12th Workshop on Computational Chemistry and Molecular Spectroscopy

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EN QUÍMICA COMPUTACIONAL Y
ESPECTROSCOPÍA MOLECULAR

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The 12th Workshop on Computational Chemistry and Molecular Spectroscopy is an international academic event organized by the PhD Program in Molecular Physical Chemistry at University Andres Bello. The main goal of this scientific activity is to promote fruitful academic interactions among renowned researchers and graduate students from several doctoral programs in Chile and Latin America.

This year, we gather from November 13th to 16th at Hippocampus, Conón, Viña del Mar, with the participation of more than 10 distinguished experts in the field, both local and international, who will share with us their most recent developments and, the insights into the future of the field.

Additionally, we count with 16 oral presentations and 2 poster sessions, to provide to graduate students, postdocs, and academics with a platform to communicate their own scientific advancements, both theoretical and experimental research are welcome.

Please, enjoy the knowledge contains in this book.

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Mayr’s scales revisited

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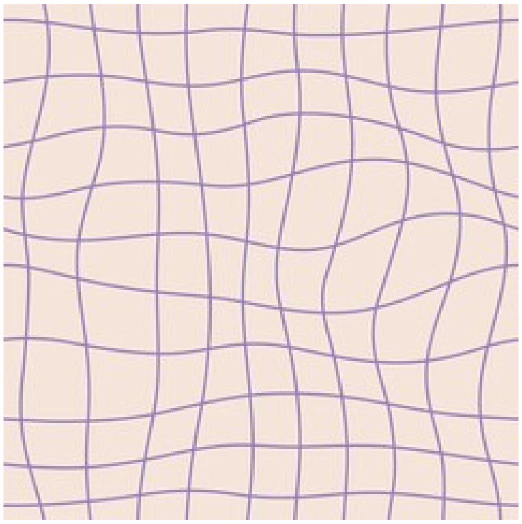
An alternative to calculate the nucleophilicities and electrophilicities of Mayr’s scale is presented. Considering that there is a good correlation between the reaction rate constant and the amount of charge transferred calculated with the Parr and Pearson model and with the two parabolas model, one obtains an expression with an identical form to that empirically proposed by Mayr. It is possible to identify the three terms appearing in Mayr’s scale: nucleophilicity, electrophilicity, and sensitivity. Values for these descriptors obtained with DFT calculations and machine learning will be discussed.



On the Representability of Chemical Reactions

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The conceptual representability of chemical reactions is a barely reviewed subject, its classic characterization based on the energy changes, the E-representation, has dominated the analysis, models and empirical approaches aimed at explaining chemical reactions. In this presentation we will explore different ways to represent chemical reactions. New concepts and ideas that have been proposed in the last few years allows one to expand the classical description of chemical reactions. Within the frame of the reaction force 1,2, we introduce the F-representation of chemical reactions, a reaction force-based representation that allows a better appraise of the reaction force concept and produce a complementary, alternative and innovative way to characterize chemical reactions. On the other hand, within the context of the reaction electronic flux (REF) 3,4, defining the electronic activity taking place during a reaction, multiple representations that rise significance and physical meaning of the property are allowed. It will be shown that a chemical representation of the REF based on reactivity indexes complements the physical representation grounded on electron polarization and transfer.

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Can we capture chemical concepts?

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Chemical concepts are century-old. One can define them in the context of quantum mechanics. But are these definitions consistent with our expectations, or is reality more complex than can be covered by them? In order to support the latter viewpoint, we discuss simple examples that questions the notion of an atom in a molecule, of atomic shells, . . .
We define the region of the space for which the probability to find a number of electrons is maximal. To give a trivial example, we find a region of space around a nucleus with charge Z, such that the probability of having a number of electrons equal to Z is maximal, and take this as a reasonable definition of an atom in a molecule (or solid). Probably many people would agree that in an ionic crystal, one better uses regions of space with a number of electrons larger or smaller than Z. Further examples are discussed.

Positron-Bonded Systems: Exploring Novel Molecules and Analyzing Bond Energies

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In a recent investigation, an exploration was undertaken to examine the energy stability of a unique kind of positronic compound [1]. This compound exhibits a curious composition, consisting of two hydride anions that would normally experience repulsion. However, the introduction of a single positron (e+[H_2^{-2}]) brings about a stable configuration.

This discovery attracted significant attention within the scientific community, resulting in further inquiries into the energy stability of alternative diatomic systems bonded by positrons, including 2e+[H_2^{-2}] [2], 3e+[H_2^{-2}] [3], as well as homo- and heteronuclear e+[X^-Y^-] compounds involving halide anions (X, Y = F, Cl, Br) and a single positron [4].

Here, we examine a novel matter-antimatter molecular entity comprising two positrons and three hydride anions, namely 2e+[H_3^{-3}] [5]. Our study provides compelling evidence that the repulsive trihydride system [H_3^{-3}] can achieve stabilization through the formation of a three-center two-positron bond. Intriguingly, the 2e+[H_3^{-3}] system bears resemblances to its purely electronic analogue, the [Li^{3+}] trication, which is held together by two electrons. Despite sharing similar physical attributes, including molecular symmetry, internuclear distance, vibrational parameters, and ground-state positron density within the internuclear region, data concerning bond energies indicates that positron bonding is comparatively weaker than electronic bonding in trication systems.

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"Exploration of potential energy surfaces based on linear notations for both molecular and extended systems"

Armando González-Ortíz, Jessica Arcudia, Gabriel Merino

Exploring the potential energy surface can be conducted through various methods, each with its own advantages and limitations. However, most of these methods rely on geometric information. In this presentation, I will delve into an approach centred on linear notations. This involves using character strings to represent chemical space.

For smaller systems like C_6H_6, just 217 character strings (of the SMILES type) are sufficient to encompass the chemical space, excluding species that may violate classical organic chemistry rules (and enantiomers). As the number of atoms increases and heteroatoms are introduced, the number of isomers grows significantly.

To achieve this purpose, we propose an algorithm that amalgamates principles from Darwinian evolutionary theory (using a genetic algorithm), Lamarckian evolution (employing a local optimizer), and the theory of physiological development in living organisms (depicting the phenotypic expression of solutions).

Conversely, there is no equivalent of SMILES for crystalline systems. In this scenario, we introduce a notation for crystalline layered materials called joining and arrangement of multilayers (JAM). Because the symmetry of the systems allows several JAM strings to denote the same arrangement, we also define rules and procedures for JAM canonicalization, allowing one to identify all N-layered stacking configurations. As a result, the JAM notation may be used to represent any 2DLM with a high-symmetry honeycomb lattice via a string.

In summary, we are taking initial steps towards exploring the intricate function of molecular structures by leveraging rules rooted in language theories.

Modeling the binding of metallic species to proteins.

JeanDiMaréchal

Molecular modeling has emerged as a significant asset in biomolecular chemistry. Despite notable achievements using quantum or classical mechanics models, there still needs to be more research on the modeling of interactions between metallic species and proteins. Given that approximately one-third of all known genomes involve bioinorganic systems, surmounting these limitations can significantly advance our comprehension of life, facilitate the development of novel enzymes, and aid in drug design.

In this presentation, I will elucidate the strides made by our research group in this domain, encompassing multi-scale strategies (QM, MD, etc.), updated docking methodologies, and novel predictors for identifying metal binding sites in proteins. Furthermore, I will delve into evaluating the inherent flexibility exhibited by the cofactor-protein complex and its consequential impact on the catalytic mechanisms of metalloenzymes. Prominent examples will center on the design of artificial metalloenzymes and therapeutic agents.

From quantum topology to properties. A focus on superconductivity

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A room temperature superconductor is probably the most desired system in solid state physics. So far, the greatest advances, cuprates, pnictides and number of others were obtained in a serendipitous way. As there is no clear theory for these superconductors, it is difficult to predict where progress will be made. In contrast the Bardeen-Cooper-Schrieffer (BCS) theory gives a clear guide for achieving high Tc, and hydrogen seems to be a main clue. Within this approach, the recently reported superconductivity at 190 K in compressed H2S [1] has been arguably the biggest discovery in the field since the superconducting cuprates nearly 30 years ago. However, a microscopic understanding of why this particular material features such a strong coupling is still missing. We have recently shown that the underlying chemical structure and bonding need to be characterized for a good comprehension of the chemical composition-superconductivity relation. We have constructed simple metal and BCS models showing that the Electron Localization Function [2] can be used to define a quantity called the networking value, which should provide insight into the superconducting activity.

By analyzing through DFT calculations the structural and electronic properties of nearly 200 compounds predicted to be superconductors in the literature, we have shown that the networking value correlates well with the predicted critical temperature, much better than any other descriptor analyzed thus far. And this, for all bonding types [3]. The discovery of the positive correlation between superconductivity and the bonding network offers the possibility of screening easily hydrogen-based compounds and, at the same time, sets clear paths for chemically engineering better superconductors.

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BIOPOLYMER-BASED MATERIALS WITH ABILITIES TO REMOVE POLLUTANTS FROM WASTEWATER

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Currently, there is a variety of contaminants in aqueous environments that can cause serious effects on the health of plants, animals and humans. These contaminants may be of organic (eg, dyes, pesticides, antibiotics) or inorganic (eg, heavy metals, metalloids) origin. Several treatment processes are normally used, such as coagulation/flocculation, photodegradation, membrane filtration, adsorption, chemical oxidation, and biological degradation, to remove these contaminants from wastewater. Among these proposed methods, adsorption technology is considered one of the most effective methods due to its simplicity of preparation, high efficiency in contaminant removal and adsorbent regeneration. The objective of this research is the preparation of cross-linked polymeric materials for the removal of organic and inorganic contaminants. The preparation of these materials is through polymerization reactions, in the presence of functional vinyl monomers (anionic and cationic)[1]. In addition, in the search for more sustainable materials, bio-based nanocomposites of polymer-nanocellulose [2], polymer-hemicellulose [3], polymer-lignin [4], have been prepared to compare them with their synthetic analogs. In addition, these materials are characterized by various spectroscopic techniques (1H-NMR, FTIR), thermal (TGA, DSC), and morphological (SEM, TEM).

Later, these materials were used in the removal of metals such as copper, chromium, metalloids such as arsenic, among others. In addition, they were tested in the removal of organic contaminants such as methylene blue and methyl orange dyes, and also in antibiotics such as sodium nafcillin. The results generally show a high capacity for contaminant removal, over 90% in some cases. Molecular dynamics simulations distinguish the existence of π-π stacking interactions between aromatic rings from nafcillin in the polymer + nafcillin system.

Polymer-nanocellulose nanocomposites show a porous morphology, which explains their high capacity to remove dyes. These materials have also presented a good desorption and regeneration capacity, and can be applied in several cycles of adsorption-desorption. In addition, the theoretical results showed a preferential interaction between dye and the semiflexible polymer chains at the lowest energy setting [5]. In future investigations we have considered the application in columns methods and using real wastewater samples.

Acknowledgements: FONDECYT [grant number 1231498], ANID, PCI [grant number NSFC190021], and the National Natural Science Foundation of China.

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Molecular Dynamics Simulations and Networks Analysis as Tools to Interpret How Mutations Shape Enzyme Activity During Evolution

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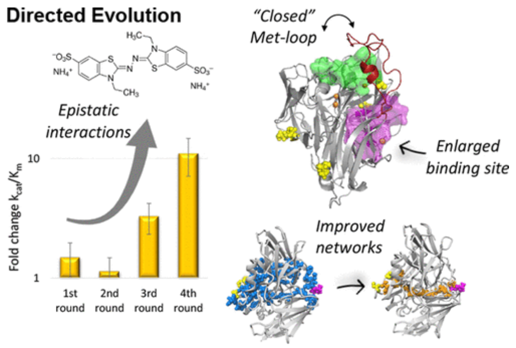
The (re)design of enzymes is often needed to improve their properties for and efficient application as biocatalysts in industry. One of the families in increasing demand as innovative solutions in the green chemistry and biorefinery fields are laccases, as they are capable of oxidizing a variety of compounds (some derived from biomass) and without the need of expensive cofactors. Here, I will present a study [1,2] in which we have combined mutagenesis with structural, kinetic and *in silico* analysis to characterize the molecular features that cause the evolution of a hyperthermostable metallo-oxidase from the multicopper oxidase family into a laccase (k_{cat} 220 s^{-1} for a bulky aromatic substrate). We show that six mutations scattered across the enzyme, collectively modulate binding site shape and protein dynamics to improve the binding and catalysis of a bulky aromatic substrate. Analysis of WT and mutant molecular dynamics simulations by the Weighted Implementation of Optimal and Suboptimal Paths (WISP)[3] software has been done. Allosterically coupled, long-range dynamic networks have been characterized, whose changes when distal mutations are introduced could explain the observed increase in catalytically competent conformational states that are more suitable for recognition and stabilization of the aromatic substrate.



