitted manuscript.*
[5] C. Nieuwland, C. Fonseca Guerra, *Chem. Eur. J.* **2024**, *30*, e202304361.

PN³P-Ruthenium Pincer Catalysis: Exploring MLC vs. Non-MLC Pathways in FA Dehydrogenation

Manjaly J. Ajitha, Mohammad Misbahur Rahman, Indranil Datta, Kuo-Wei Huang*
KAUST Catalysis Center & Division of Physical Science and Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia
kuowei.huang@kaust.edu.sa



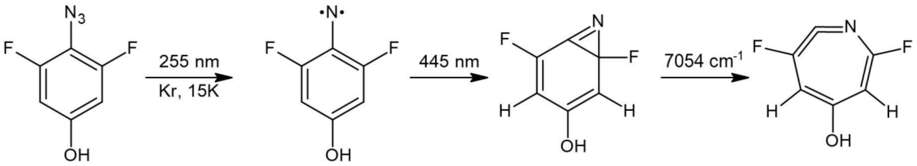
Formic acid (FA) is an emerging clean energy carrier due to its advantageous properties, including high volumetric hydrogen (H_2) storage capacity, low toxicity, inflammability, and favorable dehydrogenation temperature.[1] Unlike H_2, which faces significant safety and storage challenges, FA offers a safe and efficient alternative for fuel cells, contributing to low carbon emissions.[2] Extensive research has been dedicated to optimizing FA's dehydrogenation pathway using various catalysts. In this study, computational methods are employed to investigate the PN³P-Ru catalyzed dehydrogenation of FA,[3] focusing on the comparison between metal-ligand cooperation (MLC) and non-MLC pathways. Our findings reveal that the acidity of FA is a critical factor, favoring the non-MLC pathway through an acid-base interaction with the catalyst. Additionally, triethylamine plays a dual role in both formate ion generation and catalyst activation by creating a vacant site on the central metal atom. These insights are valuable for designing efficient catalysts for hydrogen generation from FA and highlight the potential of MLC mechanisms in reactions involving less acidic substrates. This study enhances our understanding of FA dehydrogenation and paves the way for more sustainable and effective energy solutions.

[1] J. Eppinger, K.-W. Huang, *ACS Energy Lett.* **2017**, *2*, 188.
[2] I. Dutta, S. Chatterjee, H. Cheng, R. K. Parsapur, Z. Liu, Z. Li, E. Ye, H. Kawanami, J. S. C. Low, Z. Lai, X. J. Loh, K.-W. Huang, *Adv. Energy Mater.* **2022**, *12*, 2103799.
[3] Y. Pan, C.-L. Pan, Y. Zhang, H. Li, S. Min, X. Guo, B. Zheng, H. Chen, A. Anders, Z. Lai, J. Zheng, K.-W. Huang, *Chem. Asian J.* **2016**, *11*, 1357.

Manipulating chemical bonds with IR radiation.

Leonardo José Duarte,[a,b] Cláudio M. Nunes,[b] Rui Fausto[b,c], Ataualpa A. C. Braga[a]
[a]Institute of Chemistry - University of São Paulo, São Paulo, Brazil
[b]CQC-IMS, Department of Chemistry, University of Coimbra, Coimbra, Portugal
[c]Faculty of Sciences and Letters, Department of Physics, Istanbul Kultur University, Istanbul, Turkey
ljduarte@iq.usp.br

Infrared induced isomerization was first discovered in the early 60`s by Pimentel *et. al.* when irradiating a sample of nitrous acid on cryogenic matrices. Upon the interaction with the radiation, the nitrous acid undergoes a conformational change observed by differences in the infrared absorption bands[1]. Recently, it was show that infrared radiation is also able to cause the breaking of chemical bonds. By isolating precursor molecules and performing a series of irradiation experiments, Nunes and coworkers produced[2] the benzazirine IV (see **Figure 1**) by exciting the first overtone of the OH stretch normal mode, which acts as an antenna, capturing the infrared radiation and redistributing it to the reaction coordinate.



I II III IV

Figure 1: Photochemical route for the obtention of benzazirine IV in cryogenic matrix. Molecule I is trapped into the matrix and converted in II and III by successive UV irradiations. The conversion of III in IV undergoes by Infrared excitation of the first overtone of OH stretch.

By modelling the vibrational Hamiltonian in terms of normal coordinates and solving the Schrödinger equation for such systems, we were able to find possible vibrational energy redistribution paths from the excited OH stretch eigenstate to the reaction coordinate, allowing the precise control of chemical bonds using infrared radiation. The physical interpretation of the antenna effect and the coupling between normal modes can offer the basis for an efficient control of the intermolecular vibrational energy redistribution process, thus unlocking a fourth paradigm for chemical reactivity, alongside with thermodynamic, kinetics, and tunneling [3] effects.

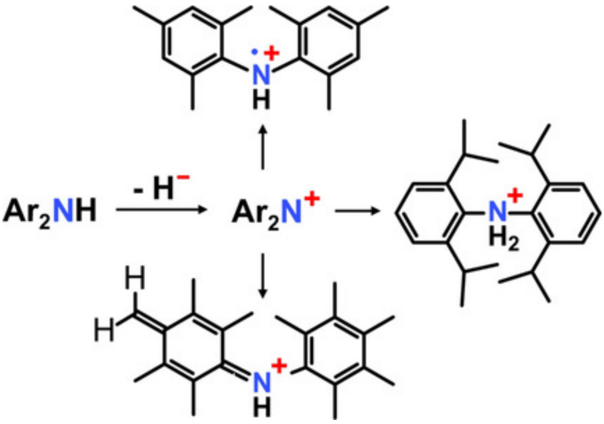
[1] R. T. Hall, G. C. Pimentel, *J. Chem Phys.*, **1963**, 38, 1889. [2] C. M. Nunes, N. A. M. Pereira, L. P. Viegas, T. M. V. D. Pinho e Melo, R. Fausto, *Chem. Comm., **2021**, 57,* 9570. [3] P. R. Schreiner, *J. Am. Chem. Soc.*, **2017**, 139, 15276.

Reactivity of Diarylnitrenium Ions

Agnes Kütt,[a] Gunnar Jeschke,[b] Lauri Toom,[a] Jaak Nerut,[a] Christhopher A. Reed[c]
[a] Institute of Chemistry, University of Tartu, Tartu, Estonia
[b] Department of Chemistry and Applied Biosciences, ETH Zurich, Zurich, Switzerland
[c] Department of Chemistry, University of California, Riverside, USA
agnes.kutt@ut.ee

Nitrenium ions, R_2N^+, isoelectronic with carbenes, are highly reactive intermediates of dicoordinate positively charged nitrogen having two free electrons. It is known from the previous works, that their lifetimes are generally short and, based on transient spectra and product analysis, their electronic states are deduced to be singlets. In general, singlets act as Lewis acids adding nucleophiles whereas triplets act as diradicals, sequentially abstracting H-atoms.

Herein, we communicate results from attempts to generate bulky diarylnitrenium ions on a synthetic scale.[1] We found that formed diarylnitrenium cations as intermediates acted as radical species, having either triplet state or singlet exited electronic state, not common singlet state.



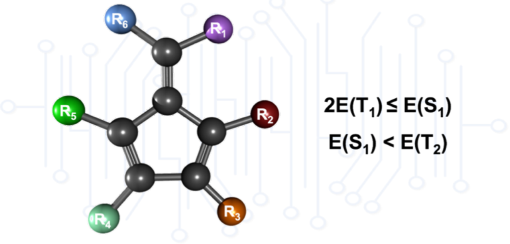
[1] A. Kütt, G. Jeschke, L. Toom, J. Nerut, C. A. Reed. *Chem. Eur. J.* **2020**, *26*, 8871.

Pursuit of Singlet Fission Fulvenes Candidates Using Inverse Design

Irene Casademont-Reig,[a] Roger Monreal-Corona[a, b], Eline Desmedt, [a] Freija Vleeschouwer, [a] Mercedes Alonso[a]
[a] General General Chemistry-Eenheid Algemene Chemie (ALGC), Department of Chemistry, Vrije Universiteit Brussels (VUB), Pleinlaan 2, 1050 Brussels, Belgium
[b] Institut de Química Computacional i Catàlisi and Departament de Química, Universitat de Girona, C/ Maria Aurèlia Capmany 69, 17003 Girona, Catalonia, Spain
E-mail address: irene.casademont.reig@vub.be

Electron excitation by photons is a key fundamental process to enhance the efficiency of photovoltaic devices.[1] Singlet-fission (SF) materials have the potential to surpass the efficiency of such devices as they can generate two excitons from a single photon, affording quantum efficiencies up to 200%.[2] A central bottleneck in this field is the limited number of suitable SF chromophores beyond linear acenes which are susceptible to photochemistry degradation.

In this project, we used fulvenes[3] as a test bed to establish a robust and innovative inverse design[4] protocol that will be later applied to accelerate the discovery of new promising porphyrinoids as SF chromophores.[5] 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 singlet fission. On the generated database, general design criteria spanning a wider chemical space are devised, including the role of ground- and excited-state aromaticity and the diradical character.



$R_{1\text{-}6}$ = NMe_2, NH_2, OH, OMe, SH, Me, SiH_3, H, BH_2, BF_2, F, Cl, CF_3, CN, $N0_2$

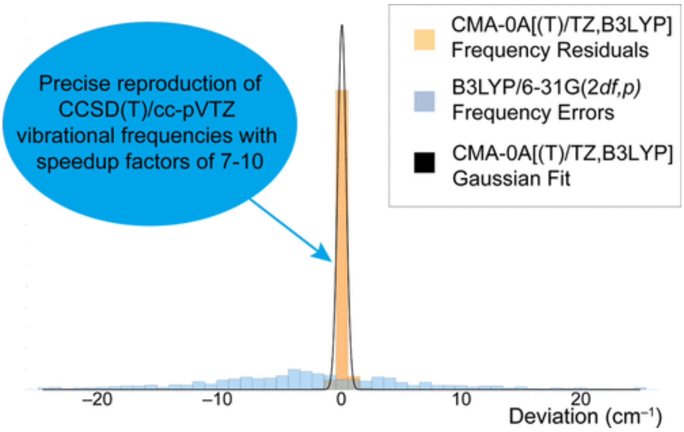
Figure 1. Targeted fulvenes for developing novel SF chromophores with enhanced stability.

[1] A. J. Baldacchino, M. I. Collins, M. P. Nielsen, T. W. Schmidt, D. R. McCamey, M. J. Y. Tayebjee, Chem. Phys. Rev. **2022**, *3*, 021304; [2] T. Ullrich, D. Munz, D. M. Guldi, Chem. Soc Rev. **2021**, *50*, 3485; [3] O. El Bakouri, J. R. Smith, H. Ottosson, J. Am. Chem. Soc., **2020**, *142*, 5602; [4] E. Desmedt, D. Smets, T. Woller, J. L. Teunissen, M. Alonso, F. De Vleeschouwer, Phys. Chem. Chem. Phys. 2023, 25, 17128-17142; E. Desmedt, L. Serrano Gimenez, F. De Vleeschouwer, M. Alonso, Molecules, **2023**, *28*, 7371; [5] I. Casademont-Reig, R. Monreal-Corona, E. Desmedt, F. Vleeschouwer, M. Alonso, *in preparation*.

Concordant Mode Approach for Molecular Vibrations

Mitchell E. Lahm,[a] Nathaniel L. Kitzmiller,[a] Henry F. Mull,[a] Wesley D. Allen,[a,b]
Henry F. Schaefer III[a]
[a] University of Georgia, Athens, GA, USA
[b] Allen Heritage Foundation, Dickson, TN, USA
Mitchell.Lahm@uga.edu

The Concordant Mode Approach (CMA) is a novel hierarchy for increasing the system size and level of theory feasible for quantum chemical computations of harmonic vibrational frequencies. The key concept behind CMA is that transferrable, internal-coordinate normal modes computed at an appropriate lower level of theory (B) comprise a superb basis for converging to vibrational frequencies given by a higher level of theory (A). Accordingly, high-level harmonic frequencies can be evaluated via CMA from a collection of single-point energies that essentially scales linearly in the number of atoms, providing nearly order-of-magnitude CPU time speedups. The accuracy of CMA methods was established by comprehensive tests on over 120 molecules for target Level A = CCSD(T)/cc-pVTZ with auxiliary Level B choices of both CCSD(T)/cc-pVDZ and B3LYP/6-31G(2df,p). Remarkably, the frequency residuals given by the diagonal CMA-0A(nc) scheme exhibit mean absolute deviations (MADs) of only 0.2 cm^{-1} and standard deviations less than 0.5 cm^{-1}; the corresponding zero-point vibrational energies (ZPVEs) have negligible errors in the vicinity of 0.3 cm^{-1}. [1]

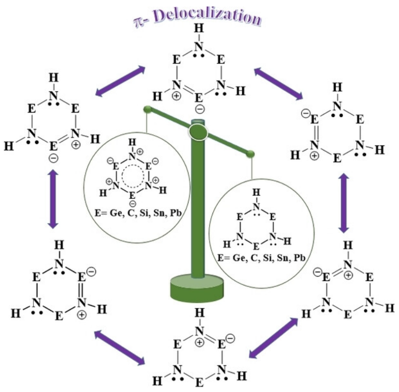


[1] ME Lahm, NL Kitzmiller, HF Mull, WD Allen, HF Schaefer, *JACS*, **2022**, *144*, 51.

Unlocking the Secrets of Charge-Shift Bonding, Delocalization, and Aromaticity in Germanazene and Its Heavier Group 14 Analogues: A Valence Bond Theory

Shailja Jain[a,†], David Danovich,[a] Slavko Radenković,*[b] and Sason Shaik*[a]
[a] The Hebrew University of Jerusalem, Jerusalem 9190401, Israel.
†Present address: University of Stuttgart, Pfaffenwaldring 55, 70569, Stuttgart, Germany.
[b] Faculty of Science, University of Kragujevac, 12 Radoja Domanovica, 34000 Kragujevac, Serbia.
E-mail address shailjanclwork@gmail.com

Our study investigates the structure, bonding, and aromaticity of low-valent compounds in group 14, focusing on the $E_3(NH)_3$ (E = Ge, C, Si, Sn, Pb) series. We employ modern *ab initio valence bond theory* and magnetically induced current densities to examine *π-bonding* and aromaticity. Our findings reveal that while (4n+2)π systems in carbon rings exhibit aromaticity due to cyclic π delocalization, the $E_3(NH)_3$ rings display non-aromatic behaviour. Instead, they feature the *hopping of one localized π-E=N* double bond at a time, with the remaining π-electron density localized on the two N atoms. Nevertheless, these molecules demonstrate significant covalent-ionic resonance energies of 153.0, 86.6, 74.2, 61.2, and 58.9 kcal/mol for E = C, Si, Ge, Sn, and Pb, respectively. The covalent-ionic mixing in $E_3(NH)_3$ leads to the formation of stabilized π systems through *charge-shift bonding*. This substantial charge-shift resonance energy contributes to the stability observed in $Ge_3(NH)_3$ and potentially extends to the heavier congeners yet to be synthesized. Thus, *charge-shift bonding* extends beyond two-center bonds to cyclic systems, showcasing single π-bond cyclic delocalization.



[1] S. Jain, D. Danovich, S. Radenković, S. Shaik, *Chem. Eur. J.*, **2023**, *29*, e202300992.