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A reinterpretation of fundamental concepts in Organic Chemistry within Molecular Electron Density Theory (MEDT).

Luis Domingo

In the 20's of the last century, renowned chemists such as K. Ingold, A. J. Lapworth or G. N. Lewis established a number of fundamental concepts in the study of reactivity in organic chemistry. These concepts, proposed before the establishment of quantum mechanics, were based on empirical observations or on very elementary concepts of atomic structure.

The development at the end of the last century of a series of tools within quantum chemistry, such as CDFT, ELF or AIM, allows today the study of the structure and reactivity of molecules based solely on the analysis of the electron density.

After more than 20 years of studying the reactivity of organic molecules, in 2016 Domingo proposed the Molecular Electron Density Theory (MEDT), which has allowed a reinterpretation of the basic concepts, giving a modern vision of Organic Chemistry.

Luminescent materials: Synthesis, applications and emergent properties

Dr. Víctor Jiménez

En la plática describiremos los avances mas recientes del grupo de investigación sobre materiales luminiscentes derivados de boro y estaño. Hemos estudiando sus propiedades fotofísicas, su citotoxicidad, y sus aplicaciones en bioimágenes in vitro, tinción de biomateriales, así como la fabricación de dispositivos optoelectrónicos. La química verde la aplicamos en su síntesis de estos materiales ya que usamos las microndas, el ultra sonido y la mecanosíntesis. También veremos algunas propiedades poco reportadas en la química del estaño y boro como el criocromismo, viscocromismo y termocromismo reversible. Finalmente, mostraremos algunos de nuestros avances respecto a la obtención de materiales fluorescentes solubles en agua a partir de la biomasa y su aplicación en la tinción de fibroína de seda.

Non-bonded parameters for biological force fields derived from Atom-in-molecules approaches.

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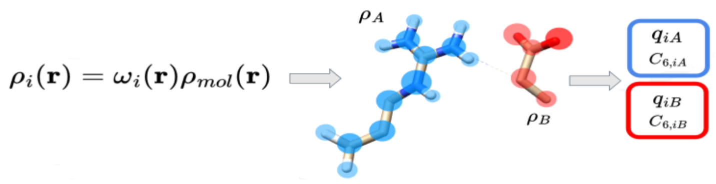
Molecular dynamics (MD) simulations are very powerful tools to get energetic and structural insights into large biological systems on an atomistic scale. At the heart of most MD simulations, we find the force field, a set of mathematical functions that model the interactions between atoms based on classical physics and combined with an integrator to model the evolution of the system over time[1]. The force field functions require atom-specific parameters to model the interactions of (non-)bonded atoms which are often obtained from empirical or fitting methods. The main shortcoming of this procedure is the results are accurate just for the class of observables for which it was developed.



In recent years, there's a renewed interest in deriving force field parameters from quantum electronic structure calculations for modeling protein and small molecule interactions[2]. In this work, we present a novel approach to derive non-bonded force-field parameters directly from atoms-in-molecules (AIM) partitioning of the electron density[3]. We derived parameters for a dataset of sidechain-sidechain residues with mostly dispersion and electrostatic interactions in 610 conformations (Arginine, Glutamic acid, Aspartic acid, Phenylalanine, Tryptophan, Glutamine, Asparagine, and Tyrosine). Electrostatic and dispersion interactions obtained at the force field level were compared to ALMO-EDA2 reference energies with the wB97XV/def2TZVPD method[4]. Our results show that atomic charges derived from the MBIS scheme provide the best model for reproducing electrostatic interactions. Conversely, C6 parameters derived from the MB-AVH scheme predict dispersion interactions more effectively when compared to other AIM schemes, as well as the biomolecular force fields CHARMM36m and AMBER99sb[5].

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Exploring stereoselective models of hydride transfer in methylotrophic metabolism: The case of MtdA.

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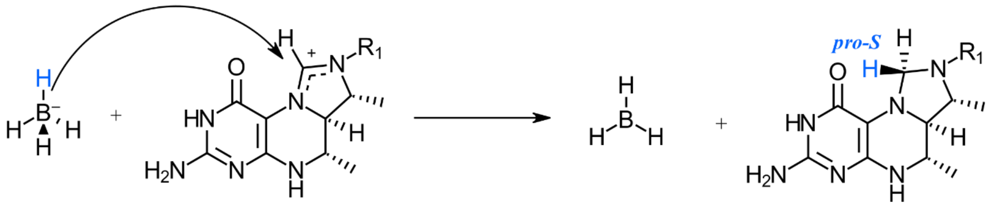
Methylotrophs are microorganisms capable of using C1 compounds as a source of energy and carbon. The set of enzymes and reactions allowing methylotrophs to use C1 compounds as a carbon and energy source is conserved among different species. A crucial element in this route is the enzyme Methylene-tetrahydrometanopterin (methylene-H_4MPT) dehydrogenase, specifically in its "A" variant (MtdA).[1] The reaction catalyzed by MtdA is the stereospecific transfer of a hydride ion from methylene-H_4MPT to $NADP^+$. It has been observed that MtdA, just like all H_4MPT-dependent dehydrogenases, catalyze the transfer of the *pro-R* hydride unit. Given the prvalence of this preference, it has been suggested that this hydrogen atom is easier to subtract than its *pro-S* equivalent. This hypothesis has been challenged by the observation of the non-enzymatic reduction of methenyl-H_4MPT^+ by $NaBH_4$. Based on the principle of microscopic reversibilty, one would expect the reduction happening on the *Re*-face of methenyl-H_4MPT^+. On the contrary, it has been observed that in this reaction the hydride is incorporated to the *Si* face of the molecule.[2] Some authors proposed that the ionic nature of BH_4^- would hinder the approximation on the *Re* face, enhancing a stereochemical outcome different to that observed in the enzyme, where the hydride donor bears no charge. According to some authors, the non-enzymatic reduction by neutral donors should keep the stereoselectivity observed in MtdA. In this work we analyze the potential energy surface for the non-enzymatic reaction between methenyl-H_4MPT^+ and BH_4^- ion. Transition structures and reaction coordinates with diverse stereoselectivity have been identified, and the intermolecular interactions favoring the *Re* or *Si* preference have been characterized using symmetry adapted perturbation theory (SAPT). Also, a hypothetical reaction with the neutral hydride donor pyridine has been analyzed, to evaluate the influence of electrostatic interactions on the stereochemical outcome of the reduction.



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Glycosidic Bond Biosynthesis: An Exploration of Glycosyltransferase Mechanisms through Quantum Mechanics/Molecular Mechanics Methods

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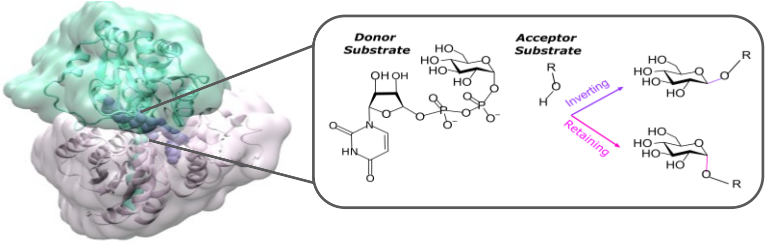
Glycosyl transfer reaction is one of the most important biochemical reactions, given two-thirds of the carbon in the biosphere exists as carbohydrates. Glycosylated compounds occur as polysaccharides, glycoconjugates and small glycosides. All of them carry out a wide range of functions, including energy storage, maintenance of cell structural integrity, molecular recognition, cell–cell interaction, immune response, etc. In addition, glycosylation usually plays key roles in the physico-chemical properties and functional performance of natural products, providing many possibilities for novel bioactive substance exploitation.[1]



Scheme 1. Three-dimensional representation of a GT, showing the C-terminal and N-terminal domains in green and light pink, respectively. The substrates are depicted as lilac spheres between the interdomain region. The two possible stereochemical outcomes arising from glycosylation reactions are illustrated in the right panel.

Glycosyltransferases (GTs) use two substrates to catalyze the formation of a new glycosidic bond: the donor substrate, that provides the pyranosyl moiety, and the acceptor substrate that will engage to the pyranose ring **(Scheme 1)**. The reaction is a nucleophilic substitution at the anomeric carbon and can proceed with either retention or inversion of the anomeric configuration. Consequently, there are two types of GTs: the retaining GTs (ret-GTs) and inverting GTs (inv-GTs).[2] Computational techniques like the QM/MM (Quantum Mechanics/Molecular Mechanics) approach has been proved as a valuable tool to investigate the enzymatic mechanisms catalyzed by GTs, providing the molecular bases of both retaining and inverting mechanisms.

This work will present the findings of different computational studies that have deeply contributed to the field of glycoscience, as well as the elucidation of the catalytic and molecular details of these important biochemical reactions.

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Molecular recognition and non-covalent inhibition of gliptins in DPP-4 enzyme

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Diabetes type 2 is a chronic metabolic disease that affects millions of people worldwide. Due to its beneficial results, the most promising treatment is to block the regulatory enzyme Dipeptidyl Peptidase-4 (DPP-4), prolonging the action of insulin. The blocking compounds are called gliptins and the crystalline structure of many complexes DPP4/inhibitor have been reported.[1–3] Recently, we established the protonation state of the catalytic site of DPP-4 enzyme through the study of different protonation states of selected residues, whose pKa is close to the physiological pH. In this research, DPP-4 complexes with vildagliptin, saxagliptin, alogliptin, teneligliptin, sitagliptin, and linagliptin were modelled with the protein in the previously established protonation state, to insight into the molecular recognition and non-covalent inhibition of this gliptins. Molecular dynamics simulations of 150 ns were performed with protein-ligand complexes in Amber and GAFF force fields. The binding free energies were calculated with the MM/PBSA method. H-bond tool allowed the detection of protein-ligand hydrogen bonds. Throughout the simulations, the inhibitors remain positioned like in the crystal structure. The binding free energies are comparable to experimental values and depend on the electrostatic interaction of the amino group of the ligand with the N-terminal recognition site of the enzyme. Unlike classical static modeling, dynamic behavior reveals important conformational changes in drugs and elucidates the most relevant interactions in molecular recognition. These findings contribute to the development and improvement of DPP-4 inhibitors.

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Spin-polarized chemical reactivity at finite temperatures: Changes in multiplicity at constant charge.

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We extend spin-polarized conceptual density functional theory [1] to finite temperatures within the framework of the grand canonical ensemble [2], utilizing the density matrix operator. Our focus is on the derivation of new spin-polarized reactivity indices that incorporate temperature effects. We start by introducing the expressions needed to calculate the average values of key quantities such as energy, total electron number, spin number, electron density, and spin density. These expressions are further derived leading to the general form of global and local reactivity indices that account for temperature variations.

Furthermore, we present a three-states model for a carbon atom, with a triplet state as a reference. This model allows for changes in multiplicity, shifting between the reference state to singlet and quintet states while maintaining a constant charge (Fig. 1). Within this framework, we derive the electronic spin potential, electronic spin hardness, and electronic Fukui functions. Finally, we illustrate how the energy varies as a function of the spin number, demonstrating that the function is now continuous and smooth, ensuring differentiation at any order and resolving the "Ns-differentiability problem".

Acknowledgments: We are grateful for the support and collaboration of the “Centro de Química Teórica & Computacional (CQT&C)” and the Chemistry department of Cinvestav.

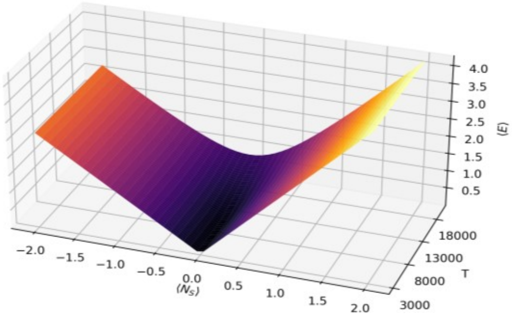

Figure 1: Average energy of an ensemble of a carbon atom in singlet, triplet and quintet state versus the spin number and temperature, experimental values from Nist [3].

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Exploration of mechanical properties in two-dimensional materials M_2X, (M=Cu, Ni, Co and X=Si, Ge) with planar hypercoordinated atoms

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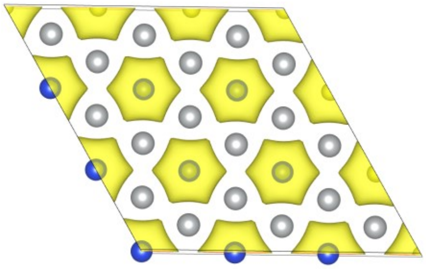
Two-dimensional materials with planar hypercoordinate atoms (phA) exhibit unconventional mechanical properties, such as significantly large isotropic elastic moduli and uniformly atypical deformations within the linear elasticity regime at finite strains. The exploration of these systems through theoretical studies can prove valuable for mechanical applications, with the anticipation that they may lead to experimental designs featuring intriguing physicochemical functionalities.(1-3) Using ab initio calculations within the framework of density functional theory (DFT), adapted for modeling periodic systems as implemented in the VASP package, we investigate the M2X systems, where (M=Cu, Ni, Co, and X=Si, Ge). We attribute the emergence of these remarkable properties to the presence of multicenter bonds in the M2X materials, a consequence of the phA's presence, which exhibits favorable elastic behavior as evidenced by the analysis of second derivatives of energy.



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Removing Self-interaction Error from Density Functional Theory Calculations with Fermi-Löwdin Orbitals

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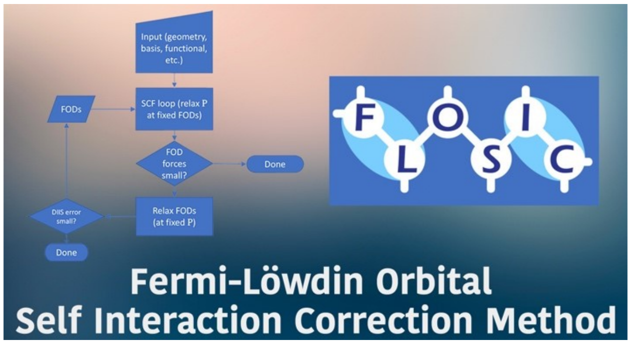
The effect of DFT self-interaction error (SIE) on calculated molecular and solid-state properties has been known for more than 40 years. The most widely accepted framework for removing SIE in DFT in an orbital-by-orbital basis is due to Perdew and Zunger (PZ) [1]. The high computational cost associated with minimizing the PZ energy functional and the poor performance of local and semi local functionals after SIE removal made the calculation of self-interaction-free molecular properties elusive. Recently, an efficient implementation for SIE removal based on Fermi orbitals was proposed [2]. This method explicitly avoids the unitary transformation from canonical to localized orbitals that is needed in standard PZ and replaces it with a Fermi-Löwdin transformation which depends only on one vector descriptor per occupied orbital, also called Fermi orbital descriptor. The Fermi-Löwdin orbital self-interaction correction (FLOSIC) provides a computationally efficient alternative to the traditional PZ approach. [2] I will describe the FLOSIC methodology, and its advantages and drawbacks compared to traditional PZ-SIC. I will show our recent efforts to make FLOSIC more efficient though a formulation based on the density matrix. [3] As an illustration of the capabilities of the FLOSIC method, I will review some recent results of diverse properties in cases where SIC is important and discuss current opportunities. This work is supported by the US Department of Energy DE-SC0018331.



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Diseño y síntesis racional de nuevos análogos de Brasinoesteroides y su evaluación promotora de crecimiento en *Arabidopsis thaliana*.

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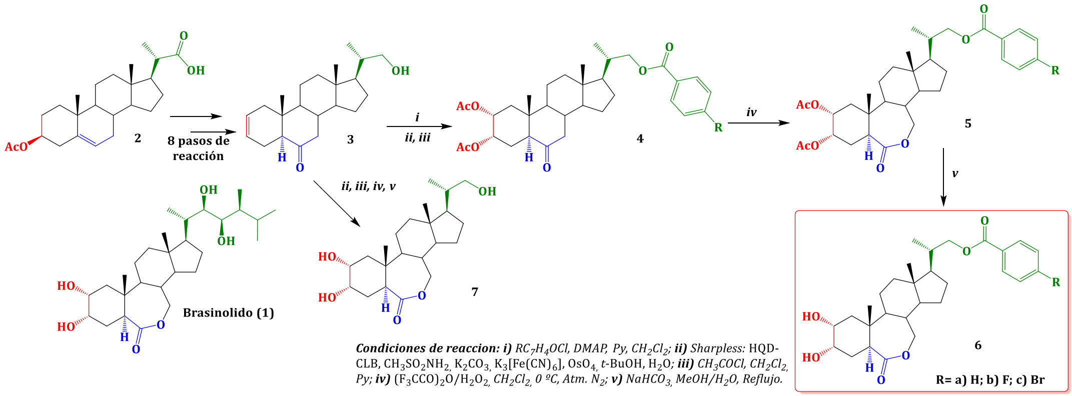
Los brasinoesteroides BRs son un grupo de hormonas vegetal involucradas en la regulación de muchas actividades fisiológicas vitales de las plantas, promoviendo el crecimiento de estas y, además, les otorgan resistencia a diferentes tipos de estreses, siendo el Brasinólido (**1**) el compuesto natural más activo [1]. Por lo ello, en este trabajo se presenta el diseño computacional por Docking Molecular basado en la evaluación de afinidad de acoplamiento de los ligandos a la proteína receptora de BRs (BRI1 y BAK1) [2] y la síntesis de una serie de nuevos análogos de BRs **6(a-c)** que cuentan con un esqueleto esteroidal similar al del brasinolido (**1**) pero con una cadena lateral con función benzoilada *p*-sustituida en C22 y el precursor **7**. La síntesis se ha realizado a partir del ácido 23,24-bisnorcolenicos **2,** de acuerdo con el Esquema 1 [3, 4]. Además, se presentará la evaluación promotora de crecimiento vegetal de los nuevos compuestos en el bioensayo de elongación de hipocótilo y raíz de *Arabidopsis thaliana*.



Condiciones de reaccion:* i)** *RC_7H_4OCl, DMAP, Py, CH_2Cl_2;* ***ii) *Sharpless:* HQD-CLB, $CH_3SO_2NH_2$, K_2CO_3, $K_3[Fe(CN)_6]$, OsO_4, *t*-BuOH, H_2O; ***iii)*** *CH_3COCl, CH_2Cl_2, Py;* ***iv)*** $(F_3CCO)_2O/H_2O_2$, *CH_2Cl_2, 0 ºC, Atm. N_2;* ***v)*** *$NaHCO_3$, MeOH/H_2O, Reflujo.*

Esquema 1. Ruta de síntesis de los nuevos análogos de BRs **6**(**a-c**) y del precursor **7**.

Agradecimientos: Proyecto Fondecyt N°1231502.

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ffparAIM: A Python workflow for non-covalent force field parameter derivation and its applications

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We introduce a workflow based on the QM/MM methodology and the Minimal Basis Iterative Stockholder (MBIS) partitioning of the polarized electron density to derive atomic charges and Lennard-Jones (LJ) parameters of molecules in condensed phases. Our Python-based protocol combines molecular dynamics simulation carried out with OpenMM and the QM/MM approach to obtain force field parameters from several configurations of the trajectory. Electron densities can be obtained for every level of theory and basis set available in ORCA 5.0.3 software. Combining IOData [1] and other libraries from the Horton3 package, we derive atomic charges and effective atom volumes, partitioning the polarized electron density of each configuration with the MBIS method. Values are averaged from all extracted configurations and replaced in the topology before initialization of a new cycle of MD simulations and QM/MM calculations until convergence. Bond-based symmetrization and atom type correction is considered for the final topology output.

Derived non-covalent force field parameters were tested with different condensed phase systems: thermodynamic properties of liquids, absolute binding affinities of host-guest systems [2] and protein-ligand complexes. For these evaluated systems, the prediction of thermodynamic observables is mainly limited by the accuracy of the force fields.

Our results shows that the thermodynamic properties estimated with environment-specific MBIS-derived parameters are in better agreement with experimental data. These modified force fields are competitive compared to data-driven optimized force fields in property estimation and are capable to predict absolute binding free energies with chemical accuracy (RMSE < 1 kcal/mol) for the L99A/M102Q T4 Lysozyme dataset.

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Role of the environment in the antioxidant strength

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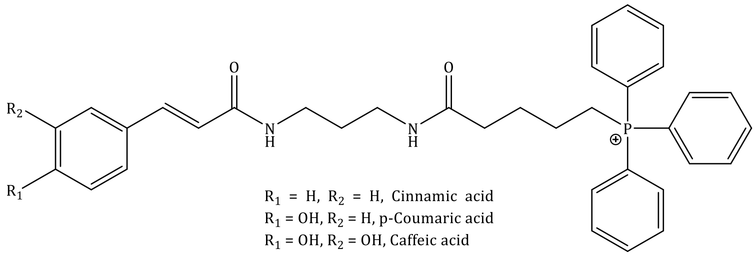
Phenolic antioxidants can be found in a variety of natural sources, such as fruits, vegetables and medicinal herbs. These species are capable of neutralizing free radicals, which in high concentrations can cause oxidative stress. When oxidative stress occurs in the cell, it can damage mitochondrial DNA leading to mitochondrial dysfunction, which has been associated with various diseases such as type 2 diabetes, heart failure, and neurodegenerative diseases such as Parkinson's.[1,2] One strategy to combat oxidative stress in mitochondria is to selectively transport antioxidants to this organelle by delivery vectors. However, the structure of the mitochondrial bilayer and its high negative potential hinder the transport of active molecules into the organelle. One strategy for their transport is through vectorization guided by delocalized lipophilic cations. These are capable of delivering compounds to the mitochondria as they are attracted to the mitochondria due to the high negative potential of the mitochondrial inner membrane, where one that has been successfully tested is the triphenylphosphonium cation (TPP).[3,4] On the other hand, the use of dendrimers for the encapsulation and transport of antioxidants improves their solubility, biocompatibility and pharmacokinetic properties. In this work, we studied the role of the polarity of the medium on the antioxidant capacity of cinnamic acid, p-coumaric acid, and caffeic acid, together with the changes in the mechanism resulting from their conjugation with TPP.

The calculated oxidation potentials of the antioxidants conjugated with TPP in different environments showed that these complexes are inactivated in apolar solvents, whereas in polar environments it is highly activated, thus transporting it in apolar environments and releasing the antioxidants into the mitochondria would increase its efficiency and selectivity. Finally, a detailed explanation is presented to understand the issues underlying the oxidation mechanisms of the different antioxidants presented.



TPP-conjugated antioxidants

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Topological analysis of the electron density to study the nature of chemical bond: case of polymer complex $(C_{200}H_{166}Cu_{12}N_4P_6Se_{12})_n,6n(C_4H_{10}O_2)$

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The topological analysis of the electron density (ρ) distribution provides the evidence of a bond critical point (bcp) in the intermolecular region. The topological properties of $\rho(r_{bcp})$ characterize the interaction between the atoms involved. A first classification of the distribution of $\rho(r_{bcp})$ is determined by the magnitude of their Laplacian, $\nabla^2\rho(r_{bcp})$. A shared – shell chemical interaction is evidenced by a negative value of the Laplacian (local concentration) of the electron density distribution, $\nabla^2\rho(r_{bcp}) < 0$; closed – shell chemical interactions, on the other hand, exhibit positive values of the Laplacian (local depletion) of the electron density distribution, $\nabla^2\rho(r_{bcp}) > 0$ [1,2]. However, for the full understanding of the electronic environment distribution in complex systems is necessary to establish a series of relationships derived from these three initial parameters [3,4]. The fourth criterion used in our analysis is the $|V(r_{bcp})|/G(r_{bcp})$ index where $V(r_{bcp})$, the local electronic potential energy density, represents the capacity of the system to concentrate electrons at the critical point, and $G(r_{bcp})$, the local electronic kinetic energy density, gives the tendency of the system to dilute electrons at the same point [2]. Espinosa classified the $|V(r_{bcp})|/G(r_{bcp})$ indicator in three regions, I) $|V|/G < 1$ and positive total energies ($H > 0$), pure closed – shell, II) $1 < |V|/G < 2$ ($-G < H < 0$), between close – shared shell and III) $|V|/G > 2$ ($H < -G$), shared – shell [1]. In this work the monomer of polymer complex $(C_{200}H_{166}Cu_{12}N_4P_6Se_{12})_n,6n(C_4H_{10}O_2)$ [5] was studied, establishing the nature of the interaction Cu–Se(II), Cu–N(II), Cu–Cu (character metallophilic), N–C(III) and C-C(III) by topological analysis of electron density and electron location function (ELF), determined by the Quantum Theory of Atom in Molecules (QTAIM) using the Density Function Theory (DFT).