Understanding the Bonding of N-heterocyclic Carbenes on Pd/Cu(111) Single Atom Alloys

Scott M. Simpson,[a]
[a] Department of Chemistry, St. Bonaventure University, St. Bonaventure, NY, 14778, USA
ssimpson@sbu.edu

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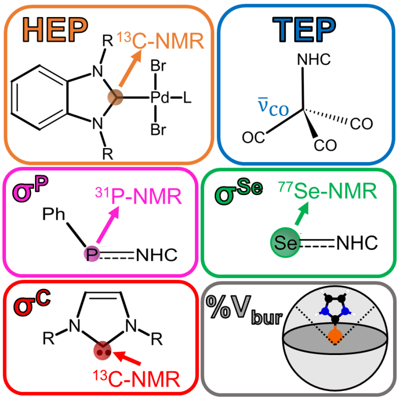

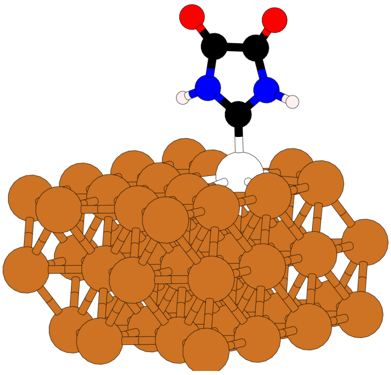

N-heterocyclic carbenes(NHCs) have garnered the attention of material scientists and chemists for their tunable electronic properties. NHCs anchored to surfaces have attractive features and may provide new applications that traditional self-assembled monolayers (SAMs) have yet to be employed. In-fact, NHCs have been utilized to functionalize surfaces to tune reactivity and/or selectivity. However, the underlying mechanisms to control the surface-adsorbate interaction is still in its infancy, especially for SAAs. Herein we utilize periodic non-local density functional theory (DFT) in conjunction with molecular DFT calculations to better understand how changing the NHC backbone influences the bonding between the surface and the adsorbate with the end goal to utilize a relatively new mechanism to store hydrogen.[2,3] To further rationalize the bonding mechanism of NHCs to SAAs explore different spectroscopic techniques to explain the bonding mechanisms.

[1] H.V. Huynh. *Chem. Rev.*, **2018**, *118*, 9457.
[2] M. Hanson, S. Simpson. *ACS Omega*, **2023**, 8, 37402.
[3] S. Simpson. *JCIS Open*, **2021**, *3*, 100013.

Posters

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Poster 1

Superexchange Interaction and Chemical Bonding

Inés Sánchez-Movellán,[a] Toraya Fernández-Ruiz[a], Ángel Martín-Pendás[b], Richard Dronskowski[c], Pablo García-Fernández[a], Miguel Moreno[a], José Antonio Aramburu[a]
[a]University of Cantabria, Santander, Spain
[b]University of Oviedo, Oviedo, Spain
[c]Institute of Inorganic Chemistry RWTH, Aachen, Germany
ines.sanchez@unican.es

Magnetic insulators have been largely studied since the advent of quantum mechanics. Their wide range of properties makes these materials interesting at both fundamental and applied level. Regarding applications, magnetic insulators are instrumental in spintronics, microwave devices or quantum computing[1], to name a few. However, the chemical mechanism for superexchange interaction that stabilizes an antiferromagnetic order (AFM) in cubic perovskites, remains elusive since the well-known models developed by Kramers[2] (1934), Anderson[3] (1959), Goodenough-Kanamori[4,5] (1950s) and Hay-Thibeault-Hoffmann[6] (1975). During the last 20 years, significant research efforts have been devoted to analyzing and quantifying this interaction, connecting it to the previous models, but the subtlety of magnetic interactions remains challenging. In our work, first principles calculations together with both orbital-based (LOBSTER[7]) and density-based (QTAIM[8], TOPOND[9]) techniques are used to determine the chemical mechanism for superexchange interactions. The model systems KMF_3 ($M = Ni^{2+}$, Mn^{2+}, V^{2+}) are used to show that the larger delocalization of spin-minority electrons in AFM state is pivotal in its stabilization below ferromagnetic state, as verified by chemical bonding analysis (COHP, COBI, kinetic energy at bond critical point). This larger delocalization is related to a slightly higher covalency, leading to an AFM ground state.

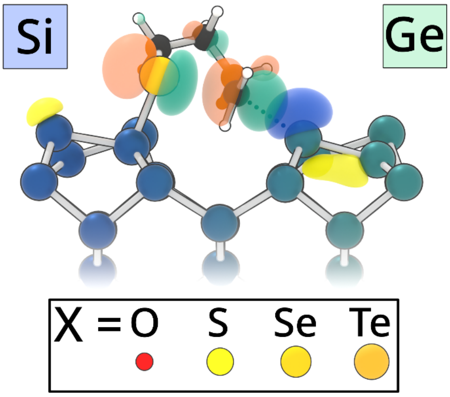
[1] A. Ardavan, G. A. D. Briggs, Phil. Trans. R. Soc. A, **2011**, *369*, 3229.
[2] H. A. Kramers, *Physica*, **1934**, *1*, 182.
[3] P. W. Anderson, *Phys. Rev.*, **1959**, *79*, 350.
[4] J.B. Goodenough, *Phys. Rev.*, **1955**, 100, 564–573.
[5] J. Kanamori, *J. Phys. Chem. Solids*, **1959**, *10*, 87.
[6] P. J. Hay, J. C. Thibeault, R. Hoffmann, *JACS*, **1975**, *97*, 4884.
[7] R. Nelson, C. Ertural, J. George, V. Deringer, G. Hautier, R. Dronskowski, *J. Comput. Chem.* **2020**, 41, 1931.
[8] R. Bader, *Atoms* in Molecules: A Quantum Theory*, **1994**, Oxford University Press.*
[9] S. Casassa, A. Erba, J. Baima, R. Orlando, J. Comput. Chem.*, **2015**, 36, 1940.*

Poster 2

Trends in the Reactivity of Pentacyclic Ether Derivatives on Silicon and Germanium Surfaces Revealed by Energy Decomposition Analysis for Extended Systems

Franz Thiemann,[a] Hendrik Weiske,[a] Ralf Tonner-Zech[a]
[a] Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnéstraße 2, 04103 Leipzig, Germany
franz.thiemann@uni-leipzig.de

Organic functionalization has emerged as a promising way of tailoring surface properties of semiconductors to fit a wide range of applications. Especially silicon and germanium are of great interest due to their industrial relevance. Therefore, we analyzed the adsorption and ring-opening reaction of pentacyclic chalcogen alkyls with chalcogen atoms ranging from oxygen to tellurium using simulations. This extends our previous investigation of THF on silicon[1] to the germanium surface and the heavier chalcogen homologues. Following the dative bound state, subsequent ring-opening reactions were found to proceed via a nucleophilic back-side attack, similar to a molecular S_N2 reaction.
We present data from periodic energy decomposition analysis[2] (pEDA) for precursor and transition state structures that reveal distinctive differences between silicon and germanium. Reaction energies and barrier heights exhibit a maximum at the sulfur derivative, with the lower barrier of THF being caused by the ring strain.



[1] L. Pecher, S. Laref, M. Raupach, R. Tonner, *Angew. Chem. Int. Ed*, **2017**, *56*, 15150.
[2] M. Raupach, R. Tonner, J. Chem. Phys, **2015**, 142, 1941195.

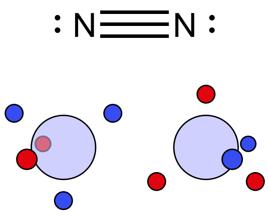
Poster 3

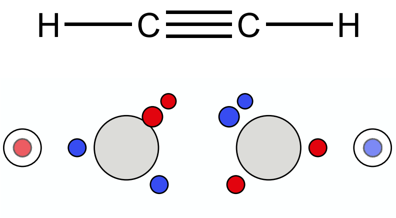
An in-Depth Study of the Bonding Situation for the Many-Electron Bonds in N_2 and C_2H_2 with Probability Density Analysis

Emma Gorgas,[a] Nicole Maser,[a] Michel V. Heinz,[a] and Arne Lüchow[a]
[a] Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany
emma.gorgas@rwth-aachen.de

A century ago, Lewis introduced the concept of electron sharing and the famous Lewis structures,[1] shaping the chemical language. Recently, it was shown that, by studying the electron positions maximizing the many-electron probability density $|\Psi|^2$ via probability density analysis, Lewis structures can be retrieved from ab initio calculations for most two-center two-electron bonds.[2] For two-center many-electron bonds, however, the maxima of $|\Psi|^2$ diverge from the familiar Lewis picture. While the maxima for acetylene remain consistent to the Lewis structures, the maxima of $|\Psi|^2$ for N_2 diverge from them. Therefore, a thorough investigation, using Jastrow-correlated Slater determinant wave functions, was conducted for both systems.

Moreover, the topology for the N_2 wave function drastically differs from the topology of the C_2H_2 wave function. Expanding the analysis to the maximum probability paths, connecting the maxima, differences in the electron delocalization were revealed: the electrons in N_2 move more freely than those in C_2H_2. These differences were traced primarily to the presence of hydrogen atoms, which was further compounded by a study of C_2H_6, C_2H_4, HCN, and HCC^-. Considering the different chemical behaviors of both molecules, different topologies of their wave functions should be expected.





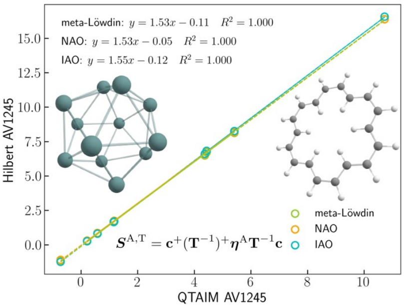
[1] G. N. Lewis, *J. Am. Chem. Soc.*, **1916**, *38* (4), 762.
[2] A. Lüchow, *J. Comput. Chem.*, **2014**, *35*, 854.

Poster 4

Evaluating electronic aromaticity indicators from robust, cheap and error-free Hilbert-space partition schemes

Joan Grèbol-Tomàs[a,b], Eduard Matito[b,c], Pedro Salvador[a]
[a] Departament de Química, Universitat de Girona, 17071 Girona, Spain
[b] Donostia International Physics Center (DIPC), 20018 Donostia, Gipuzkoa, Spain
[c] Ikerbasque Foundation for Science, 48009 Bilbao, Euskadi, Spain
joangrebol@gmail.com / joan.grebol@dipc.org

Aromaticity is a fundamental concept in chemistry that explains the stability and reactivity of many compounds by identifying atoms within a molecule that form an *aromatic ring*. Reliable aromaticity indices focus on electron delocalization and depend on atomic partitions, giving rise to the concept of an *atom-in-the-molecule* (AIM). Real-space atomic partitions present two important drawbacks: a high computational cost and numerical errors, limiting some aromaticity measures to medium-sized molecules with rings up to 12 atoms. This restriction hinders the study of large conjugated systems like porphyrins and nanorings. On the other hand, traditional Hilbert-space schemes are free of the latter limitations but can be unreliable for the large basis sets required in modern computational chemistry. This paper explores AIMs based on three robust Hilbert-space partitions – meta-Löwdin[1], Natural Atomic Orbitals (NAO)[2], and Intrinsic Atomic Orbitals (IAO)[3] – which combine the advantages of real-space partitions without their disadvantages. These partitions can effectively replace real-space AIMs for evaluating the aromatic character. For the first time, we report multicenter index (MCI) and I_{ring} values for large rings and introduce ESIpy, an open-source Python code for aromaticity analysis in large conjugated rings.[4]



[1] Q. Sun, G. K.-L. Chan, *J. Chem. Theory Comput.* **2014**, 10, 3784.
[2] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, 83, 735.
[3] G. Knizia, *J. Chem. Theory Comput.* **2013**, 9, 4834.
[4] J. Grèbol-Tomàs, E. Matito, P. Salvador, *Chem. Eur. J.* **2024**, e20241282.

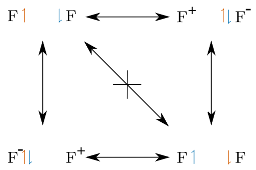
Poster 5

Identifying a Real Space Fingerprint of Charge-Shift Bonding with Probability Density Analysis

Michel V. Heinz,[a] Leonard Reuter,[a] and Arne Lüchow[a]
[a] Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany
heinz@pc.rwth-aachen.de

Three decades ago, the charge-shift bond was introduced by the valence bond community as a third type of electron pair bond, in addition to the covalent and ionic description. A charge-shift bond is characterized by a large energy difference between the covalent and the full valence bond wave functions, the charge-shift resonance energy. Therefore, these bonds are stabilized by the mixing of the covalent and the ionic valence bond structures.[1] As a result of this definition being limited at first to valence bond calculations, a multitude of different quantum chemical tools, like QTAIM or ELF, have already been employed to characterize charge-shift bonds.

Here we present the results obtained with probability density analysis: we analyzed the maxima of the 3N-dimensional probability density $|\Psi|^2$ and the maximum probability paths connecting these maxima.[2] By defining a probability barrier for each path and comparing these barriers, the bond electron exchanges can be investigated for any wave function. Two different paths connecting the covalent electron arrangements were identified: a concerted two electron exchange and a stepwise exchange via ionic electron arrangements. The differences between these barriers proved to be a reliable real space measure for charge-shift bonding in good agreement with valence bond results.[3]



[1] S. Shaik, D. Danovich, J. M. Galbraith, B. Braïda, W. Wu, P. C. Hiberty, *Angew. Chem. Int. Ed.*, **2020**, *59*, 984.
[2] L. Reuter, A. Lüchow, *Nat. Comm.*, **2021**, *12*, 4820.
[3] M. V. Heinz, L. Reuter, A. Lüchow, *Chem. Sci.*, **2024**, *15*, 8820.

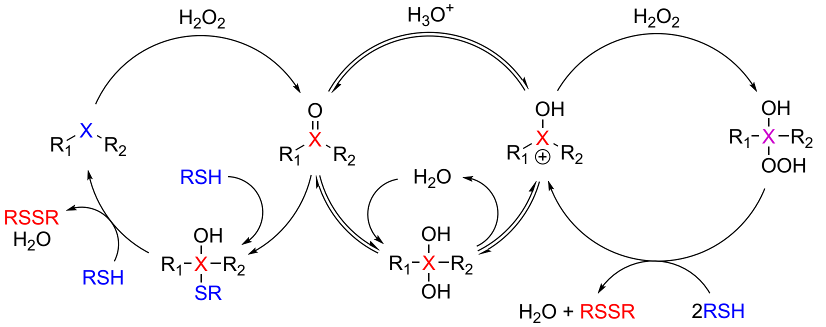
Poster 6

Oxidation of Diorganochalcogenides by H_2O_2 in Aqueous Solution

Alessandro Rubbi,[a] Antônio Luiz Braga,[b] Laura Orian[a]
[a] Dip. di Scienze Chimiche, Università di Padova, via Marzolo 1, 35131 Padova, Italia.
[b] Dep. de Química, Univ. Fed. de Santa Catarina, 88040-900 Florianópolis/SC, Brasil.
alessandro.rubbi@phd.unipd.it

Sulfur and selenium redox chemistry plays a pivotal role in living beings. While the former is present in numerous proteins, peptides and metabolites, the latter is almost exclusively found in a few enzymes that are essential for homeostasis, such as glutathione peroxidases (GPxs).[1] GPxs prevent the buildup of damaging hydroperoxides species through a sophisticated Se(II)/Se(IV) redox equilibrium. Likewise, diorganochalcogenides display an analogous reactivity, although it is not fully clear which species is the active catalyst.[2-4] Further knowledge on the mechanism of the GPx-like activity of dialkyl and diaryl chalcogenides is very valuable, for an application as antioxidants and green catalysts in organic synthesis for the activation of H_2O_2.

Our theoretical investigation aims at modelling the reactivity of simple diorganochalcogenides in aqueous solution with H_2O_2. By means of a Density Functional Theory approach, we have studied the mechanism of oxidation of chalcogenides, as well as the equilibria mediated by solvent molecules. The role of the chalcogen and substituent effects as well as the relative trends have also been assessed. Based on our results, we suggest that hydroxy perhydroxy chalcogenanes are likely key intermediates in the redox process.



[1] L. Flohé, S. Toppo, L. Orian, *Free Rad. Biol. and Med.*, **2022**, *187*, 113.
[2] L. Orian, L. Flohé, *Antiox.*, **2021**, *10*, 1560.
[3] V. Nascimento *et al.*, *J. Am. Chem. Soc.*, **2012**, *134*, 138.
[4] G. Ribaudo *et al.*, *Chem. Eur. J.*, **2017**, *23*, 2405.