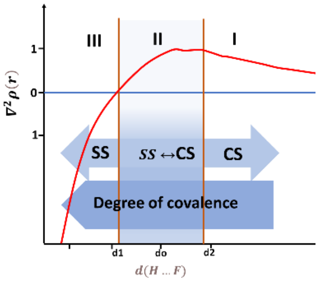

Figure 1. Laplacian characteristic regions of electron density.

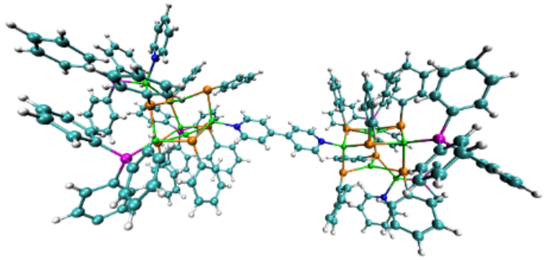

Figure 2. Monomer of the polymer **$(C_{200}H_{166}Cu_{12}N_4P_6Se_{12})_n,6n(C_4H_{10}O_2)$.**

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Activation of Strong σ-bonds by Low Valent Alumnyl Anions

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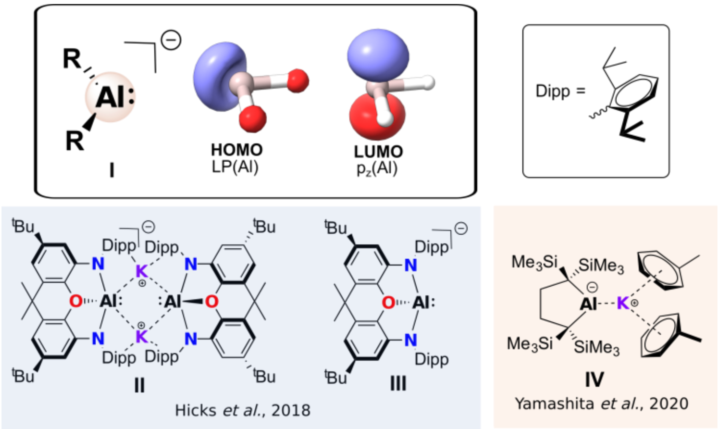
Aluminyl anions are electron-rich systems with a low valent Al(I) center, presenting a lone electron pair and an empty-p orbital perpendicular to it. These low valent aluminyl species are known to be significant σ-donors, which have been theoretically predicted to have the ability to carry out small-molecule activation reactions, a rather crucial step in the construction of catalytic cycles. Furthermore, these systems are very reactive toward the activation of σ-bonds and in reactions with electrophiles.

In this work, the activation of H_2 is studied using the simplest substituted AlR_2^- systems (**I**) employing high-level coupled cluster theory. Moreover, the computational characterization of the reaction mechanism for the activation of variated -bonds (H_2, CH_4, H_2O, NH_3, PH_3, SiH_4) was also studied using the monomeric (**II**) and dimeric (**III**) Hicks's complexes as well as Yamashitas's complex **IV**.



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Enantiospecific electron transport in chiral-modified molecular junctions

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We shall disclose the theoretical dependence of electronic transport with geometrical chirality in a molecular electronic device in which the source electrode is modified by attaching a chiral gold cluster (chAu34) [1], and in the middle part, a chiral organic molecule (label as HB) is connected (see Fig. 1a,b). The presence of chAu34 in these devices triggers enantioselective transport, this means, a difference in transmission function (see Fig. 1c) and in the conductance: 43.4 µA/V for the R case vs. 34. 5 µA/V for the L case (see Fig. 1d). It's worth mentioning that these devices could be an alternative to other chiral detection techniques, such as optical methods or those that depend upon the spin state of the system, as occurs in the Chiral-Induced Spin Selectivity effect [2]. Also, this work could be a model that describes an intrinsically chiral STM dip, as is experimentally observed in Ref. 3. As a final comment, all calculations were performed in SIESTA and in Transiesta codes, which are based on DFT theory and Non-Equilibrium Green's Function method respectively.

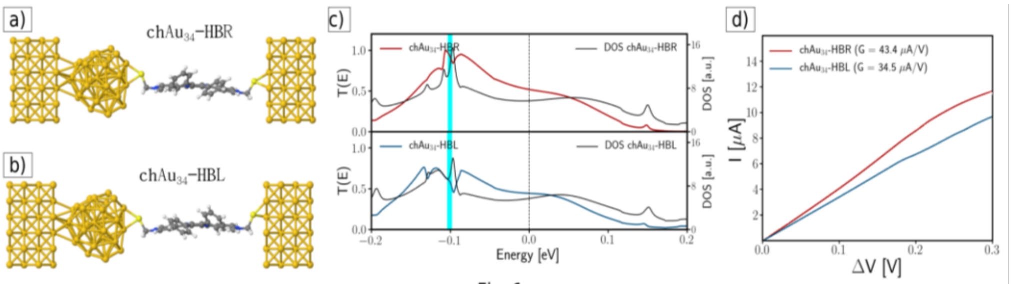

Fig. 1

Acknowledgments: OHM acknowledges UNAB (Chile) for the funding to attend this "12° Workshop en Química Computacional y Espectroscopía Molecular" and CONAHCYT for a graduate student scholarship. JEBV acknowledges funding from CONAHCYT Frontera 428214 and PAIP-FQ(UNAM) 5000-9173. ILG thanks the funding of CONAHCYT-Mexico under Project 285821, DGAPA-UNAM-Mexico under Project IN106021, and DGTIC-UNAM-Mexico under Project LANCAD 049.

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Quantum chemical exploration of the inner working of SAM-dependent epigenetic writers and halogenase enzymes

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Enzymes are macromolecular systems capable of performing fascinating chemical transformation that otherwise would be difficult or even impossible. These molecular machines are the main responsible of life, and its continuous understanding has leaded towards the design of new promising devises in fields such as remediation, chemical catalysis, biomedical applications, among others. Here we proposed to uncover the main factors that govern the mechanisms by which two different groups of enzymes are able to perform their specific role. On a first stage, we will expose the molecular intricacies associated to the inner working of SAM-dependent methyltransferases involved in epigenetic regulation process, and how according to our calculations, specific mutants can change its product specificity, and even increase its activity (Figure 1(a)).[1,2] These enzymes are in charge of the addition of a methyl group to the N-terminal domain of histones, process known as writing an epigenetic mark. The reading of this mark may trigger the expression or silencing of a gene. The malfunctioning of these enzymes is associated to the generation of cancer, as it may lead to the activation of the expression of an oncogene or the silencing of a tumor suppressor gene. On a second stage, we will present the results obtained from the exploration of the reaction mechanism for the carbon-halogen bond formation catalyzed by SAM-dependent halogenases (Figure 1(b)).[3,4]

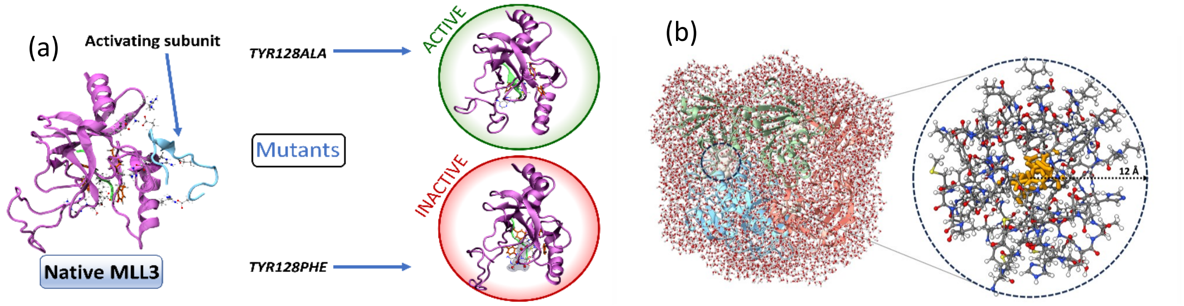

Figure 1. (a) Representation of the effect of 2 possible mutants on a methyltransferase enzyme (MLL3). (b) Representation of a fluorinase enzyme, and its catalytic site.

Acknowledgement: This research was funded by FONDECYT 1221898

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Theoretical kinetic study of the reaction of 2,5-Dihydrofuran with ozone: Mechanism and atmospheric fate of reaction products

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The 2,5-dihydrofuran (2,5-DHF) is an unsaturated heterocyclic molecule used as additive to diesel engines and is employed as a component of second generation biofuels [1]. Therefore, the production and use of this compound could increase its concentration in the troposphere. One of the main loss processes in the atmosphere for unsaturated compounds is the reaction with tropospheric ozone. This reaction can be described by the Criegee mechanism where very reactive birradical species, called Criegee Intermediates (CIs), are formed [2]. They can undergo unimolecular reactions or react with atmospheric species to produce different compounds, some of which could be aerosol precursors, affecting quality of air and contributing to climate change. The two reported experimental rate coefficients of the studied reaction are in good agreement with a value of (1.65±0.31) x 10^{-17}cm^3 molecule^{-1}s^{-1} at 298 K and 1 atm [3,4]. Additionally, an investigation based in matrix isolation technique proposes an alternative pathway to the Criegee mechanism, with the formation of complex furan--H_2O_3 through a dehydrogenation process [5].

In order to analyse the potential atmospheric competition between both processes, we present a theoretical investigation of the energetics and kinetics of the reaction of 2,5-DHF with O_3. The functional M08-HX/6-311++g(3df,3pd) was used to characterise the species and higher levels of theory, like CCSD(T)/aug-cc-pVTZ and DLPNO CCSD(T)/aug-cc-pVTZ, were employed for a reliable estimation of electronic energy. The rate coefficients were derived applying the canonical transition state theory. The results are in excellent agreement with the experimental values, being of 1.74x10^{-17}cm^3 molecule^{-1}s^{-1} at the DLPNO CCSD(T)/aug-cc-pVTZ//M08-HX/6-311++g(3df,3pd) level of theory. The present results suggest that the Criegee mechanism is dominant in tropospheric conditions. In addition, the kinetics of possible unimolecular processes of the generated CI were investigated, and the reaction between CI and H_2O was analysed.

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Advancing Insights into the Bonding in f-Element Complexes

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When considering f-element bonding in complexes, it is generally accepted that the lanthanides exhibit ionic interactions, whereas in the light actinides the bonds are more covalent in nature (due to the radial extent of the 5f shell). In addition, it is often stated in the literature that the heavy actinides behave like the corresponding lanthanides.[1] However, recent research has developed selective ligands capable of separating Bk^{3+} from the lanthanide ions, Am^{3+} from Nd^{3+} and even Bk^{3+} from Bk^{4+}, among others.[2-3] Therefore, authors point to a certain covalency in the heavier actinides, a concept now extended in terms of orbital overlap or orbital energy degeneracy[4]. These findings could place them heavy actinides as less hard acids, according to Lewis acidities and consequently incorporate soft donor atoms into ligands as a means of potentially increasing covalency[3-5].

Theoretical studies of the covalence of actinides (An) have helped to better understand this remaining open question.[4-6] In our work, we have performed a systematic study of the metal-ligand interaction in $[An(S_2CNH_2)_4]^n$ (n=0,1) and $[AnO_2(L)_x]^{n-/+}$ complexes, i.e with dithiocarbamate ligands and actinyl ion derivatives, respectively. We used a methodologies based on wave function analysis (nephelauxetic effect), Quantum Theory of Atoms in Molecules (QTAIM) and Natural Bond Orbital (NBO) analysis. Our research shows that covalency is favored when soft base donor atoms are involved. QTAIM metrics, especially total energy density (H), virial ratio (|V/G|), and delocalization index ($\delta_{(A,B)}$), consistently indicate that covalency is more pronounced in heavy actinides than in lanthanides, even in An(IV) complexes compared to An(III) complexes. Thus, a better understanding of f-element bonding can be achieved by combining several computational methods.