Poster 7

Ground and excited state aromaticity in azulene-based helicenes

Amisadai Lorenzo Reyes, [a] Fatim Ndeye Ndiaye, [a] Albert Artigas, [b] Yoann Coquerel, [a]
Cyril Terrioux, [c] Nicolas Prcovic, [c] Denis Hagebaum-Reignier, [a] Yannick Carissan[a]
[a]Aix Marseille Université, CNRS, Centrale Marseille, iSm2, Marseille,France
[b] Facultat de Ciències, Universitat de Girona, Campus Montilivi, Girona, Catalunya, Spain
[c] Aix Marseille Université, Université de Toulon, CNRS, LIS, Marseille,France
E-mail: amisadai.LORENZO-REYES@etu.univ-amu.fr

The combination of chirality and the peculiar photophysical properties of azulene looks like a promising strategy for the development of new chiroptical probes and sensors, spin filters or chiroptical switches.[1] Recently, new modified azulene helical systems have been successfully synthetized. [2] At the same time, theoretical studies have shown how azulene-containing compounds can modulate the excited state properties. [3] However, the understanding of how the presence of five- and seven-membered rings influences the properties remains limited.

Our work aims to provide a comparative theoretical analysis of the aromaticity of azulene-based [n]-helicene[1] compared to classical benzenoid helicene analogues. Based on the analysis of magnetic properties (3D Isotropic Magnetic Shielding (IMS3D) and Anisotropy of the Induced Current Density (AICD)) and localization/delocalization of the wave function (Electron Density of Delocalized Bonds (EDDB)), we study the ground and first triplet states of azulene-based helicenes at the B3LYP/6-311++G(d,p) level of theory.

We will show how the aromatic characters of helicenes with azulene units only ([n]-azu), differ from the behavior of the azulene and analogous benzenoid-azulene helicene hybrids ([n]-hel-azu). Our findings indicate that in azulene-based helicenes with 6 and 8 cycles, the energy gap between singlet and triplet states narrows, and the triplet state exhibits greater aromaticity than their isoelectronic analogues. [4]

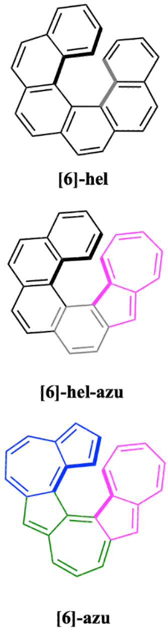


Figure 1. *Example of azulene-based isoelectronic helicene compounds under study.*

REFERENCES
[1] J. Huang, S. Huang, Y. Zhao, B. Feng, K. Jiang, S. Sun, C. Ke, E. Kymakis, X. Zhuang, *Small Methods,* **2020**, *4* (10), 2000628
[2] C. Duan, H. Xin, X. Gao, *Tetrahedron Letters*, **2023**, *123*, 154553.
[3] C. Yang, W. Q. Tian, *ChemPlusChem*, **2023**, *88 (8)*, e202300279.
[4] A. Lorenzo Reyes *et al.*, *Chemistry a Europen Journal*, under revision.

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[1] n: total number of ortho-fused cycles in the helicenes, here for n =4,6,8.

Poster 8

Generalized Davidson algorithm for partial diagonalization of large non-Hermitian matrices

F. BROECKER [a,b], T. NOTTOLI [b], F. LIPPARINI [b]
[a] Institute of Physical Chemistry, RWTH Aachen, Landoltweg 2, 52074 Aachen, Germany
[b] Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi 13, 56124, Pisa, Italy
felix.broecker@rwth-aachen.de

Quantum chemical methods facilitate the elucidation and comprehension of spectroscopic and photochemical phenomena in molecular systems by computing excitation energies and transition properties. Belonging to the systematically improvable coupled cluster (CC) family, equation of motion (EOM) CC provides an accurate description of excited state properties. The diagonalization of the full vast non-Hermitian EOM CC Hamiltonian matrix with dense linear-algebra routines is costly and limited to a matrix dimension of about 10,000. Thus, the Davidson method is employed to obtain a few lowest or highest eigenpairs.

We present a numerically stable nonsymmetric Davidson solver, capable of determining a range of desired eigenpairs. The solver can compute either only right or both right and left eigenpairs in a simultaneous or consecutive manner.[1,2] For the orthogonalization of the approximate Ritz vectors itself, Cholesky decomposition is used, whereas for the biorthogonalization of the left and right vectors a singular value decomposition approach is employed.[3,4] The performance of the new routine is evaluated on EOM-CC-like matrices with dimensions ranging from 1,000 to 10,000 with up to 100 desired eigenpairs. Besides, the routine has been interfaced with the CFOUR[5,6] suite of quantum chemistry programs and results are presented on a small range of systems.

[1] M. Caricato, G. Trucks, M. Frisch, *J. Chem. Theory Comput.*, **2010**, *6*, 1966.
[2] D. Zuev, E. Vecharynski, C. Yang, N. Orms, A. I. Krylov, *J. Comput. Chem.,* **2015**, *36*, 273.
[3] T. Nottoli, I. Giannì, A. Levitt, F. Lipparini, *Theor. Chem. Acc.,* **2023**, *142*.
[4] R. Alessandro, I. Giannì, F. Pes, T. Nottoli, F. Lipparini, *J. Chem. Theory Comput.*, **2023**, *19*, 9025.
[5] D. A. Matthews, L. Cheng, M. E. Harding, F. Lipparini, S. Stopkowicz, T.-C. Jagau, P. G. Szalay, J. Gauss, J. F. Stanton, *J. Chem. Phys.,* **2020**, *152*, 210901.
[6] J. F. Stanton, J. Gauss, *et al.* For the current version, see http://www.cfour.de.

Poster 9

Selectivity tuning of graphene quantum dots based trimethylamine gas sensor by tailoring the oxygen functional groups: A DFT based approach

Bruno S. Sampaio[a], Murilo H. M. Facure[b], Rafaela S. Andre[b], Daniel S. Correa[b],
Tiago V. Alves[a], Luiza A. Mercante[a]
[a] Instituto de Química, Universidade Federal da Bahia, Salvador, Brazil
[b] Nanotechnology National Laboratory for Agriculture, Embrapa Instrumentation, 13560-970, São Carlos, São Paulo, Brazil
brunosamp08@gmail.com

When it comes to the design of new gas sensors, the coupling of experimental and computational methods is an effective approach to obtain improved sensing response [1]. In a previous work [2], three graphene quantum dots (GQDs), with different proportions of hydroxyl, carboxyl and epoxy groups, were obtained through a hydrothermal method. In order to evaluate the influence of these functional groups on the GQDs electrical sensor performance, in this work, we investigated the interaction of these GQDs with trimethylamine (TMA) molecule. The sensor with a larger proportion of hydroxyl groups showed the greatest electrical response. To explain this result, potential energy curves were built through scan calculations of the interaction between TMA and three GQDs models (Fig. 1), each with one of the oxygen functional groups at the M06-2X/6-31+G(d,p) level, where three sites were selected for each model.

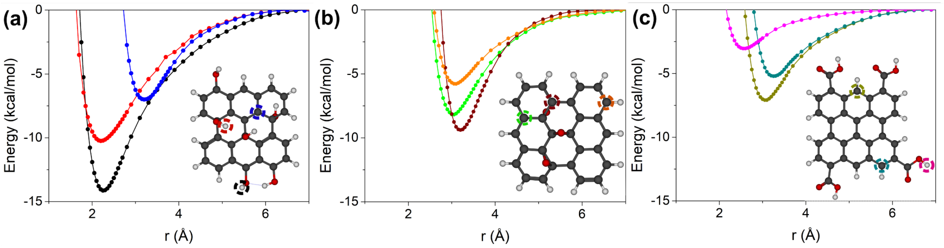


Fig. 1: Potential energy curve of the scan between TMA and a GQDs model with only: (a) hydroxyl groups; (b) epoxy groups; (c) carboxyl groups

To explain the difference in energy of each scan, atoms in molecules and non-covalent interaction analysis were employed at the equilibrium distance of each scan. The GQDs with only OH groups exhibited the greatest dissociation energy, followed by the GQDs with epoxy groups at the carbons closer to the epoxy group. The topological study adopted in this work was able to explain the experimental results.

[1] Z. Yan, Y. Zhang, W. Kang, N. Deng, Y. Pan, W. Sun, J. Ni, X. Kang, *Nanomat.*. 2022, 12, 20..
[2] M. H. M. Facure, R. Schneider, L.A. Mercante, D.S. Correa. *Mater. Tod. Chem.*. 2022, 23.

Poster 10

[1,n]-Metal Migrations for Directional Translational Motion at the Molecular Level

Emma L. Hollis, [a] Michael N. Chronias, [a] Carlijn L. F. van Beek, [a] Paul J. Gates [a] and Beatrice S. L. Collins[a]*

[a] University of Bristol, Bristol, United Kingdom
emma.hollis@bristol.ac.uk
bs.lefanucollins@bristol.ac.uk

We present carbon-to-carbon rhodium migrations as a new approach to mimicking the dynamic association that underpins directional translational molecular level motion displayed by biological systems such as DNA polymerase and myosins.[1] To date, artificial rotaxane or molecular walker systems which display controlled translational molecular level motion either utilise mechanical bonds and ratcheting mechanisms to achieve directional movement.[2] Or, for the walker systems that do not utilise a mechanical bond, the stepwise intervention of an experimentalist is required to achieve directionality.[3] The system detailed herein represents the first example of autonomous directional translational motion at the molecular level in a fully synthetic system that does not rely on mechanical bonds.

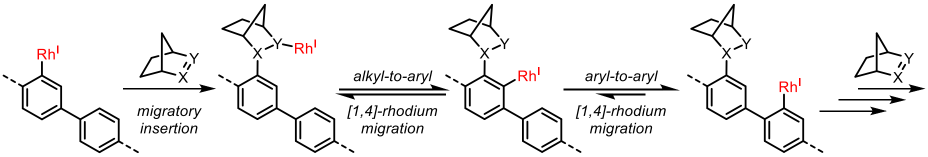


Figure 1: Three-step system using norbornene as a hydrocarbon chemical fuel (X=Y) and rhodium migrations for the directional translation of a rhodium centre along archetypal track 1,4-polypheneylene.

Upon a polyaromatic track, rhodium may be translated unidirectionally *via* repeating cycles of the following three-step process: incorporation of the strained hydrocarbon fuel norbornene (X=Y), followed by an alkyl-to-aryl rhodium migration, then an aryl-to-aryl rhodium migration. The incorporation of large norbornene groups onto various polyaromatic tracks has been shown to ratchet the system and achieve the directional translation of a rhodium centre over extended distances, without the requirement of a mechanical bond.

[1] Breyer, W. A. and Matthews, B.W. *Prot. Sci.* **2001**, 10, 1699.
[2] S. Borsley, D. A. Leigh and B. M. W. Roberts, *J Am Chem Soc*, **2021**, 143, 4414.
[3] M. Von Delius, E. M. Geertsema and D. A. Leigh, *Nature Chemistry,* **2009**, 2, 96.

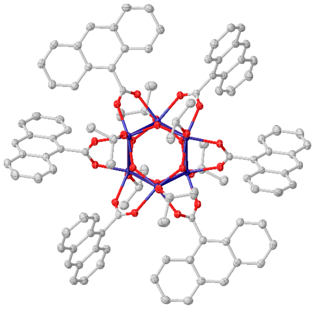
Poster 11

ELEVATING PHOTOCATALYSIS: UNLEASHING THE POTENTIAL OF TITANIUM-OXO CLUSTERS THROUGH HOMO/LUMO GAP ENGINEERING FOR SUSTAINABLE TRANSFORMATIONS

Ashwani Ashwani,[a,b] **Bin Wang,**[b] **Frederik Tielens,**[b] **Frank De Proft,**[b] **Sebastian D. Pike,**[a]
[a]Department of Chemistry, University of Warwick, Coventry, UK
[b]Algemene Chemie, Vrije Universiteit Brussels, Belgium
Email: ashwani.ashwani@vub.be

Abstract: Titanium-dioxide (TiO_2) is a pivotal semiconductor material widely utilized in applications such as self-cleaning windows and photocatalysis[1]. At the nanoscale, titanium-oxo clusters bridge the gap between molecular and materials chemistry, presenting unique opportunities for photocatalytic applications due to their distinctive structural and electronic properties[2]. This study focuses on the electronic structure and photochemical properties of a series of Ti6-oxo clusters and their impact on photocatalytic performance[3]. Through time-dependent density functional theory (TD-DFT) calculations, we demonstrate that the ligand-based energy levels can significantly influence the band structure of these clusters, akin to the HOMO/LUMO gap modulation in nanomaterials[4]. Our findings reveal that varying the ligand environment, including the use of dye and non-dye ligands, can optimise the photocatalytic efficiency by engineering the electronic properties. These insights enhance our understanding of chemical bonding in titanium-oxo clusters and open new avenues for their application in sustainable energy conversion, environmental remediation, and chemical synthesis[5].

Figure: Molecular structure of $[Ti_6O_6(O^iPr)_6(9\text{-}AC)_6]$, H atoms omitted for clarity with Ti (blue), O (red) and C (grey).



References

1. Haider, A. J.; Jameel, Z. N.; Al-Hussaini, I. H. M., *Energy Procedia* **2019,** *157*, 17-29.
2. Schubert, U., *Chemistry – A European Journal* **2021,** *27* (44), 11239-11256.
3. Chen, X.; Mao, S. S., *Chemical Reviews* **2007,** *107* (7), 2891-2959.
4. Krämer, T.; Tuna, F.; Pike, S. D., *Chemical Science* **2019,** *10* (28), 6886-6898.
5. Brown, S. E.; Mantaloufa, I.; Andrews, R. T.; Barnes, T. J.; Lees, M. R.; De Proft, F.; Cunha, A. V.; Pike, S. D., *Chemical Science* **2023,** *14* (3), 675-683.

Poster 12

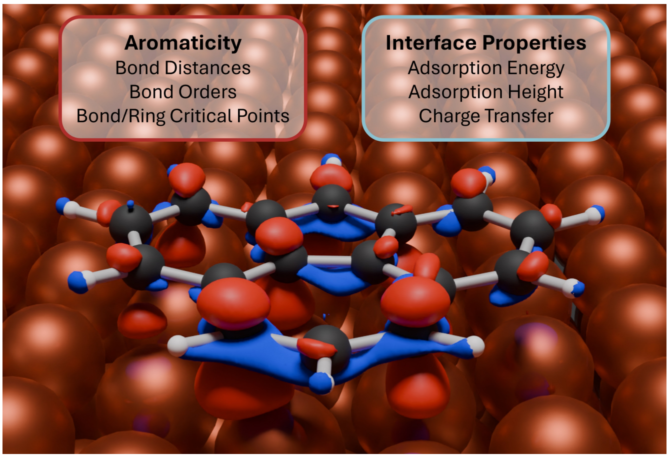
Aromaticity of Adsorbed π-Electron Systems

Jakob Schramm,[a] Ralf Tonner-Zech[a]
[a] Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnéstraße 2, 04103 Leipzig, Germany
jakob.schramm@uni-leipzig.de

The interactions between polycyclic hydrocarbons (PCHs) and metal surfaces are a crucial factor in the performance of organic electronic devices. Therefore, a deeper understanding of such metal-organic interfaces is necessary. An important chemical concept for the description of PCHs is aromaticity. Over the past years, numerous aromaticity indices have been proposed, which can be broadly divided into four categories: energetic, geometric, electronic, or magnetic.

Upon interaction of the π-electron system of a PCH with a metal substrate, the aromaticity of the PCH can, however, be significantly altered. To evaluate this effect, we investigated a set of 11 non-alternant and 11 alternant PCHs adsorbed on a Cu(111) surface. We previously showed that these systems exhibit different strengths of interactions ranging from physisorption to weak and strong chemisorption.[1]

Using density functional theory with periodic boundary conditions, we were able to use geometric and electronic aromaticity indices to investigate the aromaticity of the adsorbed molecules. Comparison with their gas phase aromaticity showed significant changes upon adsorption. Those changes in aromaticity seem to be a promising extension to the usual interfacial properties, addressing effects not covered by them and contributing to a better understanding of metal-organic interfaces.



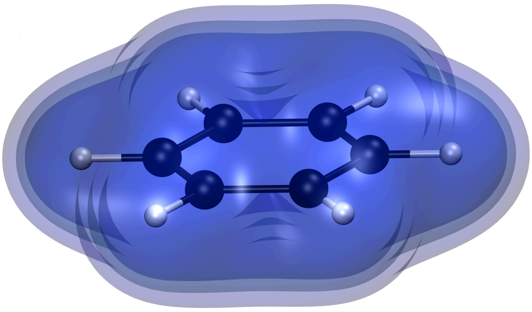
[1] J. Schramm, R. Tonner-Zech, in preparation.

Poster 13

Aromaticity Descriptors under Isotropic Pressure

Jochen Eeckhoudt,[a] Alexander Dellwisch[b], Tim Neudecker[b], Mercedes Alonso[a], Frank De Proft[a]
[a] Vrije Universiteit Brussel, Brussels, Belgium
[b] University of Bremen, Bremen, Germany
Jochen.pedro.eeckhoudt@vub.be

In the past decades, the interest in high pressure chemistry has taken up again, bringing with it developments in quantum mechanical models for describing pressure at the single molecular level. While some of these, such as X-HCFF[1], start from mechanochemical principles, others, such as GOSTSHYP[2], apply the pressure directly through the Hamiltonian operator. These models have allowed for the evaluation and analysis of many atomic and molecular properties[3] and are now used to study the elusive aromaticity concept, which has only been sparsely investigated under pressure[4,5]. In our work, we consider some of the most widely used descriptors and indices for quantifying aromaticity and examine their behaviour under pressure for benzene, the archetypal aromatic system. We consider the effects of different pressure models and determine what causes changes in aromaticity, how they are meaningful and where they (dis)agree.



[1] T., Stauch, *J. Chem. Phys.*, **2020**, 153, 134503.
[2] M., Scheurer, A., Dreuw, E., Epifanovsky, M., Head-Gordon, T., Stauch, *Chem. Theory Comput.*, **2021**, 17, 583.
[3] J., Eeckhoudt, T., Bettens, P., Geerlings, R., Cammi, B., Chen, M., Alonso, F., De Proft, *Chem. Sci.*, **2022**, 13, 9329.
[4] S., Fanetti, M., Citroni, R., Bini, *J. Phys. Chem. C*, **2014**, 118, 13764
[5] N., Casati, A., Kleppe, A.P., Jephcoat, P., Macchi, *Nat. Commun.*, **2016**, 7, 10901.

Poster 14

Study of non-covalent interaction in asphaltene models

Leonardo Baptista,[a] Kelly F. P. Laeber[b], Maurício T. M. Cruz[b]
[a] Departamento de Química e Ambiental, Universidade do Estado do Rio de Janeiro, Faculdade de Tecnologia, Resende – RJ, Brasil
[b] Departamento de Química Geral e Inorgânica, Universidade do Estado do Rio de Janeiro, Rio de Janeiro – RJ, Brasil
leobap@gmail.com
fpkelly@hotmail.com
cruzmtmr@gmail.com

Asphaltenes aggregation is a huge problem for the oil industry since it impacts the oil field production[1]. According to the literature, this issue is associated with the π-π interactions between two or more asphaltene molecules and is impacted by the presence of functional groups in the asphaltene main carbon chain. Also, the injection of gaseous CO_2 back into the oil wells can also affect the aggregation process. This study aims to investigate the non-covalent interactions related to the asphaltene aggregation, considering the coronene moiety (functionalized or not with nitrogen and sulfur) as an asphaltene model. DFT methods were used to obtain the structural and electronic parameters, while QTAIM and the evaluation of the reduced density gradient (RDG) plots were used to access the non-bonded interaction for the coronene dimerization and its interaction with CO_2. Figure 1 presents the RDG for the interaction between non-substituted coronene and CO_2. According to the plot, the attractive interaction is mainly van der Waals interaction, while the QTAIM analysis shows that only carbon and one oxygen interact with the coronene.

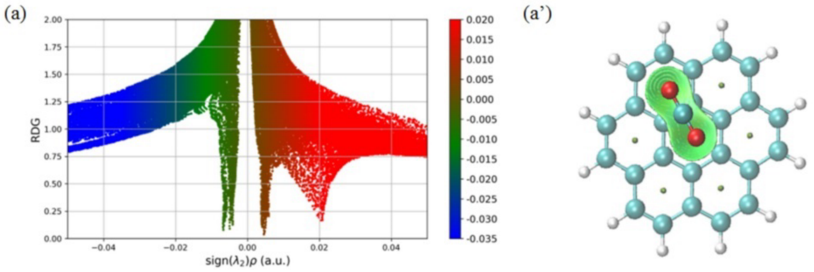


Figure 1: a) 2D plot of the reduced density gradient of the interaction between coronene and CO_2.a') 3D RDG plot.

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[1] Mullins, Oliver C., et al. *Energy & Fuels* **2012,** 26.7, 3986.

Poster 15

Exploring Electronegativity in Reciprocal Space

Parameswaran Parvathy,[a] Alena Vishina[b], Martin Rahm*[a]
[a] Chalmers University of Technology, Gothenburg, Sweden
[b] Uppsala University, Uppsala, Sweden
parvathy.parameswaran@chalmers.se

Electronegativity is a well-known chemical concept that can used to guide and explain molecular structure and behavior. While there are many ways to quantify this useful concept, we prefer to define electronegativity as the average binding energy of valence electrons, $\bar{\chi}$.[1] This definition has made explicit the connection between electronegativity and total energies through an energy decomposition analysis,[2] and allowed the development of a topological partitioning scheme applicable to molecules, [3] and crystals. [4] In this work, we extend the analysis of electronegativity to reciprocal space. Through this development, we introduce a complementary perspective for analyzing electronic structure of extended systems. Electronegativity resolved in reciprocal space, $\bar{\chi}(k)$, can to a first approximation be estimated from averaging energies of occupied crystal orbitals in each reciprocal k-point. The maximal variation of $\bar{\chi}(k)$ over the first Brillouin zone is introduced to quantity the sensitivity of the electronic structure with respect to periodicity, and is shown to distinguish classes of materials, such as covalent, ionic, and molecular crystals within a space group. The maximum variation of $\bar{\chi}(k)$ also shows tantalizing correlation to mechanical hardness.

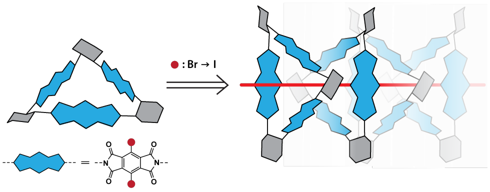
[1] M. Rahm, T. Zeng, R. Hoffman, *J. Am. Chem. Soc.*, **2019**, *141*, 342.
[2] M. Rahm, R. Hoffman, *J. Am. Chem. Soc.*, **2017**, *137*, 10282.
[3] S. Racioppi, M. Rahm, *Chem. Eur. J.*, **2021**, *27*, 18156.
[4] S. Racioppi, P. Hyldgaard, M. Rahm, *J. Phys. Chem.*, **2024**, *128*, 4009.

Poster 16

Crystal Engineering with Molecular Triangles

Sergey Fisher,[a,b] Lorraine A. Malaspina,[b] Cristian Gozálvez Martínez,[c] Alessandro Prescimone,[c] Yaser Balmohammadi,[b] Simon Grabowsky,[b] and Tomáš Šolomek*[a,b]
[a] University of Amsterdam, Amsterdam, The Netherlands
[b] University of Bern, Bern, Switzerland
[c] University of Basel, Basel, Switzerland
s.fisher@uva.nl

Balancing H–bonds and X···X interactions to form supramolecular nanotube



Functional nanoporous materials have the potential to find broad industrial application and to surpass traditional methods in fields such as gas storage and separation, water purification, and energy storage.[1] The metal-organic-frameworks (MOFs) and covalent-organic-frameworks (COFs) are highly porous as reflected in the high surface areas.[2] However, their polymeric nature limits their solubility and complicates post-synthetic modifications without disrupting their crystallinity. Shape-persistent macrocycles can be viewed as basic units of the layers in 2D COFs. However, macrocycles are discrete molecules that allow for a chemical modification prior to the crystallization process.[3] As a result, the formation of both intrinsic and extrinsic voids can be precisely tailored. Here, we will present the synthesis of functionalized macrocyclic equilateral triangles based on pyromellitic diimide substituted with halogens.[4] They direct the intermolecular interactions between individual macrocycles in successive layers in the solid-state varying the packing density. Such manipulation of the crystal structure allows to engineer crystal morphologies with either small intrinsic channels, large extrinsic pores, or columnar superstructures. The nature of the intermolecular interactions is investigated computationally based on structures obtained from single crystal diffraction. Finally, attempts to construct tubular supramolecular co-polymers using halogen-bonding will be disclosed.

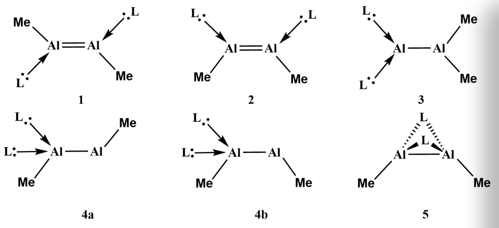
[1] W. R. Dichtel, *Nature*, **2016**, *529*, 190; O. M. Yaghi et al., *Nanotechnol.*, **2020**, *15*, 384.
[2] O. M. Yaghi, *Science*, **2010**, *5990*, 424.
[3] A. I. Cooper, *Adv. Func. Mater.*, **2020**, *30*, 1909832.
[4] J. Gawroński, *Chem. Eur. J.* **2002**, *8*, 2484 ; J. F. Stoddart, *J. Am. Chem. Soc.* **2017**, *139*, 6635.

Poster 17

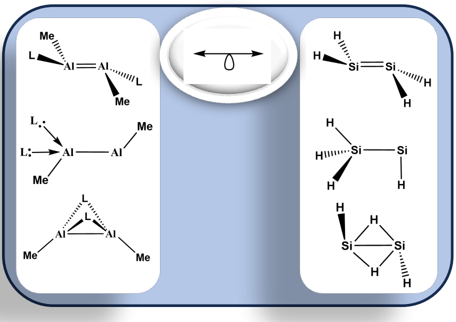
Structure and Bonding in $Al_2Me_2L_2$ (L=CO, PMe_3, NHC, cAAC) isomers isoelectronic to Si_2H_4

Shahnaz Sultana Rohman[a] and Pattiyil Parameswaran[a]*
[a] Department of Chemistry, National Institute of Technology Calicut, Kozhikode 673601, India
*E-mail : param@nitc.ac.in

Abstract: The chemistry of multiple bonding in main group compounds has witnessed remarkable advances after the contravention of the so called ‘double bond rule’. Beginning with the isolation of Si=Si double bond by West and co-workers a plethora of heavier main group multiply bonded compounds have been synthesized.[1] The study of multiple bonding in heavier group 14 and 15 elements is now well-established with merely very few reports on their group 13 analogues.[2,3] Hence an investigation of structure and bonding in multiply bonded aluminum compounds and its comparison with isoelectronic group 14 congeners is expected to provide a nuanced idea of their reactivity and potential applications. Herein, density functional theory-based calculations have been performed to study the structure and bonding in various isomers of $Al_2Me_2L_2$ where L=CO, PMe_3, NHC, and cAAC (Scheme 1). Structural analysis indicates that isomers **1** and **2** possess a typical trans-bent and twisted geometry. Al-Al double bond character is observed in these isomers and validated by molecular orbital analysis. However, NBO analysis shows that the strength of the π-interaction is weaker than that in isolobal Si_2H_4 species. The relative stability of various isomers was gauged to find that **3** is energetically the most stable isomer which is also rationalized based on its high singlet-triplet energy gap.



Scheme 1. Various isomers of $Al_2Me_2L_2$ where L=CO, PMe_3, NHC, cAAC.



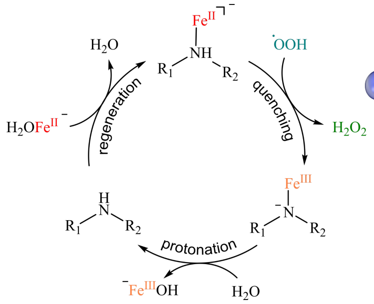
[1] R. West, M. J. Fink, J. Michl, *Science*, **1981**, *214*, 1343.
[2] P. Bag, C. Weetman, S. Inoue, *Angew. Chem. Int. Ed.*, **2018**, *57*, 14394.
[3] C. Weetman, A. Porzelt, P. Bag, F. Hanusch, S. Inoue, *Chem. Sci.*, **2020**, *11*, 4817.

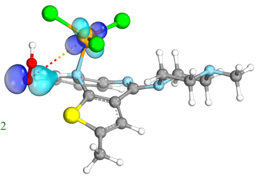
Poster 18

Radical Scavenging and Anti-Ferroptotic Molecular Mechanism of Olanzapine: Insight from a Computational Analysis

Davide Zeppilli,[a] Giacomo Grolla,[a] Valerio Di Marco, [a] Giovanni Ribaudo,[b] and Laura Orian[a]
[a] Dipartimento di Scienze Chimiche, Università degli Studi di Padova, Via Marzolo 1, 35131 Padova, Italy.
[b] Dipartimento di Medicina Molecolare e Traslazionale, Università degli Studi di Brescia, Viale Europa 11, 25123 Brescia, Italy.
davide.zeppilli@phd.unipd.it

Olanzapine is an antipsychotic drug which has been reported to suppress ferroptosis,[1] a recently discovered form of regulated cell death.[2] The ROS scavenging activity of olanzapine is investigated *in silico* using state-of-the-art DFT calculations (level of theory: (SMD)-M06-2X/6-311+G(d,p)//M06-2X/6-31G(d)). Indeed, this reactivity is linked to the therapeutic activity of many antipsychotic drugs and ferroptosis inhibitors.[3] In detail, the distinction between Hydrogen Atom Transfer (HAT) and concerted Proton Coupled Electron Transfer (cPCET) is elucidated for the most reactive sites of the studied molecule. An anti-ferroptotic cyclic mechanism is proposed for ferrostatin-1, a well-known ferroptosis inhibitor,[4] as well as for olanzapine, involving the oxidation of Fe^{II} to Fe^{III}, the quenching of hydroperoxyl radicals and the subsequent regeneration of the reactant (level of theory: M06/6-311+G(d,p),def2TZVP//M06/6-31G(d),LANL2DZ), paving the route to a molecular explanation of this complex biological process.





[1] X. Jiang, X. Teng, H. Shi, L. Cao, L. He, Q. Gu, *Bioorg. Chem.* **2023**, *133*, 106393.
[2] S. J. Dixon, K. M. Lemberg, M. R. Lamprecht, R. Skouta, E. M. Zaitsev, C. E. Gleason, D. N. Patel, A. J. Bauer, A. M. Cantley, W. S. Yang, B. Morrison, B. R. Stockwell, *Cell* **2012**, *149*, 1060–1072.
[3] G. Ribaudo, M. Bortoli, C. Pavan, G. Zagotto, L. Orian, *Antioxidants* **2020**, *9*, 714.
[4] G. Miotto, M. Rossetto, M. L. Di Paolo, L. Orian, R. Venerando, A. Roveri, A.-M. Vučković, V. Bosello Travain, M. Zaccarin, L. Zennaro, M. Maiorino, S. Toppo, F. Ursini, G. Cozza, *Redox Biol.* **2020**, *28*, 101328.