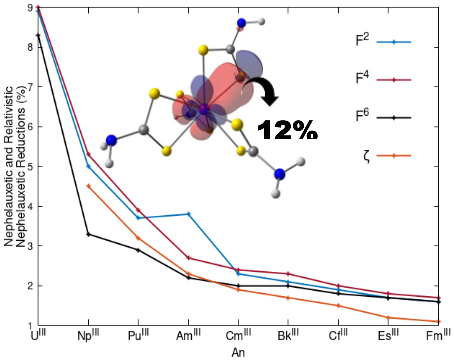

Figure 1. Nephelauxetic Effect in $[An(S_2CNH_2)_4]^-$ and NLMO Analysis for $[Am(S_2CNH_2)_4]$ Molecule

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Substituent effect on frustrated Lewis pairs (FLPs) based on 2-[bis(R)boryl]-N,N-dimethylaniline in catalytic hydrogenations of polar and nonpolar double bonds: A theoretical study.

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Frustrated Lewis pairs (FLPs) emerged as a metal-free alternative for inert bond activation and catalytic reductions of unsaturated compounds.[1,2] The intramolecular FLP 2-[bis(pentafluorophenyl)boryl]-N,N-dimethylaniline demonstrated the ability to activate the H-H bond, being subsequently used in the catalytic reduction of a variety of alkynes. In this work, the substituent effect on the 2-[bis(R)boryl]-N,N-dimethylaniline backbone was studied to tune the Lewis acidity of the boron atom using electron donating groups (EDGs = Me, Et, Ph and Mes) and electron extracting groups (EWGs = CF_3, pFPh, p-NitroPh and FMes) attached to the B atom. The performance in H-H bond activation and catalytic reduction of polar and non-polar substrates was analyzed. While the former was studied with the global/local electrophilicity index defined by Parr,[3] the latter was characterized using the theoretical TOF proposed by Kozuch and Shaik[4] to obtain the efficiency of a catalytic cycle using the complete reaction mechanism.[6] The proposed mechanism for the reduction of alkynes with 2-[bis(pentafluorophenyl)boryl]-N,N-dimethylaniline consists of a first step releasing an R-substituent, forming the catalytically active species, followed by a hydroboration of the alkyne, finally releasing the alkene.[5] This mechanism was studied for the catalytic reduction of ethene and formaldehyde, but in view of the need to deepen the knowledge of the mechanism, alternative routes for the catalytic reduction of unsaturated compounds and deactivation routes were also studied. For ethene, the initially proposed internal conversion mechanism (hydroboration route) was found to be feasible, while the alternative route of direct reduction by double H^-/H^+ transfer to ethene by different species of FLPs was also found, but with different degrees of catalytic efficiency. In contrast, the reduction for formaldehyde only proved feasible for direct double H^-/H^+ transfer from FLP, whereas the hydroboration route yields methoxy-substituted FLPs.

Acknowledgements. The authors acknowledge Fondecyt grants with projects Nºs 1181914 and 1231241.

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Physicochemical and Theoretical Characterization of (E)-4-amino-3-((3,5-di-tert-butyl-2-hydroxybenzylidene)amino) benzoic acid harbor a Differential Antimicrobial Effect against Gram-Positive Bacteria

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Searching for adequate and effective compounds displaying antimicrobial activities, especially against Gram-positive bacteria, is an important research area due to the high hospitalization and mortality rates of these bacterial infections in both the human and veterinary fields.[1] In this work, we explored (*E*)-4-amino-3-((3,5-di-tert-butyl-2-hydroxybenzylidene)amino) benzoic acid (**SB-1**, harboring an intramolecular hydrogen bond). Results demonstrated that **SB-1** showed an antibacterial activity determined by the minimal inhibitory concentration (MIC) against Staphylococcus aureus, Enterococcus faecalis, and Bacillus cereus (Gram-positive bacteria involved in human and animal diseases such as skin infections, pneumonia, diarrheal syndrome, and urinary tract infections, among others), which was similar to that shown by the classical antibiotic chloramphenicol.[2] By contrast, this compound showed no effect against Gram-negative bacteria (Klebsiella pneumoniae, Escherichia coli, and Salmonella enterica). Furthermore, we provide a comprehensive physicochemical and theoretical characterization of SB-1. We also performed a computational study through the DFT theory level, including geometry optimization, TD-DFT, NBO, and global and local reactivity analyses.

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fac-Re(CO)3(5,6-epoxy-5,6-dihydro-1,10-phenanthroline)Br: Physicochemical and Staining assay in Gram-negative bacteria and yeast

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Coordination d^6 metal complexes, such as Re (I) tricarbonyl complexes have exposed highly suitable properties for cellular imaging (especially for fluorescent microscopy) such as low cytotoxicity, good cellular uptake, and differential staining.[1] These features can be modulated or tuned by modifying the ligands surrounding the metal core. However, most of Re(I)-based complexes have been tested for non-walled cells, such as epithelial cells (skin, blood vessels, and organs).[1] In the present work, we show *fac*-Re(CO)$_3$(5,6-epoxy-5,6-dihydro-1,10-phenanthroline)Br complex, obtaining the first neutral Re(I)-based complexes able to stain walled cells (bacteria and yeasts).[2] In this study, we show a complete structural characterization. We also assessed the cytotoxicity of *fac*-Re(CO)$_3$(5,6-epoxy-5,6-dihydro-1,10-phenanthroline)Br against walled-cells, including Gram-negative bacteria (*Salmonella enterica serovar Typhimurium*), non-sporulated Gram-positive bacteria (*Staphylococcus aureus*), sporulated Gram-positive bacteria (*Bacillus cereus*), and yeasts (*Candida albicans*), all cell models involved in human diseases.[2] We observed that this complex exhibited very low or no cytotoxicity, and also found that *fac*-Re(CO)$_3$(5,6-epoxy-5,6-dihydro-1,10-phenanthroline)Br exhibited good properties as a luminescent probe for this kind of cells. Accordingly, we found that this complex showed good potential to be directly used as a luminescent probe for walled cells, including yeasts (e.g., *Candida albicans*) and Gram negative bacteria (e.g., *Salmonella enterica*), which can be observed by confocal microscopy. This work open a new use of Re(I)-based complexes as fluorophores for walled cell, and has gained increasing biology inorganic chemistry attention in recent years.

Acknowledgments: FONDECYT Regular 1230917 (ANID) and Núcleo UNAB DI-01-22/NUC

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Metabolites in endemic Agaves species from the region of the Caribbean and its lipid-lowering effect.

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Hyperlipidemia is a major determinant of cardiovascular diseases. Natural products are a valuable source of new active agents capable of reducing plasma lipids without secondary effects. Steroidal saponins are major metabolites from agaves with reported hypolipemiant activity. For all these precedents, in this work the authors studied the behavior of agaves species in that way, choosing initially the Agave brittoniana ssp brittoniana, Agave acicularis and Agave grisea. The principal metabolite types were determined qualitatively using phytochemical screening were proof the presence of saponins, coumarins, flavonoids and alkaloids. Experimental conditions established for hydroalcoholic (42-43%) and n- butanolic (8-10%) extracts obtaining, similar results with the Agave brittoniana trel1 were studies. The presence of yuccagenin and diosgenina was evidence like majority sapogenins using chromatographic tecniques.

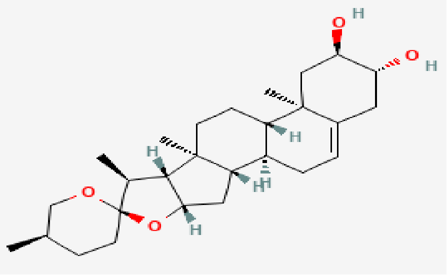

Figure 4. Structure of a spirostan Sapogenin. 25R-espirost-5-en-2α, 3β-diol (Yuccagenin)[2]

The hypolipemiant activity was evaluate producing cholesterol and triglyceride in blood superior values with exception of Agave grisea, although these values were saw affected by a high percent of mortality.

Acknowledgments: We thank the financial support of ANID/Chile under Project FONDECYT 1230917.

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Predicción de Entalpias de Formación en Aleaciones de Alta Entropía (HEA): $Fe_{20}Mn_{20}Ni_{20}Co_{20}Cr_{20}$ y $Fe_{50}Mn_{30}Co_{10}Cr_{10}$

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Las aleaciones de alta entropía (HEA) forman soluciones sólidas que pueden construir diferentes estructuras cristalinas, como FCC, BCC y HCP, dependiendo de la disposición de los átomos. [1] Este trabajo se centra en las aleaciones equiatómicas, que son mezclas de elementos metálicos en proporciones iguales. Estas se caracterizan por tener una estructura cristalina cúbica centrada en la cara (FCC) y se les conoce también como aleación de Cantor, como en el caso de la composición ($Fe_{20}Mn_{20}Ni_{20}Co_{20}Cr_{20}$).[2] Por otro lado, se estudian las aleaciones no equiatómicas o duales, como en el caso de la composición (Fe50Mn30Co10Cr10), que tienen proporciones diferentes y presentan una conversión de estructura cristalina FCC a una fase compacta hexagonal (HCP) al enfriarse desde una región de alta temperatura. Estas aleaciones duales conducen a una mayor resistencia, reducción térmica y estabilidad de las fases de alta temperatura, lo que resulta en una mayor fortaleza del material. [3]Para llevar a cabo este estudio, se crearon estructuras de supercelda para la aleación $Fe_{50}Mn_{30}Co_{10}Cr_{10}$ utilizando estructuras cuasi-aleatorias especiales (SQS). Luego, se optimizaron estas superceldas mediante el método de la teoría de la función de densidad (DFT) implementado en el programa Vienna ab initio simulation package (VASP), analizando los cambios en la estructura cristalina y encontrando la energía electrónica total de cada sistema, incluyendo correcciones magnéticas debido a los diferentes estados de espín. Para la aleación de Cantor, se construyó una supercelda de 60 átomos que representa un reordenamiento aleatorio de los elementos metálicos en la estructura cristalina. Posteriormente, se siguieron los mismos procedimientos que para las aleaciones no equiatómicas. Los resultados muestran que, en la aleación de Cantor, los elementos Fe y Cr presentan una estructura cristalina más estable en forma de BCC, mientras que para Ni, Co y Mg las estructuras más estables corresponden a FCC, HCP y Mg20, respectivamente.

Agradecimientos: Fondecyt de iniciación 11200264

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Electronic and structural properties of B6 clusters doped with Be—a computational study.

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Researchers have recently delved deeply into the structural diversity of boron clusters. This interest stems from their electron-deficient characteristics and the existence of delocalized multicentric bonds, which bestow them with aromatic properties. Moreover, the effects of doping these clusters with different metals have been studied, broadening their potential applications [1,3]. A significant discovery in this domain is stabilizing boron clusters, notably B60 and B80, by incorporating beryllium atoms [2]. This addition addresses the electronic deficiency and unveils unique properties like fluxionality and enhanced aromaticity. A particularly intriguing observation is the notably short distances between beryllium atoms in the $Be_2B_7^-$ and Be_2B_8 clusters, measuring 1.90 Å and 1.91 Å, respectively. This finding has sparked considerable academic curiosity [3,4]. Inspired by the abovementioned research, in this study, we delve into beryllium-doped boron clusters, specifically focusing on M_nB_6 (where M=Be and n ranges from 1 to 6). We performed a computational study, utilizing the AUTOMATON program to identify global minimum structures combined with local optimizations at DFT level. Intriguingly, introducing three or more beryllium atoms into the B_6 cluster led to significant structural alterations, promoting the emergence of three-dimensional configurations as global minima. To further analyze the electronic structure properties, techniques such as natural population analysis (NPA), Wiberg bond indices (WBI), and the Adaptive Density Natural Partitioning (AdNDP) method were employed. The insights from this research will enrich our comprehension of the electronic structure of beryllium-doped boron clusters, marking a significant stride in this burgeoning research area.

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Síntesis Asistida por Microondas de Complejos Derivados de Iminas con Potencial Catalítico en Reacciones Click

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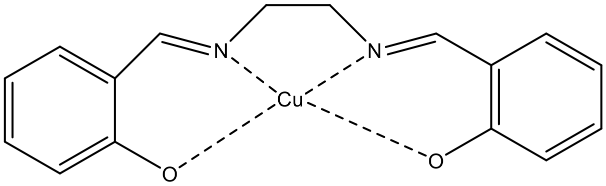
El desarrollo de diversas metodologías para la obtención de triazoles ha llevado a explorar el uso de nuevas fuentes catalíticas que permitan potenciar el rendimiento de la reacción.[1] En este trabajo, se sintetizan una serie de complejos de cobre y hierro, utilizando ligandos tipo imina, derivados de salicilaldehido. Mediante el uso de microondas, se sintetizan iminas derivadas de salicilaldehido y aminas como etilendiamina, acido 4-aminosalicílico y p-toluidina. Estas, se hacen reaccionar con CuI y $FeCl_3$ para obtener compuestos de coordinación.



Los compuestos obtenidos son caracterizados mediante espectroscopía infrarroja, en donde se identifica la conversión del grupo carbonilo al grupo imino, y análisis termogravimétrico, identificando puntos de descomposición y fenómenos de estabilidad térmica. Como resultado preliminar, se han sintetizado los complejos Bis-saliciletilendiiminCu (I) y Bis-saliciletilendiiminFe (III). Se espera que dichos compuestos puedan utilizarse en la síntesis de triazoles y corroborar su efectividad catalítica respecto al uso de CuI convencional.

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Understanding the Transition from Statistical into Non-Statistical Reactivity Regimes in Cycloaromatizations of Eneyne-Allenes. A Reaction Force Constant Based Study

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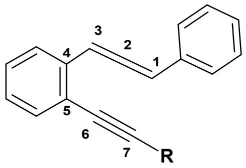
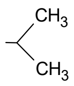
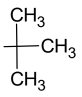
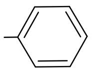
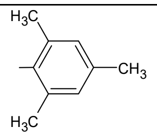
Myers-Saito and Schmittel cycloaromatization reaction pathways were computed to gain physical insights in the transition from a well-described classic statistical reaction into a non-statistical scenario using seven prototypes of benzoannulated eneyne-allenes. To achieve this goal we used the reaction force constant introduced in the reaction force frame. was further decomposed into a linear combination of active modes (LCAM) along the transition region in both 5-endo and 6-endo paths by a static approach (PLS-VIP decomposition models) inspirated by the decomposition of the reaction force constant proposed by Toro-Labe et all. LCAM-based procedure revealed the following two main features. First, the vibrational contributions of the *H-wagging* type in the allene group, the *bending* type of the alkyne moiety, and also the vibrational contribution of the fourth vibrational character mode of the benzene substructure in the benzoannulated moiety contribute towards the Schmittel and Myers-Saito cyclization in favor of risen quasi-degenerated transition states, and secondly, an overall tendency shows a linear dependency in the distance of the free energy barriers ($\Delta\Delta G^{\ddagger}$) with the exergonicity difference ($\Delta\Delta G$) in the competitive paths of cycloaromatization reactions. In line with the last mention, we propose that specific vibrational coupling (*H-wagging* of the allene group, a *bending* type of the eneyne group and the fourth vibrational character mode of the benzene ring in the benzonnulated moety) in the exit channels of reaction between quasi-degenerated transition states will explain the risen of non-statistical perturbation due to deviations of the Boltzmann distribution.



System	1	2	3	4	5	6	7
R	$-H$	$-CH_3$	$-CH_2CH_3$	 $-CH(CH_3)_2$	 $-C(CH_3)_3$		

Acknowledgments: FONDECYT projects № 1181914 (PJ), 1221803 (RMM) for financial support.

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Remoción del azul de metileno presente en el agua utilizando nanocompósitos de lignosulfonato de sodio y TiO_2.

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En la actualidad, una amplia serie de contaminantes impacta los cuerpos de agua naturales debido a las descargas industriales [1,2]. Uno de estos contaminantes es el azul de metileno (MB), que, debido a su compleja estructura química, tiene una baja tasa de degradación natural, lo que suscita un interés en el desarrollo de métodos que aceleren este proceso [2]. En este contexto, ha habido una escasa investigación sobre la utilización de materiales poliméricos compuestos por hidrogeles y óxidos metálicos para la adsorción y fotodegradación de MB (ver **Figura 1**)

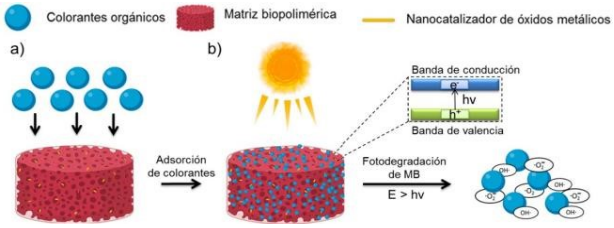

Figura 1. Representación del proceso de a) adsorción y b) degradación de MB utilizando óxidos metálicos como fotocatalizador.

En esta investigación, se desarrollaron nanocompuestos utilizando como base el poli(4-estireno sulfonato) de sodio (P(SSNa)), con diferentes proporciones de lignosulfonato sódico (LS) y nanopartículas de óxido de titanio (Np TiO_2). La formación de estos nanocompuestos se confirmó mediante técnicas de análisis, como espectroscopía infrarroja, microscopía electrónica de barrido y análisis termogravimétrico. El sistema que consiste en P(SSNa) con un 20% de LS y un 10% de Np TiO_2 demostró una eficacia máxima de adsorción de MB del 94,8% y una capacidad máxima de adsorción de MB de 780 mg g^{-1}. Los resultados obtenidos se ajustaron a modelos cinéticos de pseudo-segundo orden y a los modelos de isotermas de Freundlich, Elovich y Redlich-Peterson. En consecuencia, se evidenció que el material adsorbente investigado posee propiedades prometedoras para la eliminación de colorantes iónicos, presentes en aguas residuales. Además, podría considerarse para su uso como material capaz de concentrar y posteriormente fotodegradar los contaminantes adsorbidos.

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Accessible quantum states of molecular domains

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In this work, we propose a framework to describe the accessible quantum states of a molecular domain, based on the density matrix theory. These domains are regions in the molecular space that exchange electrons between them, and hence, are considered open quantum systems. In this sense we use the grand-canonical statistical model to describe the quantum states of a molecular domain which permits the treatment of the number of particles as a continuous variable. The model is based on the statistical contribution of three closed systems states, which consists of a neutral and two ionic (cationic and anionic) states within the Fock space. Representation of the energies in a simplex diagram and the corresponding energy variations along vertical and horizontal trajectories are also discussed.

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The inverse temperature estimator-operator

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The inverse temperature is a key quantity in both classical and quantum statistical mechanics. It appears as a Lagrange multiplier, in MaxEnt procedure, associated to the constraint that the energy of a system within a thermal bath fluctuates around its mean value [1,2]. In the literature of classical statistical mechanics, there are some definitions to an inverse temperature estimator [3,4], i.e., a quantity which gives the inverse temperature of the system after taking its expectation value. Nevertheless, to date, no works in this direction, within a quantum formalism, are reported. This communication has a twofold purpose: the first one is to show an adaptation to quantum mechanics of the conjugate-variables theorem [5] (Q-CVT) by means of the Lie derivative between linear operators; the second one is, by use Q-CVT and a Gibbs state, to show a general form of an inverse temperature estimator-operator. Applications to simple quantum systems and, comparisons with the equivalent results of classical statistical mechanics are also discussed.

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Electrical Resistance and Electronic Density of States of H_2S Crystalline Phases at Different Pressures and Temperatures

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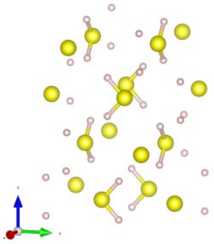
In a recent work, it was discovered conventional superconductivity of crystalline H_2S at 203K (under 153GPa of pressure), the highest temperature known actually, which was also predicted theoretically [1]. However, it is still not clear which chemical interactions and crystal structures are responsible for the observed superconductivity of H_2S at high pressures, where the chemical dissociation of this compound or the formation of metal hydrides and perovskite structures may play presumably a significant role [2]. These results have motivated the development of new works to compute different properties of H_2S crystals and to establish specific crystalline structures under high pressures.



The scope of the present work is to compute H_2S crystalline phases, at different pressures and temperatures, by means of the density functional theory (DFT) and molecular quantum dynamics, to estimate electrical resistance and electronic density of states of each phase. It be expected that these results contribute to elucidate the specific structure that promotes superconductivity of the H_2S crystal.

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New insights into H_2 activation by intramolecular Frustrated Lewis Pairs based on aminoboranes: The local electrophilicity index of boron as a suitable indicator to tune the reversibility of the process

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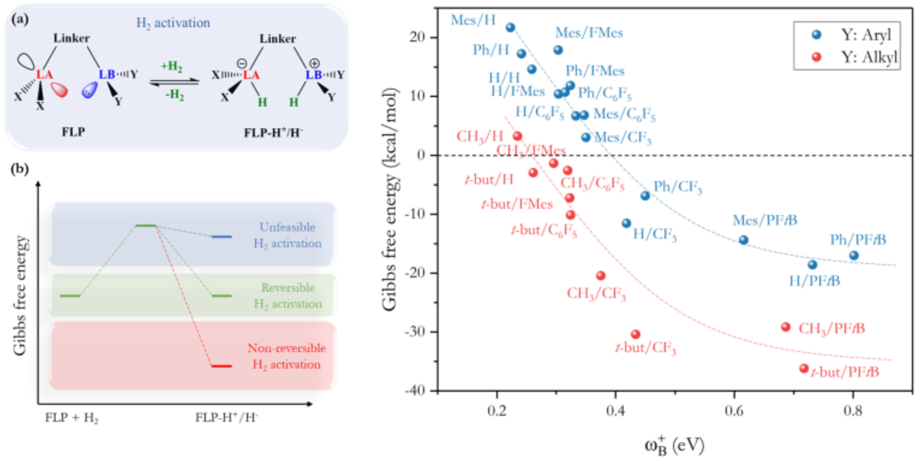
Frustrated Lewis Pairs (FLPs) have emerged as a metal-free alternative to traditional transition metal catalysis [1]. FLPs have been able to activate reversibly H_2, allowing the reduction of unsaturated organic compounds. In this work, a large set of intramolecular aminoboranes-based FLPs was studied employing Density Functional Theory in the H_2 activation process to analyze how the acidity and basicity of boron and nitrogen atoms, respectively, affect the reversibility of the process. The results show that significant differences in the Gibbs free energy of the process are found by considering all the combinations of substituents. From this, 25 different FLP systems of type 2-[bis(X)boryl]-(Y)aniline (X: H, CF_3, C_6F_5, PF*t*B, FMes and Y: H, CH_3, t-but, Ph, Mes) can be formed. By analyzing the electronic properties of each system, we have found that the condensed-to-boron electrophilicity index ω^+_B is inversely related to the ΔG_{H2}, as shown in a previous study but with a considerably smaller set of systems [2]. Interestingly, two relationships were found; the first is for alkyl groups (Y: CH_3 and *t*-but) and the second for aryl groups (Y: H, Ph, and Mes) attached to nitrogen. With this finding, a rational design of this kind of FLPs can be performed by analyzing the acidity of boron through ω^+_B and knowing the nature of the substituent of nitrogen according if the Y is alkyl or aryl, optimizing the H_2 reversible activation in a rational way, which is crucial to improve the catalytic performance.



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Electronic and steric effects in dimer formation of aminoborane Frustrated Lewis Pairs: A computational study

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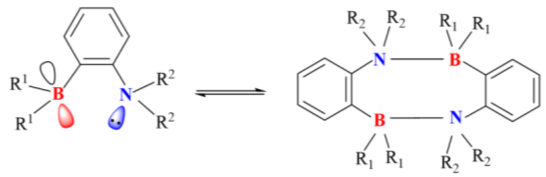
This study focuses on analyzing electronic and steric effects that influence the dimerization of intramolecular aminoborane Frustrated Lewis Pairs (FLPs), employing the Density Functional Theory (DFT). The FLPs have emerged as metal-free catalysts [1, 2, 3] of great interest, especially in the reversible H_2 activation. These molecular systems are composed of a Lewis acid and a Lewis base centers, which, due to the steric effect of bulky substituents, are hindered from forming the classic Lewis adduct. This peculiarity allows them to donate and accept electrons in the same cavity, fundamental to activating extremely stable molecules, such as H_2. However, the dimerization of FLPs limits their catalytic activity. In this sense, this study aims to elucidate how aryl or alkyl substituents attached to boron and nitrogen affect dimerization. The computational analysis reveals that unsubstituted boron or nitrogen favors the dimer formation. As the substituent increases in size, e.g., by employing methyl group in nitrogen, the dimerization is prevented, no matter which substituent in boron is employed. On the other hand, when bulky substituents are employed in both Lewis centers, covalent dimer formation is avoided, and non-covalent dimers predominate from an energetic viewpoint. The non-covalent dimer formation does not affect the acidity of boron, which relates with the ΔG of H_2 activation process, [4] preserving its capability to act as a catalyst. This study contributes to the rational design of FLP catalysts by providing a detailed comprehension of the factors that influence the formation of the dimers, which is a step in developing more environmentally friendly chemical processes.