Poster 19

The description of Atom and Bond Reactivity in the Language of Conceptual Density (Matrix) Functional Theory

Bin Wang,[a] Paul Geerlings,[a] Farnaz Heidar-Zadeh,[b] Paul W. Ayers,[c] Frank De Proft [a]

[a] Vrije Universiteit Brussel, Brussels, Belgium
[b] Queen's University, Kingston, Canada
[c] McMaster University, Hamilton, Canada

Bin.Wang@vub.be

In the context of the growing impact of conceptual density functional theory (CDFT) as one of the most successful chemical reactivity theories, response functions up to second order have now been widely applied; in recent years, among others, particular attention has been focused on the analytic evaluation of these response functions and extensions to higher order have been put forward.[1] The traditional CDFT gives sharp definitions for a set of well-known but vaguely defined concepts such as chemical potential (electronegativity) and hardness/softness. In addition, it gives access to regioselectivity, electro-/nucleophilicity through local reactivity descriptors such as the Fukui function and (hyper)polarizability via a nonlocal (non)linear response function.[2-3] In our study, their performances are compared between the analytical approach with the wildly used finite difference approximation. In the same spirit of traditional CDFT, we further extended its matrix formalism called conceptual density matrix functional theory (CDMFT) for the description of the reactivity or property of chemical bonds in molecular systems. With the quantity defined in CDMFT, i.e., Fukui matrix, we illustrate that the derivative of bond order with respect to the number of electrons is closely related to the difference of force constant and bond distance between natural and ionized systems.[4]

[1] P. Geerlings, F. De Proft, W. Langenaeker, *Chem. Rev.*, **2003**, *103*, 1793.
[2] B. Wang, P. Geerlings, C. Van Alsenoy, F. Heider-Zadeh, P. W. Ayers, F. De Proft, *J. Chem. Theory Comput.*, **2023**, *19*, 3223.
[3] B. Wang, P. Geerlings, S. Liu, F. De Proft, *J. Chem. Theory Comput.*, **2024**, *20*, 1169.
[4] B. Wang, P. Geerlings, F. Heider-Zadeh, P. W. Ayers, F. De Proft, to be submitted shortly.

Poster 20

Unravelling the changes in the geometries of sandwich compounds induced by cation-π interactions – a DFT study

Katarina A. Ćeranić,[a] Snežana D. Zarić,[b] Dušan P. Malenov[b]
[a] Innovative Centre of the Faculty of Chemistry, Studentski trg 12-16, Belgrade, Serbia
[b] University of Belgrade – Faculty of Chemistry, Studentski trg 12-16, Belgrade, Serbia.
E-mail address: katarina_ceranic@chem.bg.ac.rs

Ion-π interactions are important in numerous molecular systems. These interactions can be enhanced by the transition metal coordination of aromatic rings, which was previously show on anion-π interactions of benzene half-sandwich compounds,[1] as well as cation-π interactions of ferrocene.[2] In this work, we have studied structural changes in the geometries of three benzene sandwich compounds (Cr(benzene)$_2$, Mo(benzene)$_2$ and W(benzene)$_2$) upon the formation of cation-π interactions. Cation-π complexes of three benzene sandwich compounds with alkali and alkaline earth metal cations, as well as ammonium, were examined by the means of DFT calculations, employing the B3LYP density functional with def2-TZVP basis set. The studied sandwich compounds form stronger cation-π interactions than (uncoordinated) benzene, and these interactions are particularly strong for alkaline earth cations (W(benzene)$_2$/Mg^{2+} interaction has the energy of -196.77 kcal/mol). The formation of these cation-π interactions induces several interesting changes in the geometries of sandwich compounds. Namely, the distance between aromatic rings in the sandwich ($d_{\pi\text{-}\pi}$, Fig. 1) is relatively constant whether or not cation-π interaction is formed. However, cation-π interactions induce the shortening of the $d_{M\text{-}\pi,top}$ distance (Fig. 1) and the lengthening of the $d_{M\text{-}\pi,bottom}$ distance (Fig. 1), and this effect gets more pronounced by the strengthening of cation-π interactions.

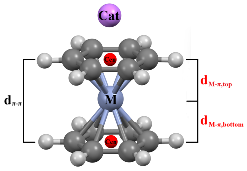


Fig. 1. Cation-π complex of a sandwich compound. **Cat** is for cation; **Cen** is for centroid; and **M** is for a transition metal: Cr, Mo or W.

[1] D. P. Malenov, S. D. Zarić, *Chem. Eur. J.*, **2021**, 27, 17862.

[2] A. H. Ilkhechi, J. M. Mercero, I. Silanes, M. Bolte, M. Scheibitz, H. W. Lerner, J. M. Ugalde, M. Wagner, *J. Am. Chem. Soc.*, **2005**, 127, 10656.

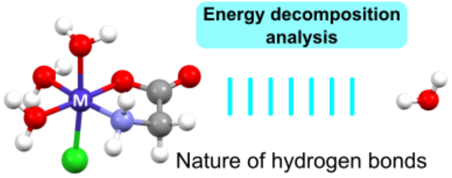
Poster 21

Nature of hydrogen bonds of coordinated glycine complexes with water

Sonja S. Zrilić,[a] Dragan B. Ninković,[a] Mihajlo R. Etinski,[b] Snežana D. Zarić[c]
[a] Innovative Centre of the Faculty of Chemistry, Studentski trg 12-16, Belgrade, Serbia
[b] Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12-16, Belgrade, Serbia
[c] Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, Belgrade, Serbia

sonjaz@chem.bg.ac.rs

Coordinated glycine can form three types of hydrogen bonds with a water molecule: NH/O involving complex's α-amino group as a hydrogen bond donor, O1/HO involving α-hydroxyl O1 oxygen of the complex as a hydrogen bond acceptor, and O2/HO involving complex's α-carbonyl O2 oxygen as a hydrogen bond acceptor. Cambridge Structural Database (CSD) search and quantum chemical calculations were done for various glycine complexes to evaluate the strength of their interactions with a water molecule.[1,2] Energy decomposition analysis was used to elucidate the nature of hydrogen bonds of different metal ion glycine complexes with a water molecule. Both perturbational (Symmetry Adapted Perturbation Theory, SAPT)[3] and variational (Localized Molecular Orbitals Energy Decomposition Analysis, LMO-EDA)[4] were deployed. The values of total interaction energies showed good agreement with CCSD(T)/CBS values. Energy decomposition analysis revealed that the electrostatic interaction is the leading attractive energy term, while orbital relaxation values are also significant. Effects of complex charge, metal oxidation number, complex coordination number, and metal atomic number on all decomposition terms were also evaluated.



[1] S. Zrilić, J. Živković, S. Zarić, *J. Inorg. Biochem.*, **2023**, *242*, 112151.
[2] S. Zrilić, J. Živković, S. Zarić, *J. Inorg. Biochem.*, **2024**, *251*, 112442.
[3] B. Jeziorski, R. Moszynski, K. Szalewicz, *Chem. Rev.*, **1994**, *94*, 1887.
[4] P. Su, H. Li, *J. Chem. Phys.*, **2009**, *131*, 1.

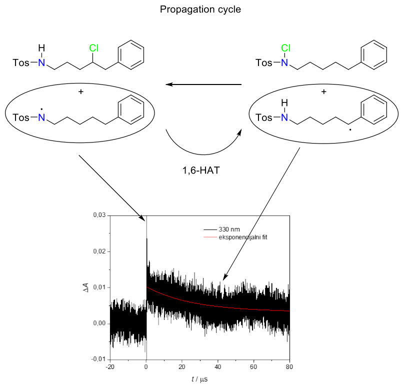
Poster 22

Experimental, computational and kinetic modelling of Hofmann–Löffler–Freytag Reaction

<u>Gabrijel Zubčić</u>,[a] Tomislav Friganović,[a] Luka Adrijanić,[a] Jiangyang You,[b] Iva Džeba,[b]
Kristina Pavić,[a] Erim Bešić,[a] Valerije Vrček,[a] and Davor Šakić[a]
[a] University of Zagreb, Zagreb, Croatia
[b] Institute Ruđer Bošković, Zagreb, Croatia
gabrijel.zubcic@pharma.unizg.hr

The Hofmann-Löffler-Freytag (HLF) reaction is a method for functionalizing distant C-H bonds[1] which predominantly results in the creation of pyrrolidine rings or C5-substituted compounds. This reaction's mechanism involves a rearrangement via 1,5-hydrogen atom transfer (HAT) from an N-centered radical. Studies by Corey[2] and Short[3] groups have reported the formation of C_5- and C_6- halogenated products via 1,5-HAT or 1,6-HAT, while Muniz[4] has selectively made piperidine rings.

Using laser flash photolysis (LFP) with NMR spectroscopy on N-chloro-N-alkyl-tosylamides, N-and C-centered radicals were produced with laser excitation at 266 nm. Experimental absorption peaks were assigned with the aid of TD-DFT calculations. Furthermore, kinetic modeling coupled with extensive DFT calculations were performed of the propagation cycle of HLF. Conclusively, kinetic modelling revealed that this type of HLF reaction is pseudo-first order, which is supported by experimental and computational data.



1. T. Cernak, K. D. Dykstra, S. Tyagarajan, P. Vachal, and S. W. Krska, *Chem. Soc. Rev.*, **2016**, *45*, 546.
2. L. R. Reddy, B. V. S. Reddy, and E. J. Corey, *Org. Lett.*, **2006**, *8*, 2819.
3. M. A. Short, J. M. Blackburn, and J. L. Roizen, *Synlett*, **2020**, *31*, 102.
4. H. Zhang and K. Muñiz, *ACS Catal.*, **2017**, *7*, 4122.

Poster 23

Urea-Based Templates in Pd(II)-Catalyzed C−H Olefination: How Noncovalent Interactions Dictate Regioselectivity

Daniel Arley Santos Oliveira,[a] Ataualpa A. C. Braga[a]
[a] Institute of Chemistry, University of São Paulo, São Paulo, Brazil.
danielarley452@usp.br

The use of molecular templates capable of directing the regioselectivity of C−H functionalization of arenes through noncovalent interactions has received great attention in recent years.[1] In this work, we present a computational study of the palladium (II)-catalyzed aryl C−H olefination reaction employing a urea-based direct template.[2] DFT calculations, along with the Quantum Theory of Atoms in Molecules (QTAIM) and Noncovalent Interaction (NCI) Index, were employed to analyze the key steps of the mechanism and elucidate the origins of reaction regioselectivity. Our results indicate a competition for activation at *meta* and *ortho* positions, while the reaction barriers for *para* C−H activation are consistently higher. In contrast to the experimental proposal,[3] the hydrogen bonds between the N−H bonds of the urea moiety and the carbonyl group from the substrate promote activation at the *ortho* position rather than at the *meta* position. On the other hand, *meta*-selectivity is governed by secondary interactions between the substituent group R (linked directly to the urea group) and the catalyst, which are maximized for R=Ph (Figure 1).

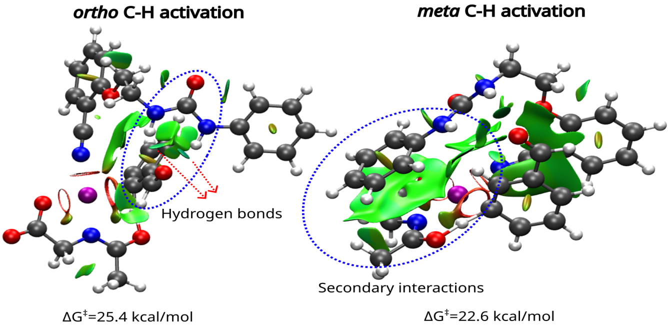


Figure 1: NCI graphs for *ortho* and *meta* C−H activations.

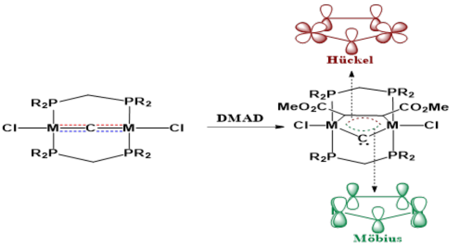
[1] A. Fernández-Figueiras, M. A. Ravutsov, S. P. Simeonov, *ACS omega* **2022**, *7*, 6439.
[2] D. A. S. Oliviera, A. A. C. Braga, Noncovalent Interactions in Palladium(II)-Catalyzed Meta-Selective C−H Functionalization: Mechanistic Insights and Origins of Regioselectivity. Submitted, **2024**.
[3] G. Li, Y. Yan, P. Zhang, X. Xu, Z. Jin, *ACS Catalysis* **2021**, *11*, 10460.

Poster 24

1,3-Dipolar Cycloadduct of Organometallic Allene with Dipolarophile – An Apparent Hückel - Möbius Aromatic Five-membered Organometallic Carbene with Ambiphilic Reactivity

Jishnu Sai Gopinath, [a] Pattiyil Parameswaran[a]
[a] National Institute of Technology Calicut, Calicut, India
jishnusai.upasana@gmail.com

1,3-dipolar cycloaddition reaction is a powerful synthetic reaction for the generation of heterocycles in organic chemistry. However, similar reactions in organometallic chemistry are limited. Here we report the structure and bonding of A-frame μ-carbido compounds $[M_2(\mu\text{-}C)Cl_2(\mu\text{-}dppm)_2]$ (1M, M = Co, Rh, and Ir), their cycloaddition reaction with a dipolarophile, dimethylacetylenediacetate (DMAD) and the structure and bonding of the resulting cycloadduct five-membered bimetallic carbene complexes $[M_2(\mu\text{-}C)(\mu\text{-}DMAD)Cl_2(\mu\text{-}dppm)_2]$ (2M). The geometrical analysis revealed that the carbido complex 1M exhibits a linear M-C-M spine with a planar environment around the metal atom. The bonding analysis indicated that the linear M-C-M spine has a bisallylic anionic type bonding scenario. Accordingly, the carbido carbon atom is highly electrophilic as indicated by the very high values of hydride affinities. The allylic anionic type delocalization enforces the compound 1M to act as 1,3-dipole. Hence, these compounds undergo stepwise cycloaddition reaction with DMAD resulting in five-membered bimetallic carbene 2M. The carbene centre shows ambiphilic reactivity as compared to the nucleophilic reactivity of Arduengo type N-heterocyclic carbene. The five-membered bimetalla cyclic ring has Hückel – Möbius type aromatic delocalization having 10π electrons, which is in contrast to Arduengo type N-heterocyclic carbene which has 6π Hückel-type aromatic delocalization.



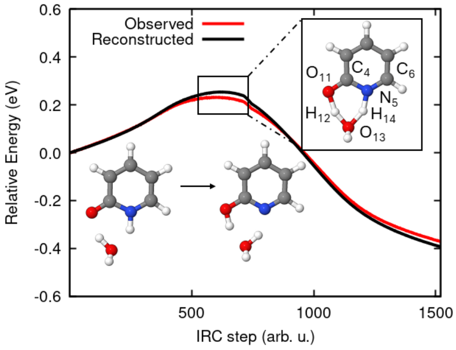
[1] J. S. Gopinath, P. Parameswaran, *Organometallics,* **2024**, 43, 1411.

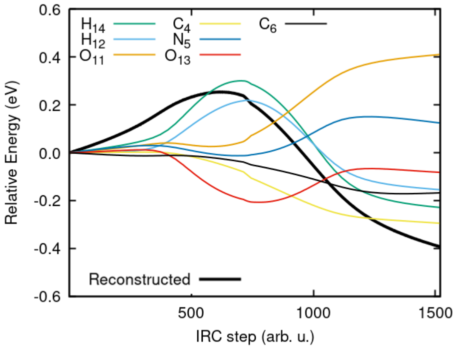
Poster 25

Decoding Reaction Energies An Interacting Quantum Atoms perspective

Miguel Gallegos[a] and Ángel Martín Pendás[a]
[a]Department of Analytical and Physical Chemistry, University of Oviedo, E-33006, Oviedo, Spain.
gallegosmiguel@uniovi.es // miguelgallegosgonzalez@gmail.com

Molecular energies (*E*) play a crucial role in modern chemical science, often used to rationalize fundamental concepts such as reactivity and stability. However, the complex interplay between kinetic (*T*) and potential (*V*) energy contributions can obscure significant features during dynamic processes, making it challenging to fully capture the nuances of molecular behaviour through conventional energy analysis. To address this, physically rigorous energy partitioning schemes, such as the Interacting Quantum Atoms (IQA) approach, [1] provide a detailed perspective by decomposing the molecular energy into locally defined atomic and interatomic terms. Unfortunately, the combinatorial growth of these local energy contributions complicates the identification of the dominant features influencing *E*, particularly in large systems. In this work, we introduce a novel strategy to efficiently identify the dominant atomic and interatomic interactions that govern the evolution of total molecular energy in dynamic scenarios. By leveraging a machine learning (ML) approach combined with the high-speed PM7-IQA energy decomposition, [2] our technique offers a systematic and scalable solution to uncover critical energy contributions that might otherwise remain hidden. We demonstrate the effectiveness of our method across a variety of chemical reactions, showcasing its potential to enhance our understanding of reaction dynamics and energetics. This study not only advances the application of ML in chemical analysis but also paves the way for exploring complex energetic landscapes in molecular systems without the biases inherent in manual analysis, in line with the REG approach.[3]





[1] E. Francisco, Á. Martín Pendás and M. A. Blanco, *J. Chem. Theory Comput.*, **2006**, 2, 90–102.

[2] H. Salazar-Lozas, J. M. Guevara-Vela, Á. Martín Pendás, E. Francisco and T. Rocha-Rinza, Phys. *Chem. Chem. Phys.*, **2022**, 24, 19521–19530.

[3] J. C. R. Thacker and P. L. A. Popelier*, Theor Chem Acc*, **2017**, 136.

Poster 26

H-Bonds between 1,3-Cyclopentadiene Derivatives and Water Clusters: Impact on Photochemical Ionization Pathways

Murillo H. Queiroz, [a] Suelen A. Santos [a], Bruno S. Sampaio [a] Tiago V. Alves, [a]
Roberto Rivelino[b]
[a] Instituto de Química, Universidade Federal da Bahia, Salvador, Bahia, Brazil
[b] Instituto de Física, Universidade Federal da Bahia, Salvador, Bahia, Brazil
murillo.halo@ufba.br

In this investigation we explore intermolecular interactions between 1,3-cyclopentadiene and its cyano derivatives and water clusters considering astrochemical conditions. The recent discovery of Aromatic Hydrocarbons (AHs) like 1,3-cyclopentadiene (CPD) and its cyano derivatives [1] in Taurus molecular cloud has spurred theoretical investigations into molecular clusters formation in space [2]. By using density-functional theory (DFT) and time-dependent DFT (TD-DFT), we examine the stability, H-bonding patterns, and ionization potentials of AH-water complexes. Key findings reveal that H-bonding (O-H···π and O-H···N) significantly influences the stability and ionization energies of these clusters.

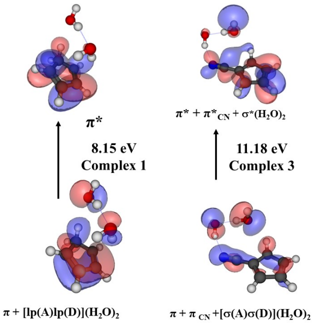


Figure.1. Molecular orbitals involved in the main CT transitions.

Our results show distinct electronic transitions and absorption properties of AH-water complexes under vacuum ultraviolet (VUV) radiation, crucial for understanding photochemical processes and molecular rearrangements in space. The research provides insights into the initial steps of AH formation and the dynamics of ionization processes influenced by H-bonding configurations.

[1] J. Cernicharo, M. Agúndez, C. Cabezas, B. Tercero, N. Marcelino, J.R. Pardo, P. de Vicente, Astron. Astrophys., 2021, 649, L15.

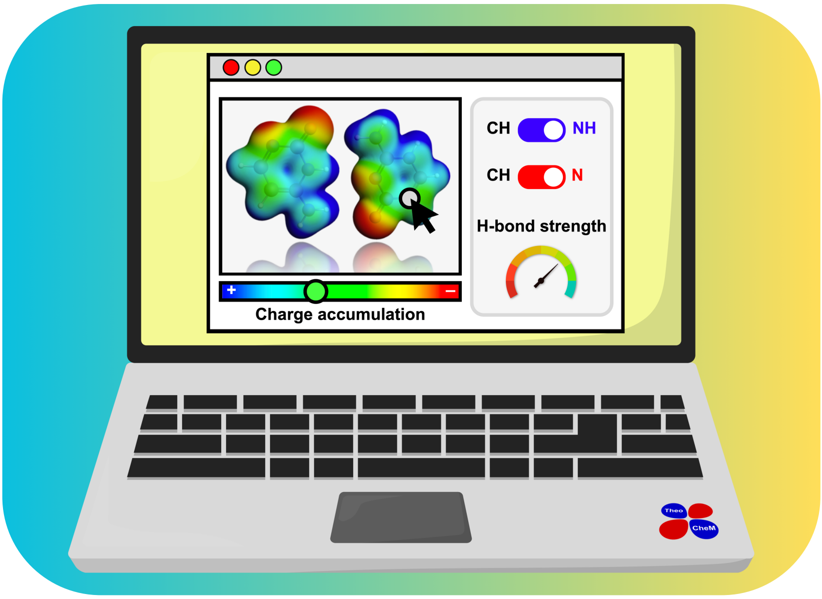
[2] M.H. Queiroz, S.A. Santos, B.S. Sampaio, T.V. Alves, R. Rivelino, Spectrochim. Acta A Mol. Biomol. Spectrosc., 2024, 320, 124637.

Poster 27

Multiple hydrogen-bonded dimers: Are only the frontier atoms relevant?

Celine Nieuwland,[a] David Almacellas,[b] Mac M. Veldhuizen,[a]
Lucas de Azevedo Santos,[a] Jordi Poater,[b,c] Célia Fonseca Guerra[a]
[a] Department of Chemistry and Pharmaceutical Sciences, Vrije Universiteit Amsterdam
[b] Universitat de Barcelona, Barcelona, Catalonia, Spain
[c] ICREA, Barcelona, Catalonia, Spain
c.nieuwland@vu.nl

Non-frontier atom exchanges in hydrogen-bonded aromatic dimers can induce significant changes in the intermolecular interaction energy (up to 6.5 kcal mol^{-1}). Our quantum-chemical analyses reveal that the relative hydrogen-bond strengths of *N*-edited guanine–cytosine base pair isosteres, which cannot be explained from the frontier atoms, follow from the charge accumulation in the monomers.[1] These findings challenge the concept of explaining hydrogen-bond strengths by the frontier atoms, revealing that the strength of the electrostatic interactions, as well as the orbital interactions, are determined by the whole backbone of the hydrogen-bond donor and acceptor fragments.



[1] C. Nieuwland, D. Almacellas, M. M. Veldhuizen, L. de Azevedo Santos, J. Poater, C. Fonseca Guerra, *Phys. Chem. Chem. Phys.* **2024**, *26*, 11306.

Poster 28

Tackling the Jastrow parameter instability with orthogonal Laguerre polynomials

Vladimir Terzi,[a] Arne Lüchow[a]

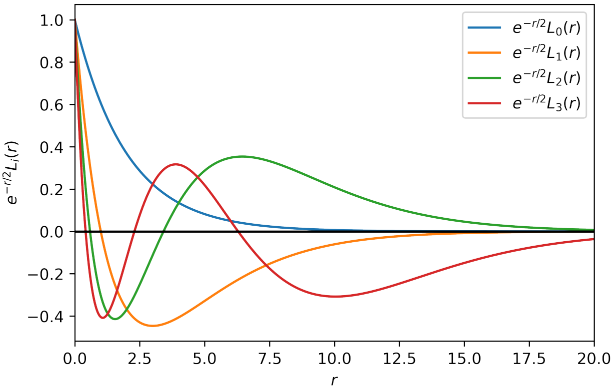
[a] Institute of Physical Chemistry, RWTH Aachen University, Germany

terzi@pc.rwth-aachen.de

For highly accurate wave functions, electron correlation has to be taken into account. This can be achieved by constructing a wave function as an expansion of Slater determinants. However, the number of determinants and, therefore, the computational complexity of such an ansatz grows with the factorial of the system size. Another approach to include correlation into a wave function is multiplying the expansion (or a single Slater determinant) with a Jastrow factor e^U, which leads to a more compact representation with significantly fewer determinants required. However, the ideal analytical form of the function U—the explicit function of particle distances—is unknown.

Commonly, a truncated power series of scaled distances is used. Here, the distances are scaled to fit in the interval [0, 1) with a sigmoidal function. However, the extension of this ansatz to high orders is problematic since the coefficients of higher powers are near-linear dependent, which renders their optimization unstable.

As is shown in this work, an ansatz with orthogonal polynomials is a promising alternative. Since distances are defined on the positive set of real numbers, the Laguerre polynomials with an exponential weighting factor are a suitable choice. Their use improves the stability of the optimization in comparison to the power series ansatz.



[1] V. Terzi, A. Lüchow, u*npublished manuscript.*

Poster 29

Understanding the Bonding of N-heterocyclic Carbenes on Pd/Cu(111) Single Atom Alloys

Scott M. Simpson,[a]
[a] Department of Chemistry, St. Bonaventure University, St. Bonaventure, NY, 14778, USA
ssimpson@sbu.edu

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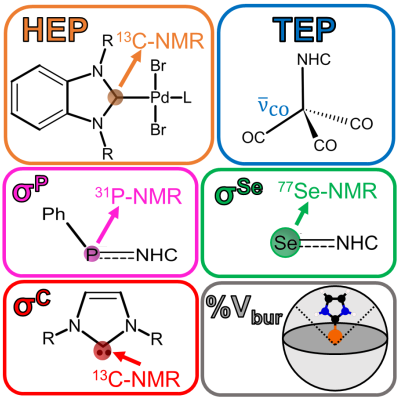
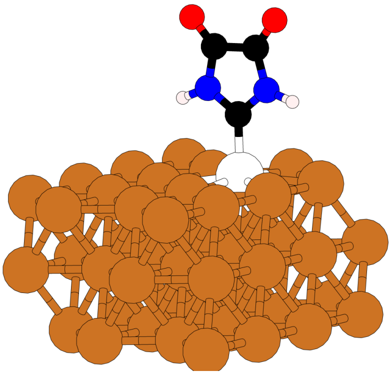




N-heterocyclic carbenes(NHCs) have garnered the attention of material scientists and chemists for their tunable electronic properties. NHCs anchored to surfaces have attractive features and may provide new applications that traditional self-assembled monolayers (SAMs) have yet to be employed. In-fact, NHCs have been utilized to functionalize surfaces to tune reactivity and/or selectivity. However, the underlying mechanisms to control the surface-adsorbate interaction is still in its infancy, especially for SAAs. Herein we utilize periodic non-local density functional theory (DFT) in conjunction with molecular DFT calculations to better understand how changing the NHC backbone influences the bonding between the surface and the adsorbate with the end goal to utilize a relatively new mechanism to store hydrogen.[2,3] To further rationalize the bonding mechanism of NHCs to SAAs explore different spectroscopic techniques to explain the bonding mechanisms.

[1] H.V. Huynh. *Chem. Rev.*, **2018**, *118*, 9457.
[2] M. Hanson, S. Simpson. *ACS Omega*, **2023**, 8, 37402.
[3] S. Simpson. *JCIS Open*, **2021**, *3*, 100013.

Poster 30

Experimental Reconstruction of one-electron reduced density matrices

Sizhuo YU,[a] Jean-Michel GILLET[a]

[a] *Structures, Properties and Modelling of Solids lab., CentraleSupelec, Paris-Saclay University,*
3 rue Joliot-Curie, 91191 Gif-sur-Yvette, France
sizhuo.yu@centralesupelec.fr

The experimental determination of electronic behaviours has been an important counterpart to theoretical computations in chemistry. For example, X-ray diffraction measurements of crystals can be used to obtain the charge density and related chemical bonding information [1]. Beyond charge densities, the one-electron reduced density matrix (1-RDM), a one-particle complete description of electrons, can also in principle be reconstructed from experiments. Starting with the work of Clinton [2], the 1-RDM reconstruction problem has been at the centre of the interplay between crystallography and quantum chemistry, namely the field of quantum crystallography [3,4].

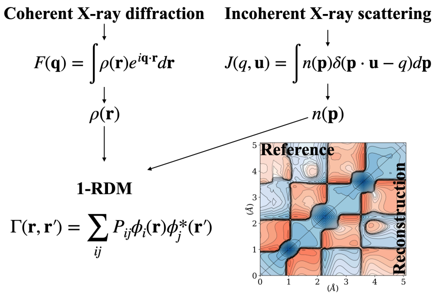


Figure 1: *A schematic illustration of experimental 1-RDM reconstruction. The figure on the lower right shows the reconstructed and reference 1-RDM on the O-C-N-H path of urea molecule in our numerical test.*

We will briefly introduce the history of experimental reconstruction of 1-RDMs and its relation to charge density refinements and report our latest results of 1-RDM reconstruction from joint use of position and momentum space measurements [5-7]. In our approach, the restricted active space 1-RDM is fitted to the experimental data while necessary constraints such as symmetry and N-representability conditions are guaranteed using convex programming. A numerical validation is carried out on the (non-centrosymmetric) urea crystal using corrupted artificial data to assess the robustness and quality of this method. Finally, our latest results using actual experimental data will be briefly discussed.

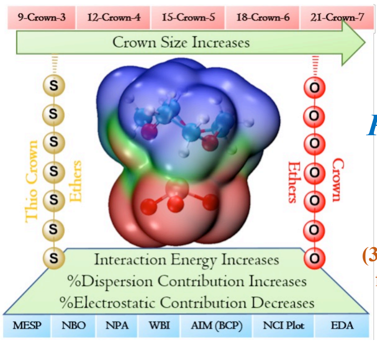
[1] Gatti, C., and Macchi, P., *Modern Charge-Density Analysis*, **2011**, Springer
[2] Clinton, W. et al., *Phys. Rev.,* **1969**, 177, 1, 1
[3] Massa, L. and Matta, C. F., *J. Comput. Chem.,* **2018**, 39.17, 1021
[4] Genoni, A. and Macchi, P., *Crystals,* **2020**, 10.6, 47,
[5] De Bruyne, B. and Gillet, J.-M., *Acta Cryst. A,* **2020**, 76.1. 1
[6] Launay, Y., and Gillet, J.-M., *Acta Cryst. B,* **2021**, 77.5, 683
[7] Yu, S. and Gillet, J.-M., *Acta Cryst. A,* **2024**, 80.3, 249

Poster 31

Going where Experimentalists Fear to Tread: Computational Chemistry to the Rescue in Understanding XeO_3 Chemistry

Soumya Ranjan Dash,[a, b] Kumar Vanka*[a, b]
[a] Physical and Materials Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pashan, Pune-411008, India
[b] Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India
srdchem@gmail.com, *k.vanka@ncl.res.in*

The hazardous nature of XeO_3 makes computational studies an ideal means of exploring its new chemistry.[1,2] To enhance the stability of this highly explosive and shock-sensitive compound, DFT calculations were conducted to investigate its potential complexation with crown ethers and their thio (-S) and aza (-NR) analogues.[3,4] Interestingly, aza-crowns exhibited superior binding to XeO_3 compared to their oxygen and thio counterparts. However, while the binding affinity was observed to increase with the size of the crown ethers in the latter cases, aza-crowns showed a variable size preference, peaking with aza-15-crown-5 and decreasing thereafter. Significant contributions from secondary C-H…O interactions were found to strengthen the σ-hole-mediated aerogen bonding in these complexes. Additionally, a rare Xe…Xe interaction was observed to influence the coordination number of xenon in a 1:2 complex of 18-crown-6 with two XeO_3 molecules, resulting in a first-of-its-kind inverse sandwich complex for a noble gas compound.[5]



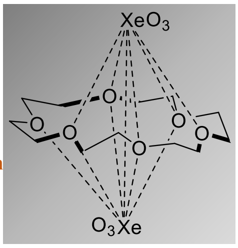
Inverse Sandwich Complex of XeO_3

Powered By

(1) Aerogen Bonding

(2) C-H…O Interactions

(3) Back-Donation from Lone Pair of Xe



[1] A. Bauzá, A. Frontera, *Angew. Chem. Int. Ed.*, **2015**, *54*, 7340.
[2] S.R. Dash, K.Vanka, *ChemPhysChem*, **2024**, *25*, e202300908.
[3] S.R. Dash, H. Sharma, M.K. Tiwari, L. Greb, K. Vanka, *Inorg. Chem.*, **2024**, *63* (9), 4099.
[4] S.R. Dash, K.Vanka, *ChemPhysChem*, **2024**, e202400302.
[5] S.R. Dash, K. Vanka, *Inorg. Chem.*, **2024** (Just Accepted: 10.1021/acs.inorgchem.4c01744)

Poster 32

Stabilization of Diborynes versus Destabilization of Diborenes by Coordination of Lewis bases

Lucas de Azevedo Santos,[a] F. Matthias Bickelhaupt,[a] M. Solà[b]
[a] Vrije Universiteit Amsterdam, Amsterdam, The Netherlands
[b] University of Girona, Girona, Catalonia, Spain.
l.deazevedosantos@vu.nl

Metallomimetic elements are the main group elements that mimic the behavior and properties of transition metals like coordination chemistry and reactivity.[1] Because of the environmental problems and high cost of transition metals, metallomimetic elements like boron have emerged as a green and cheaper alternative.[2] The metallomimetic behavior of boron is observed in one boron center connected by single or multiple B–B bonds like diboranes (B–B) that are stabilized by electron-donating ligands (L) as in diborenes ($L_2B{=}BL_2$) and diborynes ($LB{\equiv}BL$). We have quantum chemically investigated the boron-boron bonds in B_2, diborynes B_2L_2, and diborenes $B_2H_2L_2$ (L=none, OH_2, NH_3) using dispersion-corrected relativistic density functional theory at ZORA-BLYP-D3(BJ)/TZ2P.[3] B_2 has effectively a single B–B bond provided by two half π bonds, whereas B_2H_2 has effectively a double B=B bond provided by two half π bonds and one σ 2p–2p bond. This different electronic structure causes B_2 and B_2H_2 to react differently to the addition of ligands. Thus, in B_2L_2, electron-donating ligands shorten and strengthen the boron-boron bond whereas, in $B_2H_2L_2$, they lengthen and weaken the boron-boron bond. The aforementioned variations in boron-boron bond length and strength become more pronounced as the Lewis basicity of the ligands L increases.