R^1, R^2: {H, CH_3, *t*-but, Ph, Mes}

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Amines in the interstellar medium (ISM)

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The detection of amines in the interstellar medium (ISM) confirms their efficient formation through interstellar chemistry, however, the specific pathways leading to their formation in the ISM are still poorly understood. In this context, theoretical investigations can contribute by calculating spectroscopic parameters, including rotational constants, vibrational frequencies, and infrared intensities using ab initio methodologies such as coupled clusters (CCSD(T)). Thus, advancements in theoretical methodologies are required to improve the precision and accuracy of the predicted frequencies, allowing for a more robust identification of C_2NH_4O amine precursors in the ISM. For those species, a precise spectroscopy characterization will be performed. There is no rotational spectroscopy available for $C2NH_4O$, so no search for any of these precursors can be conducted in the laboratory. We will provide accurate rotational data to guide possible laboratory searches, which will be done by our collaborators at the Center of astrochemical studies at the Max Planck Institute for Extraterrestrial Physics in Garching.

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NCI-i a new descriptor based on Non-Covalent Interactions for the exploration of Potential Energy Surface

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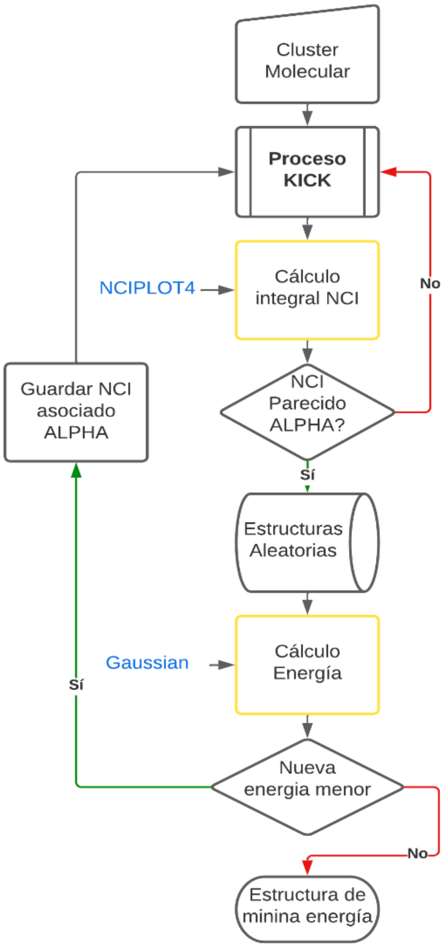
Non-Covalent Interactions (NCI)[1,2] are chemical interactions between atoms or molecules that do not involve exchanging or transferring electrons between them. Thanks to the electron density ($\rho(r)$) and its reduced gradient ($s(r)$), it is possible to notice the presence and strength of NCIs in a chemical system without the need for demanding calculations. However, this methodology's possible predictive capability in exploring the potential energy surface has not yet been addressed. We introduce the "Non-Covalent Interaction Index" (NCI-i) as a quantitative descriptor, according to the NCI integral described by Contreras[3]. We demonstrate that this index has a strong direct correlation with the energy of molecular clusters, making it a valuable tool in chemical research. In addition, we have developed a computer program that simplifies and automates calculating the NCI-i, from the preparation of input data to the interpretation of results.

To further enhance the usefulness of NCI-i, we have incorporated a search algorithm based on simple particle swarm approach, optimizing the selection of molecular structures. Initial results are promising: the use of the NCI-i-based method significantly improves the stability of isomers, outperforming random selection techniques.



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Searching for Global Minima Structures containing Planar Tetracoordinate Group 13-15 Elements

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Since its the groundbreaking introduction by Monkhorst in 1968, planar tetracoordinate carbon (ptC) has captivated chemists attention.[1] Two years later Hoffmann and his team introduced methods to stabilize ptC transition states in racemization reactions.[2] These pioneering efforts have led to a surge in the design and discovery of ptC compounds, challenging long-standing beliefs in organic chemistry.[3]

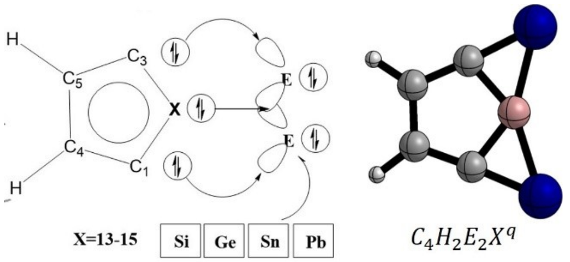

Fig. 1. Aromatic ring system with planar tetracoordinated metal.

In our computational study, we extend a stabilization strategy proposed by Yañez et al.[4] initially developed for designing ptCs. Here, our study zeroes in on the $C_4H_2E_2X^q$ combination, with E representing elements from silicon to lead, X denoting elements from groups 13-15, and q as –1 (group 13), 0 (group 14), or +1 (group 15), which had not been explored yet . Interestingly, these systems incorporate a planar tetracoordinated main group element (ptX) within an aromatic five-membered ring. We arrive at this conclusion after exploring the potential energy surface of different combinations and analyzing the chemical bonding employing different methods, including Wiberg Bond Indices (WBI), Natural Population Analysis (NPA), and Adaptive Natural Density Partitioning (AdNDP). Additionally, we examined the aromaticity of the systems through the induced current densities in response to an externally applied magnetic field oriented perpendicular to the molecular plane.

Acknowledgements: The authors acknowledge financial support from the Doctoral Scholarship Program in Molecular Physical Chemistry, the FONDECYT project number 1211128, and the supercomputing infrastructure support from NLHPC (ECM-02).

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Pyvista for Visualizing and Modeling Aromatic Compound Properties

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This study introduces a systematic approach to analyzing and visualizing aromatic molecule data using VTK and VTI files. Graphical interfaces and the Pyvista library were utilized to depict the structural and molecular information stored within these scientific visualization formats.

The methodology adopted was developed over several weeks. Initially, an extensive study was conducted to determine the most suitable libraries for the project, selecting from various options while considering compatibility, ease of use, and features offered by each. An evaluation was also carried out to choose the most appropriate text editor, and other essential resources and tools were considered to facilitate the research and development process.

Meetings were scheduled weekly, serving as essential review and feedback points. During each session, the progress made up to that point was presented, allowing for a dynamic exchange of ideas, improvement proposals, and necessary adjustments to ensure the quality and efficiency of the work. These team interactions were fundamental in guiding the direction of the project and refining specific details.

Once the tools were defined, graphical interfaces were implemented using Tkinter, allowing the user to customize visual preferences. Upon loading VTK/VTI files containing aromatic system data, these were processed using NumPy and subsequently, 3D visualizations were generated using Pyvista.

The resulting visualizations, including cross-sections, contours, and isosurfaces, provide valuable insights into aromatic properties and structures. Finally, these visualizations are exported as images to facilitate their sharing and interactive analysis

Firstly, I want to thank God for all the help provided, my Mom and Dad for their unconditional support, and my family in general for always being by my side.

Keywords: 3D display, Pyvista, VTK, VTI, Aromatic Molecules.

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Síntesis de nuevos análogos de Brasinoesteroides benzoilados en C22 con potencial actividad como reguladores de crecimiento vegetal

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Los brasinoesteroides (BRs) corresponden a hormonas vegetales que participan en importantes fenómenos fisiológicos de las plantas promoviendo su crecimiento [1]. Los BRs se comenzaron a estudiar cuando se logró aislar el brasinólido (**1**) desde extractos del polen de *Brassica napus* [2] que demostró poseer un efecto en la elongación del tallo del frijol. Este descubrimiento potenció el estudio de los BRs y debido a su baja concentración en las plantas, ha sido necesario recurrir a la síntesis de diversos análogos [3]. En esta investigación se realizó un estudio de Docking Molecular basado en la evaluación de afinidad de acoplamiento de los ligandos a la proteína receptora (BRI1 y BAK1) para diseñar una ruta sintética a partir del ácido hiodeoxicólico (**2**), del cual se obtuvieron cuatro nuevos análogos de BRs benzoilados (**3a-d**) en la posición C22 de la cadena lateral con distintos sustituyentes en posición *para* del anillo aromático (Figura 1). Todos los compuestos e intermedios de síntesis fueron completamente caracterizados mediante técnicas espectroscópicas de RMN 1D y 2D. Finalmente, los nuevos análogos sintetizados serán evaluados en pruebas de crecimiento vegetal para contrastar con los resultados observados en el estudio de Docking Molecular y validar el modelo predictivo.

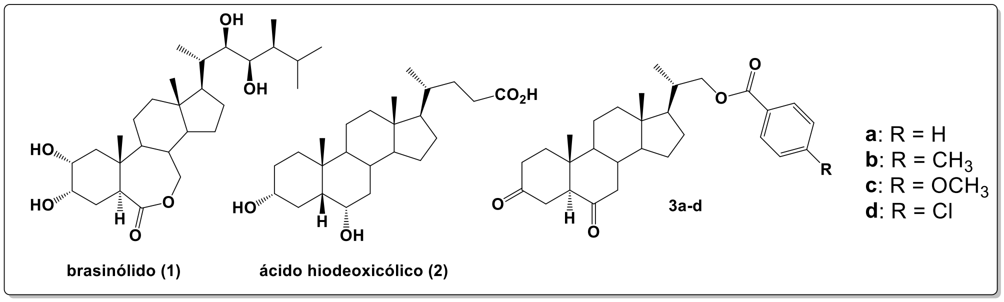

Figura 1. Estructuras del brasinólido (1), ácido hiodeoxicólico (2) y nuevos análogos 3a-d.

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Recuperación de iones litio desde soluciones acuosas de magnesio usando adsorbentes biobasados de lignina

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Para satisfacer la creciente demanda futura de litio, se han desarrollado diversas tecnologías de recuperación, que a menudo resultan en la pérdida de litio cuando hay altas concentraciones de magnesio (Mg)[1]. El método de adsorción se considera una opción prometedora para la separación de iones a gran escala con alta eficiencia[2,3]. Sin embargo, los adsorbentes selectivos para litio utilizados tienen limitaciones prácticas. En este contexto, se propone el desarrollo de materiales adsorbentes a base de lignina[4], con el objetivo de reducir la relación de concentración de Mg/Li. Esto se lograría mediante la captación de Mg, lo que potencialmente permitiría la recuperación indirecta de litio. En primer lugar, se modificó lignina con sulfito de sodio (se usó 50, 100 y 150% con respecto a los gramos de lignina) para la obtención de lignina sulfonada (LS). El grado de modificación se determinó por titulación potenciométrica y análisis elemental, y se obtuvieron valores de 11.69, 12.08 y 13.64 mmol/g de LS, con diferentes porcentajes de azufre en el material. Se confirmó la estructura molecular de LS mediante espectroscopía infrarroja por transformada de Fourier (FT-IR) y análisis termogravimétrico (TGA), que revelaron las señales características de los grupos sulfonatos y su degradación térmica. Posteriormente, se sintetizaron materiales adsorbentes biobasados mediante polimerización radicalaria utilizando acrilato de potasio 3-sulfopropilo, N,N-metilen-bis-acrilamida y persulfato de amonio. Estos adsorbentes se caracterizaron mediante FT-IR, TGA y se determinó su punto de carga cero para verificar su formación y carga superficial, respectivamente. Finalmente, se llevó a cabo un estudio preliminar sobre la retención de iones de magnesio en presencia de iones de litio mediante el método batch, logrando retener aproximadamente un 50% de magnesio en soluciones acuosas con diferentes relaciones de concentración Mg/Li (2/1 y 1/1), lo que permitió reducir la concentración de magnesio en el medio

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Is there a Covalent Au(I)-Au(I) Bond in the Trans-$(AuX)_2$ (X=F,Cl,Br,I) Structure? A Post-Hartree-Fock and Density Functional Theory Study

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Here we present an exhaustive exploration of the driving forces dominating the interaction between gold atoms in the trans-(AuX)2 dimers, where X is a halogen ligand (see Figure 1) [1]. This work would provide insights into the effect of halogen substituents on the bonding properties of aurophilic noncovalent interactions. The interaction energies were calculated at the MP2, CCSD(T), and DFT-D3 (B3LYP, PBE and TPSS) levels of theory. Then, the behavior and bonding nature of the noncovalent interactions were thoroughly analyzed and discussed by using the EDA and NCI approaches, from which we were able to define the contributions of polarization and dispersion as the most relevant at the Post-Hartree-Fock methods [2]. Finally, Wiberg indices and NBO analysis allowed discarding that the aurophilic interaction in these dimers is of covalent nature [3].