[1] P. P. Power, *Nature*, **2010**, *463*, 171.
[2] M.-A. Légaré, C. Pranckevicius, H. Braunschweig, *Chem. Rev.*, **2019**, *119*, 8231.
[3] L. de Azevedo Santos, D. E. Trujillo-González, J. O. C. Jiménez-Halla, F. M. Bickelhaupt, M. Solà, *Chem. Eur. J.*, **2024**, *30*, e202303185.

Poster 33

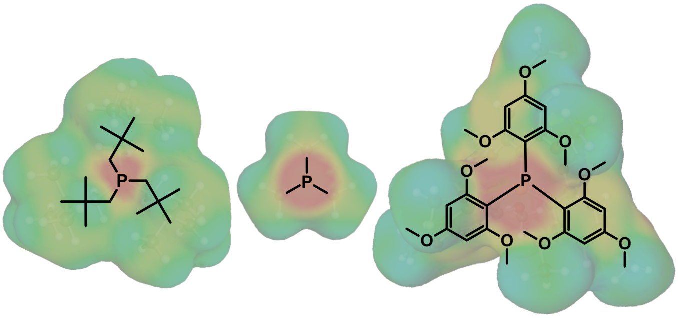
pK_{aH} values and θ_H angles of phosphanes to predict their electronic and steric parameters

Marta-Lisette Pikma,[a] Sofja Tshepelevitsh,[a] Sigrid Selberg,[a]
Ivari Kaljurand,[a] Ivo Leito,[a] Agnes Kütt [a]

[a] Institute of Chemistry, University of Tartu, Tartu, Estonia
agnes.kutt@ut.ee

Phosphanes play an important role in various applications, serving as a class of organic bases with basicities spanning more than 30 orders of magnitude. In this poster, we present basicities (pK_{aH} values) of a diverse set of phosphanes, both newly measured and calculated. [1] We demonstrate that pK_{aH} values can serve as an alternative to Tolman electronic parameters (TEP values) in evaluating the electronic properties of phosphanes. Additionally, we demonstrate parameters for assessing the steric properties of phosphanes without the need for preparation or calculation of metal-ligand complexes.

pK_{aH} values and angles from COSMO structures to predict electronic and steric properties of 56 phosphanes



pK_{aH}	12.8	15.48	19.66
θ_{CPC}	110°	111°	115°
θ_H	284°	163°	275°

[1] M.-L. Pikma, Kütt, S.Tshepelevitsh, S. Selberg, I. Kaljurand, I. Leito, A. Kütt *Dalton Trans.* **2024**, 10.1039/D4DT01430H.

Poster 34

BenzAI
A Versatile Tool for Generating and Analyzing Benzenoid Structures

Yannick Carissan,[a] Denis Hagebaum-Reignier[a], Nicolas Prcovic[b], Cyril Terrioux[b] and Adrien Varet[b]
[a] Aix Marseille Univ, CNRS, Centrale Marseille, ISM2, Marseille, 13013 France
[b] Aix Marseille Univ, Université de Toulon, CNRS, LIS, Marseille, 13013 France
yannick.carissan@univ-amu.fr

Benzenoids are an important class of polycyclic aromatic hydrocarbons with applications in materials science, astrochemistry, and organic synthesis. We present BenzAI[1], an open-source software that enables the systematic generation and analysis of benzenoid structures. Using constraint programming techniques, BenzAI can generate benzenoids with specified properties such as number of rings, symmetry, and irregularity. It provides capabilities for electronic structure analysis including local aromaticity calculations, Clar covers, and ring bond orders. BenzAI also interfaces with a database of computed infrared spectra for benzenoids up to 10 rings. We demonstrate BenzAI's utility through several case studies, including the exploration of highly irregular large benzenoids relevant to astrochemistry and the design of concealed non-Kekuléan structures with interesting magnetic properties. BenzAI provides a powerful and flexible platform for investigating the vast chemical space of benzenoid molecules.

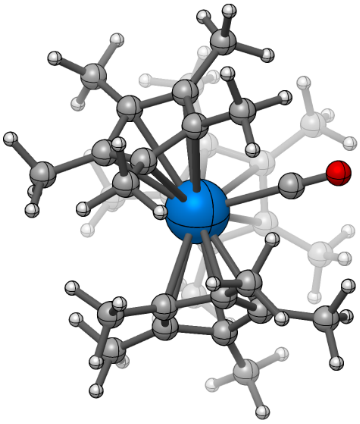
[1] Varet, A.; Prcovic, N.; Terrioux, C.; Hagebaum-Reignier, D.; Carissan, Y., *J. Chem. Inf. Model.* **2022**, *62*, 2811

Poster 35

Revisiting the U–CO bond in $(Cp^*)_3UCO$: An Energy Decomposition Analysis Perspective

Juan José Moreno,[a] Alejandra Pita-Milleiro,[a] Israel Fernández[b]
[a] Instituto de Investigaciones Químicas (IIQ), Consejo Superior de Investigaciones Científicas (CSIC) and Universidad de Sevilla, Spain
[b] Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Spain
juanj.moreno@iiq.csic.es

In 1987, Bursten and co-workers proposed a classical metal-centered backdonation model for Cp_3UCO, similar to that proposed for transition metals.[2] In 2009, Eisenstein and co-workers challenged this scheme, proposing that backdonation originated not from nonbonding metal-based orbitals but from filled ligand-based orbitals with π-symmetry used for bonding in the $[Cp_3U]$ fragment.[3] This latter model aimed to rationalize the significant substituent effect in found in these complexes. Our EDA-NOCV results bridge these two models by quantifying the participation of U-centered SOMOs and Cp*–U π orbitals in the backdonation. Our findings indicate that both contributions are present, in agreement with the high degree of backdonation and its dependency on Cp substituents.



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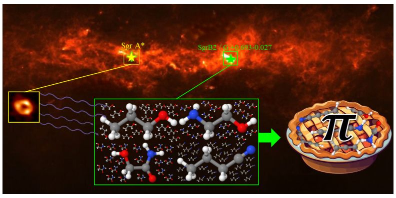
[2] B. E. Bursten, R. J. Strittmatter *J. Am. Chem. Soc.* **1987**, *109*, 6606.
[3] L. Maron, O. Eisenstein, R. A. Andersen, *Organometallics* **2009**, *28*, 3629.

Poster 36

More please: what drives the formation of unsaturated molecules in Interstellar medium?

Jhoan Londoño-Restrepo,[a] Santiago Gómez,[b] Heidy M. Quitián-Lara,[c] Felipe Fantuzzi,[d] Albeiro Restrepo *[b]
[a] Instituto de Física, Universidad de Antioquia UdeA, Calle 70 No. 52-21,Medellín, Colombia.
[b] Instituto de Química, Universidad de Antioquia UdeA, Calle 70 No.52-21, Medellín 050010, Colombia
[c] School of Physics and Astronomy, Ingram Building, University of Kent, Park Wood Rd, Canterbury CT2 7NH, UK
[d] School of Chemistry and Forensic Science, Ingram Building, University of Kent, Park Wood Rd, Canterbury CT2 7NH, UK
jhoan.londono1@udea.edu.co

A large number of molecules have been detected in the Sagittarius B2 (SgrB2) interstellar molecular reservoir near the center of the Milky Way [1], among them, four complex organic molecules are the subject of this study: Butanonitrile [2], Ethanolamine [3], Propanol [4], and Glycolamide [5], which are highly saturated. We investigate their fragmentation pathways using Born-Oppenheimer molecular dynamics and analyze post-ionization behavior. Breaking of the central C-C bond is observed In the main fragmentation pathways of all molecules leading to the formation of radical cations characterized by 2c-1e bonds. A pre-dissociative complex for the four radical cations is characterized by bond orders in the vicinity of 0.5 and the number of electrons obtained from the integration of the ELF and AdNDP basins is very close to 1. By studying the dissociation of the central C-C bond in these radical cations we found a transition state connecting two energy minima for ethanolamine and glycolamide. In this process the charge density of the unpaired electron shifts from a heteroatom to the C-C sigma bond as the C-C bond dissociates. Our results indicate that without the need of the catalytic surfaces provided by cosmic dust, the highly energetic radiation in the neighborhood of the super massive black hole at the center of our galaxy is sufficient to induce the chemical reactions that lead to the production of highly unsaturated chains that have also been detected in high abundances.



[1]. B. A. McGuire, The Astrophysical Journal Supplement Series 2022, 259, 30.
[2] A. Belloche, R. Garrod, H. Müller, K. Menten,C. Comito, P. Schilke, Astronomy & Astrophysics 2009, 499, 215.
[3] V. M. Rivilla, I. Jiménez-Serra, J. Martín-Pintado, C. Briones, L. F. Rodríguez-Almeida, F. Rico-Villas, B. Tercero, S. Zeng, L. Colzi, P. de Vicente, et al., Proceedings of the National Academy of Sciences 2021,118, e2101314118.
[4] I. Jiménez-Serra, L. F. Rodríguez-Almeida, J. Martín-Pintado, V. M. Rivilla, M. Melosso, S. Zeng, L. Colzi,Y. Kawashima, E. Hirota, C. Puzzarini, et al., Astronomy & Astrophysics 2022, 663, A181.
[5] V. M. Rivilla, M. Sanz-Novo, I. Jiménez-Serra,J. Martín-Pintado, L. Colzi, S. Zeng, A. Megías, Á. López-Gallifa, A. Martínez-Henares, S. Massalkhi,et al., The Astrophysical Journal Letters 2023, 953,L20.

Poster 37

Revisiting Rotational Isomerism of Organic Compounds

Daniela Rodrigues Silva,[a] Trevor A. Hamlin,[a] Célia Fonseca Guerra,[a]
F. Matthias Bickelhaupt[a]
[a] Department of Chemistry and Pharmaceutical Sciences, Vrije Universiteit Amsterdam
d.rodriguessilva@vu.nl

A firm grasp of the driving forces behind conformational isomerism is crucial for the rational design of molecules with tailor-made properties. With this in mind, we reinvestigate the rotational isomerism around the C–C bond in archetypal organic compounds within the framework of Kohn-Sham molecular orbital (KS-MO) theory. Our bonding analyses reveal that overall rotational energy profiles are *always* set by steric repulsion between occupied–occupied orbitals. However, the conformational preferences can be shifted if one of the two requirements are met: i) if the relative steric repulsion is too weak and thus easily counteracted by subtle attractive interactions (*e.g.*, hyperconjugation[1]; **1** → **2**, Fig. 1); or ii) if stronger intramolecular interactions take place (*e.g.*, hydrogen bonding[2]; **1**→ **3**, Fig. 1). Our analyses lead to a novel, fundamentally revisited picture of the physical mechanisms behind well-known conformational effects in organic chemistry.

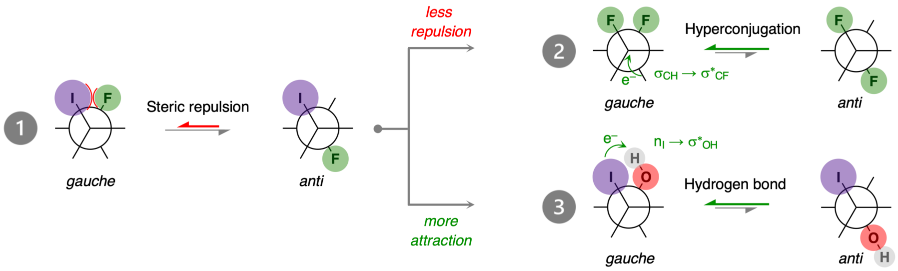


Figure 1. Conformational preferences of 1,2-disubstituted ethanes.

[1] D. Rodrigues Silva, L. de Azevedo Santos, T. A. Hamlin, C. Fonseca Guerra, M. P. Freitas, F. M. Bickelhaupt, *ChemPhysChem*, **2021**, *22*, 641.

[2] F. A. Martins, L. de Azevedo Santos, D. Rodrigues Silva, C. Fonseca Guerra, F. M. Bickelhaupt, M. P. Freitas, *J. Org. Chem.*, **2022**, *87*, 11625.

Poster 38

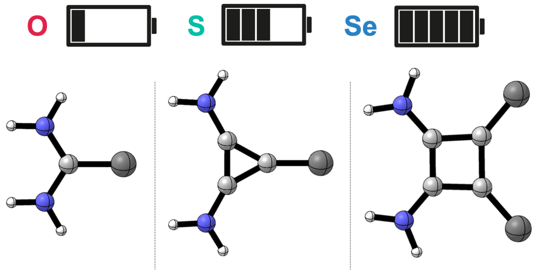
Effect of Chalcogen Atom Size on Hydrogen Bond Strength in Amide-based Linear Polymers

Siebe Lekanne Deprez[a], Lucas de Azevedo Santos[a], Celine Nieuwland[a], David Almacellas[b], Jordi Poater[b,c], Pascal Vermeeren[a], Célia Fonseca Guerra[a]

[a] Department of Chemistry and Pharmaceutical Sciences, Vrije Universiteit Amsterdam, Amsterdam, The Netherlands
[b] Departament de Química Inorgànica i Orgànica & Institut de Química Teòrica I Computacional, Universitat de Barcelona, Barcelona, Spain
[c] ICREA, Barcelona, Spain
s.j.lekanne.deprez@vu.nl

Supramolecular linear chains of urea, deltamide, and squaramide have the potential to form complex supramolecular structures due to their capability of forming hydrogen bonds[1], but what are the implications considering their sulfur and selenium analogues? Previous work with urea showed that substituting sulfur and selenium for oxygen leads to an unexpected increase in hydrogen-bond donor strength[2]. Our current work extends these insights to the supramolecular realm, utilizing dispersion-corrected density functional theory (ZORA-BLYP-D3(BJ)/TZ2P) to explore how these chalcogen substitutions influence hydrogen bonding in linear chains composed of urea, deltamide, and squaramide building blocks[3]. We reveal that as the chalcogen size increases, the larger chalcogen withdraws more charge from adjacent amino groups, amplifying the positive character of hydrogen donors and strengthening their interaction with negatively charged acceptors. This nuanced interplay of forces expands the toolkit for designing supramolecular assemblies with tailored properties.

Hydrogen-Bond Donor Capability



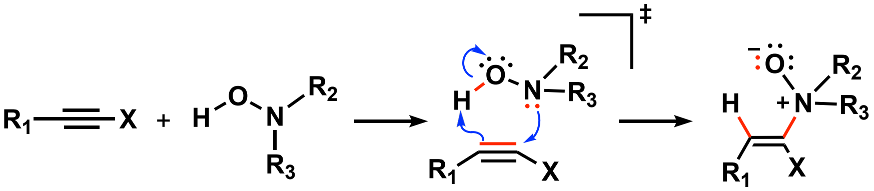
[1] L. de Azevedo Santos, D. Cesario, P. Vermeeren; S.C.C. van der Lubbe, F. Nunzi, C. Fonseca Guerra, *Chempluschem,* **2022**, *87* (2).
[2] C. Nieuwland, C. Fonseca Guerra, *Chem-Eur. J.,* **2022**, *28* (31).
[3] S. Lekanne, Deprez, L de Azevedo Santos, C. Nieuwland, D. Almacellas, J. Poater, P. Vermeeren, C. Fonseca Guerra, *Ready of Submission*

Poster 39

Understanding the Retro-Cope Reaction of Linear Alkynes

Steven Beutick,[a,b] Song Yu,[a] Laura Orian,[b] F. Matthias Bickelhaupt,[a,c,d] Trevor A. Hamlin[a]
[a] Vrije Universiteit Amsterdam, Amsterdam, The Netherlands
[b] Università degli Studi di Padova, Padova, Italy
[c] Radboud University, Nijmegen, The Netherlands
[d] University of Johannesburg, Johannesburg , South Africa
Steveneelco.beutick@phd.unipd.it

We have quantum chemically investigated the bioorthogonal retro-Cope reaction of linear alkynes R3C–C≡C–X (R3 = combinations of H, MeO, F; X = H, F, Cl, Br, I) with and N,N-dimethylhydroxylamine using relativistic density functional theory at ZORA-BP86/TZ2P. This novel reaction can be tuned through judicious substitution of the alkyne at both the terminal and propargylic position to render second-order kinetics that rival and out-compete strain-promoted variants.[1,2] Using our activation strain and quantitative MO analyses, we are the first to tease apart the physical factors at the root of this reactivity enhancement upon terminal or propargylic substitution of propyne.



[1] a) D. Kang, J. Kim, J. Am. Chem. Soc. 2021, 143, 5616–5621; b) D. Kang, S. T. Cheung, J. Kim, Angew. Chem. 2021, 133, 17084–17089; c) D. Kang, S. T. Cheung, A. Wong-Rolle, J. Kim, ACS Cent. Sci. 2021, 7, 631–640; d) D. Kang, S. Lee, J. Kim, Chem. 2022, 8, 2260–2277.

[2] a) S. E. Beutick, S. Yu, L. Orian, F. M. Bickelhaupt, T. A. Hamlin, ChemistryEurope, 2024, 2, e202300072; b) S. E. Beutick, S. Yu, L. Orian, F. M. Bickalhaupt, T. A. Hamlin, Chem. Sci., 2024, DOI: 10.1039/d4sc04211e

Poster 40

Post-translational Modification: Covalent Modification of Amino Acids in Cytochrome P460 Cofactor Maturation

Thakur Rochak Kumar Rana and Gopalan Rajaraman*
Indian Institute of Technology Bombay, Mumbai, India
E-mail: rochakrana@gmail.com

Post-translational modification (PTMs) in c-type cytochrome P460 through covalent cross-linking involves the heme porphyrin ring itself at *meso*-carbon with Lys amino acid of the protein.[1] The site-directed mutagenesis of Lys with Tyr or Leu does not cross-link and leads to catalytic inactivity for NH_2OH oxidation.[2,3] The origin of heme-Lys cross-link with leans of the functional and co-factor electronic structure remains elusive to date, and its study is highly demanding for mapping the artificial enzyme design. Specifically, the role of cross-link needs a virtuous theoretical prediction that has triggered the exciting advances in enzyme chemistry, particularly mechanistic insight.

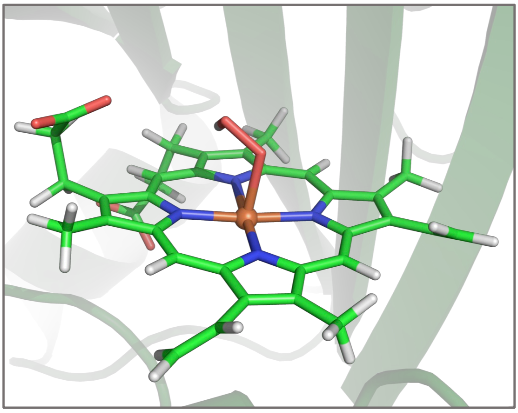


Figure 1: Active site for cyt P460 intermediate from *Nitrosomonas europea.* PDB ID: 8GAR

To this extent, we have studied the dynamics and mechanism for maturation of cross-linked cyt P460 as well as spectroscopic validation of intermediate observed by experimental studies using QM/MM calculation.

[1] Caranto, J. D.; Vilbert, A. C.; Lancaster, K. M., *PNAS* **2016**, *113 (51)*, 14704-14709.

[2] Coleman, R. E.; Lancaster, K. M., *Acc. Chem. Res.* **2020**, *53 (12)*, 2925-2935.

[3] Bollmeyer, M. M.; Coleman, R. E.; Majer, S. H.; Ferrao, S. D.; Lancaster, K. M., *JACS* **2023**, *145 (26)*, 14404-14416.

Poster 41

Single-Molecular Magnetism in n*d*-shell Transition Metal Metallocenes

Sakshi Nain,[a] Md. Ehesan Ali[a]
[a] Institute of Nano Science and Technology, Mohali, India
sakshi.ph20268@inst.ac.in

Single-molecule magnets (SMMs) showing potential in information storage have drawn the attention in recent years with the quest to achieve higher magnetic anisotropy. The iconic organometallic complex i.e., metallocene possesses intriguing bonding picture and symmetrical geometry, with a central metal sandwiched between two cyclopentadienyl (Cp) rings. We have explicitly investigated metallocenes of first-row transition metal elements, along with their one electron oxidized (cationic) and reduced (anionic) analogues, for their electronic structure and zero-field splitting (ZFS) parameters (D).[1] The covalent nature of metal-ligand bonding in such complexes play a crucial role in determining the electronic ground state of the systems. [4] The uniaxial 3d-metallocenes are observed as SMMs with sizable magnetic anisotropy (MA) that gets enhanced with increase in molecular symmetry. Applying multi-configurational calculations, we have also realized that apart from the molecular symmetry, MA escalates down the group in order of 3d<4d<5d. The record high MA among d-series is obtained in a 5d-metallocene owing large spin-orbit coupling.[2] In certain cases, specific vibrational modes are found as spoilsport for SMMs.[3]

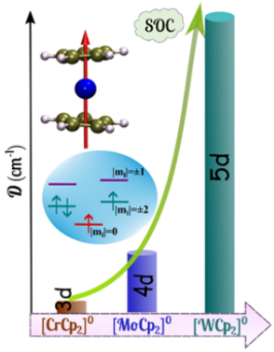


Figure 1: Enhancement of *D* value moving from 3d to 4d to 5d metallocene.

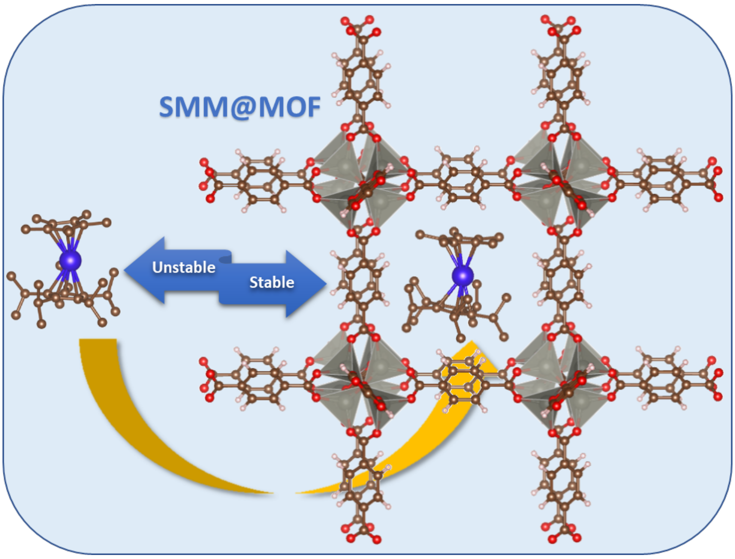
[1] Nain, S.; Khurana, R.; Ali, M. E. *J. Phys. Chem. A* **2022**, *126*, 18, 2811.
[2] Nain, S.; Mukhopadhyaya, A.; Ali, M. E. *Inorg. Chem.* **2024**, *63*, 7401.
[3] Nain, S.; Kumar, M.; Ali, M. E. *Phys. Chem. Chem. Phys.* **2023**, *25*, 14848.
[4] Swart, M. *Inorganica Chim. Acta.* **2007**, *360*, 179.

Poster 42

Achieving Ambient Stability and Suppressing Spin-Phonon Coupling in Dyprosocenium SIMs via MOF Encapsulation

Garima Bangar [a] †, Reshma Jose [a] †, Rajanikanta Rana, and Gopalan Rajaraman *[a]
[a] Department of Chemistry, Indian Institute of Technology Bombay, Mumbai-400076
214033013@iitb.ac.in , rajaraman@chem.iitb.ac.in *

Detailed ab initio Complete Active Space Self-Consistent Field (CASSCF) calculations, combined with periodic Density Functional Theory (DFT) studies, have been conducted on the $[(Cp^*)Dy(Cp^{iPr5})]^+$ [1] molecule encapsulated within a metal-organic framework (MOF). These comprehensive analyses revealed that MOF encapsulation significantly enhances the stability of these otherwise fragile molecules while preserving their effective magnetic moment (U_{eff}) values. Notably, this encapsulation effectively suppresses the critical vibrational modes typically responsible for reducing the blocking temperature. [2] This suppression presents a previously unexplored strategy for developing a new generation of Single-Molecule Magnet (SIM)–based devices, potentially revolutionising the field.



[1] F.-S. Guo, B. M. Day, Y.-C. Chen, M.-L. Tong, A. Mansikkamäki and R. A. Layfield, Science, 2018, 362, 1400-1403.

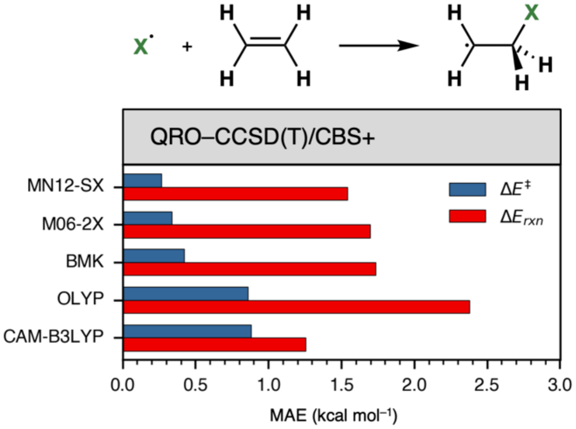
[2] J. G. Kragskow, J. Marbey, C. D. Buch, J. Nehrkorn, M. Ozerov, S. Piligkos, S. Hill and N. F. Chilton, Nat. Comm., 2022, 13, 825.

Poster 43

Radical Addition Reactions:
Hierarchical *Ab initio* Benchmark and DFT Performance Study

Yuman Hordijk,[a] Marco Dalla Tiezza,[a] Daniela Rodrigues Silva,[a] Trevor A. Hamlin*[a]
[a] Department of Chemistry and Pharmaceutical Sciences, Vrije Universiteit Amsterdam,
Amsterdam, The Netherlands
y.hordijk@vu.nl

Benchmarking is an important topic in all of computational chemistry. It is the one way to figure out if your methodology is accurate and reliable for a given chemical system. In this talk I will talk about the do's and don'ts of our benchmark on radical addition reactions.[1] We used a hierarchical[2] series of *ab initio* methods (HF, MP2, CCSD, CCSD(T)) paired with a hierarchal series of Dunning basis sets with and without diffuse functions ((aug)–cc–pVDZ, (aug)–cc–pVTZ, (aug)–cc–pVQZ). Since we work with radical systems we transformed the HF ground-state wavefunctions into quasi-restricted orbital (QRO) reference wavefunctions to address spin contamination. Following extrapolation to the CBS limit, we determined that the energies from our highest- QRO–CCSD(T)/CBS+ level were converged with respect to the *ab initio* method and basis set, respectively. Our QRO–CCSD(T)/CBS+ reference data was used to evaluate the performance of 98 density functional theory (DFT) approximations for both energetics and key geometrical parameters of the stationary points.



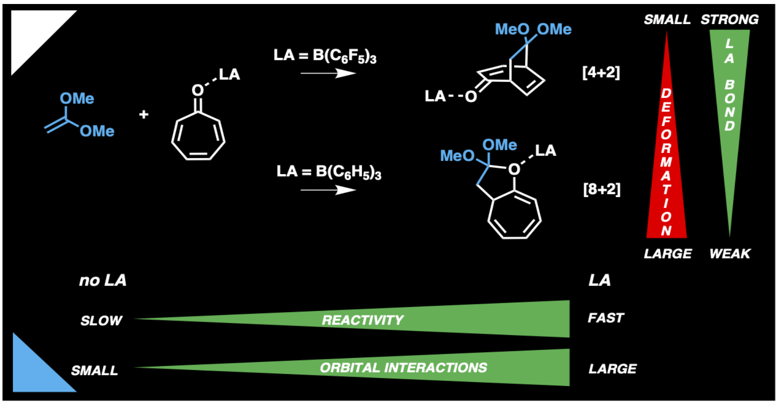
[1] Y. Hordijk, M. D. Tiezza, D. R. Silva, T. A. Hamlin, *ChemPhysChem* **2024**, e202400728.

[2] L. De Azevedo Santos, T. C. Ramalho, T. A. Hamlin, F. M. Bickelhaupt, *J. Comput. Chem.* **2021**, *42*,

Regioselectivity in Cycloaddition Reactions with Tropone

Eveline H. Tiekink,[a] Pascal Vermeeren,[a] Trevor A. Hamlin[a]
[a] Department of Chemistry and Pharmaceutical Sciences, Vrije Universiteit Amsterdam,
Amsterdam, The Netherlands
e.h.tiekink2@vu.nl

Higher-order cycloaddition reactions offer an efficient approach to synthesize bridged 3D molecular structures from simple 2D substrates. Tropone can engage in various competing higher-order cycloaddition reactions, for instance, [6+2], [6+3], [6+4], [8+2], and [8+3] cycloaddition reactions.[1] Control of the regioselectivity is crucial. Recently, Lewis acid catalysts were shown to impart total regiocontrol of the cycloaddition between tropone and 1,1-diethoxyethene: $B(C_6H_5)_3$ furnishes the [8+2] adduct while $B(C_6F_5)_3$ yields the [4+2] adduct.[2] We have studied the uncatalyzed and Lewis acid (LA)-catalyzed cycloaddition reaction between tropone and 1,1-dimethoxyethene using dispersion-corrected relativistic density functional theory.[3] The LA catalysts BF_3, $B(C_6H_5)_3$, and $B(C_6F_5)_3$ efficiently accelerate the competing [4+2] and [8+2] cycloaddition reactions by lowering the activation barrier up to 12 kcal mol^{-1} compared to the uncatalyzed reaction. Our findings reveal that the regioselectivity shift originates from the ability of the LA to absorb distortion by adopting a trigonal pyramidal geometry around the boron atom.



[1] S. Frankowski, M. Romaniszyn, A. Skrzyńska, Ł. Albrecht, *Chem. Eur. J.* **2020**, *26*, 2120.
[2] P. Li, H. Yamamoto, *J. Am. Chem. Soc.* **2009**, *131*, 16628.
[3] E. H. Tiekink, P. Vermeeren, T. A. Hamlin, *Chem. Eur. J.* **2023**, *29*, e202301223.

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