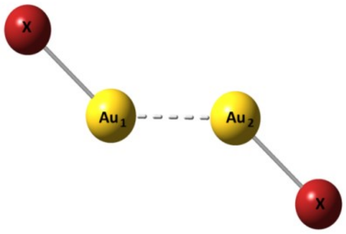

Figure 1. The conformation models trans-$(AuX)_2$ (X = F, Cl, Br, I).

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Síntesis de nuevos análogos de brasinoesteroides diseñados computacionalmente por Docking Molecular y sus evaluaciones biológicas en ensayos de crecimiento vegetal.

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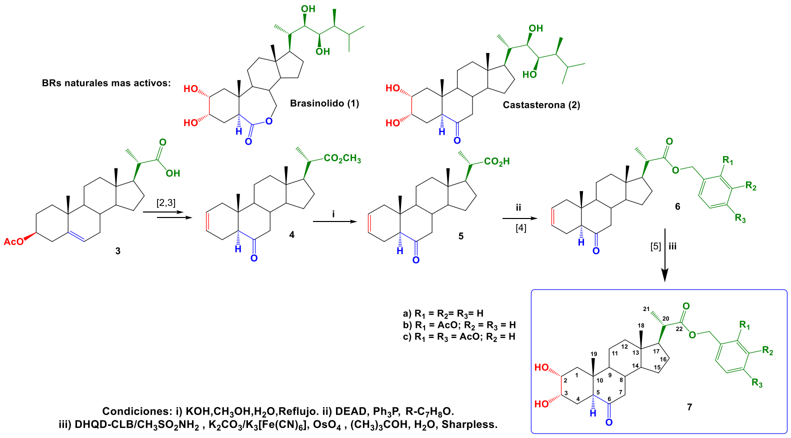
Los brasinoesteroides (BRs) son un conjunto de esteroides vegetales que se encuentran en bajas cantidades y realizan funciones importantes en las plantas, algunas tales como el aumento en el tamaño debido a la división y diferenciación celular [1]. El brasinólido (1) es el esteroide más activo, pero se han identificado más de 70 compuestos naturales que cuentan con características estructurales comunes. En el presente trabajo se aborda un enfoque computacional mediante el uso de Docking Molecular para el diseño racional de síntesis de nuevos análogos de BRs 7a-c. La síntesis de los nuevos análogos se llevó a cabo siguiendo el procedimiento descrito en la Figura 1, partiendo del ácido (3). Las estructuras fueron caracterizadas por técnicas espectroscópicas de IR y que presentan un esqueleto esteroidal similar a la Castasterona (2).



a) $R_1 = R_2 = R_3 = H$
b) $R_1 = AcO; R_2 = R_3 = H$
c) $R_1 = R_3 = AcO; R_2 = H$

Condiciones: i) KOH, CH_3OH, H_2O, Reflujo. ii) DEAD, Ph_3P, $R\text{-}C_7H_8O$.
iii) $DHQD\text{-}CLB/CH_3SO_2NH_2$, $K_2CO_3/K_3[Fe(CN)_6]$, OsO_4 , $(CH_3)_3COH$, H_2O, Sharpless.

Figura 1. Esquema de síntesis de nuevos análogos de brasinoesteroides (7a-c).

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Spectroscopic and Magnetic Properties of a Novel Squaraine-Type Dye

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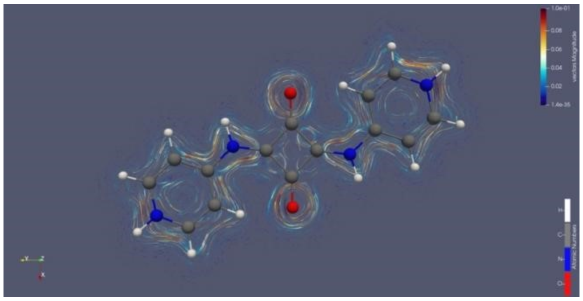
Squaraine dyes represent a class of organic dyes, in which an electron deficient central four-membered ring, derived from squaric acid, exhibit a resonance stabilized zwitterionic structure[1]. Squaraines are synthesized from a highly electron deficient aromatic squaric acid core and two electron-donating aromatic rings at diametrically opposite sides of the four-member ring. Due to this, squaraine dyes possess planar structures and zwitterionic properties, exhibiting intense and strong absorption and emission in the Visible-NIR region[2]. In this work, we calculated magnetically induced ring-current strength susceptibilities at the DFT level using the GIMIC method[3] for an aminopyridine substituted squaraine dye and their protonated species, to investigate the degree of delocalization along the structure. Our results show that electronic delocalization is affected by the degree of protonation, which modifies its optical properties, absorbing light at different wavelengths depending on the protonation state.



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Analysis of the Formation/Dissociation Processes of Molecular Aggregates Containing Hypochlorous Acid

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This study presents the formation/dissociation process of hypochlorous acid (HOCl) with water (H2O) and ammonia (NH3). Both processes were studied by analyzing the energy and electronic activity changes along the reaction coordinate. To better rationalize the results, the energy was fitted to Morse's potential to obtain analytic formulae that allow an in-depth discussion of the processes. Reaction Force Analysis (RFA) provides a unique way to analyze the chemical processes by defining reaction regions along the reaction coordinate where different mechanisms might be operating1, and the energy gain/release that occurs anywhere along the process can be easily quantified2. On the other hand, the electronic activity involved during the processes was analyzed using the Reaction Electronic Flux (REF)3; two representations of the REF were employed to get insights into the electronic phenomena: the canonical or physical representation and the chemical representation. REF profiles obtained have effectively captured the dissociation and formation processes of the two hydrogen-bonded systems. The electronic activity analysis along the reaction coordinate was complemented with the characterization of non-bonded interactions (NCI), thus visualizing the distribution of the NCIs involved4 along the reaction coordinate. Consistency between REF and NCI studies was observed in both processes.

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Probing intrinsic conformational preferences of infinite polyalanine chains by electronic structure calculations

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Proteins are one of the most important families of biomolecules for life. Deciphering the forces driving a sequence to adopt the native (functional) conformation is crucial to understand the folding process. The formation of local geometrical arrangements such as helices and β sheets are connected to energy minima in the potential energy surface (PES) of the conformational space of proteins. PES can be estimated by theoretical methods, but most approaches employ reduced models that neglect intra-chain H-bonds. Previously, we have calculated PES maps of infinite polyalanine chain using density functional theory (DFT), which fully accounts for H-bond network and cooperativity [1]. Well-defined energy minima in the PES were connected to regular secondary structures, which proved valuable to develop a novel protein secondary structure assignment method [2]. Here we have expanded such models to account for inter H-bonds that stabilize β sheets by using bidimensional periodic models of polyalanine. We have found that extended conformations (γ helix, PPII, and β strand) are significantly more stable (4-5 kcal/mol) upon formation of H-bonds between two chains, and infinite β sheets appear as the most stable conformation compared to helices (3_{10}-, α-, π helix). This outcome may shed light on the formation of amyloid aggregates. We have also derived the intrinsic structural preferences of proteinogenic amino acids using the host-guest approach based on the polyalanine model. In the absence of environmental factors like solvent and temperature, helical conformations are preferred over extended conformations. Interestingly, α-helix (the most abundant subtype) is not always the most stable conformation, where the preference order varies among the amino acids. These findings will help to further our understanding of protein folding and protein structure prediction.

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Theoretical View of Magnetic Properties in Monomeric Units PtM(X)$_4$(Y) (M=Co, Ni, X = SAc, tba and Y = H_2O, 3-NO_2py), from electronic structure and bonding

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The antiferromagnetic coupling has been observed in dimers of metal-platinum (M-Pt) complexes, where paramagnetic centers interact through a weak σ-bonding. Sandoval-Olivares et al.1 provided relevant information about the electronic structure of complexes in this form [PtCo(X)$_4$(Y)]2 (X = SAc thioacetate, tba thiobenzoate, and Y = H_2O, 3-NO_2py), highlighting the importance of the use of multiconfigurational methods that include electron correlation and the influence of bridging and axial ligands on the size of the partial σ Pt-Co bond in complexes. The charge donation from the axial ligands plays a crucial role in the metallophilic interaction (Pt---Pt); the metal bond order increases as the electron donor increases as they demonstrated compared 3-NO_2py with H_2O on monomer units. Therefore, the different electron-donor characters on the 3-NO_2py and H_2O as axial ligands are responsible for the spin-polarized mechanism on dimers. It is necessary to deepen both the role of the M-Pt interaction through an adequate description of the electronic structure and the understanding of the magnetic properties of the monomer units. In this study, we investigate the effect of the substitution of the Co^{2+} ion by Ni^{2+} ion in the monomers using SA-CASSCF calculations, choosing a suitable active space that allows the inclusion of binding orbitals with equatorial and axial ligands of the M^{2+} ion. In addition, NEVPT2 and SINGLE ANISO calculations were carried out using the ORCA 5.0.3 package. Splitting patterns in molecular orbital diagrams, energetic analysis, magnetic susceptibility patterns, and magnetization provide insight into the differences in Pt-Ni and Pt-Co interactions related to the influence of the ligands.

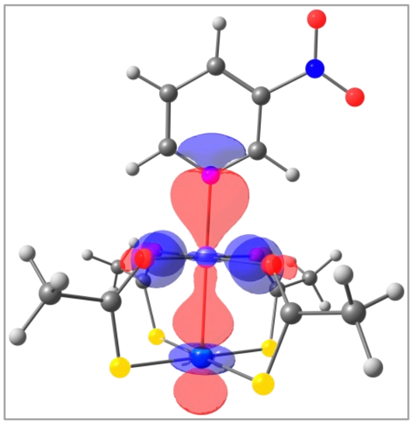

Figure 1. Representation of σ-orbital between $dz^2_{(Pt)}$ and $dz^2_{(M)}$ in [PtM(SAc)$_4$(3-NO_2py)] complex

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Computational Study of Water Adsorption in Erythrite and Pakhomovskyite Crystals Surface Through DFT Calculations

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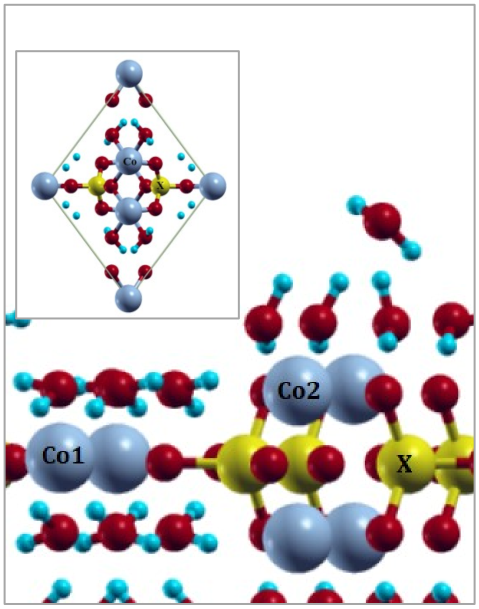

Erythrite and Pakhomovskyite crystals, belonging to the vivianite group with the formula $Co_3(XO_4)_2\cdot 8H_2O$, where X is As or P respectively, have been investigated as electrocatalysts for water splitting[1]. Surprisingly, significant catalytic activity and stability differences have been experimentally observed despite being isostructural compounds. These findings suggest that the phosphate or arsenate anion plays a key role, enhancing catalytic activity in Pakhomovskyite and imparting stability to Erythrite during the process. DFT+U calculations for structural and electronic properties have been performed by the Quantum ESPRESSO program. The initial crystal positions were determined from X-ray powder diffraction data, and band gap was measured using UV-Vis. We have computed the adsorption energies of H_2O, OH*, O*, and OOH* as OER intermediates on the exfoliated surface as a preliminary analysis to understand the aforementioned behavior. Our results reveal higher adsorption energies on metal sites and distinct behavior among cobalt sites. Cobalt coordinated to four structural water molecules and two anions exhibits lower activity compared to cobalt coordinated to two structural water molecules and four anions. Interestingly, Pakhomovskyite displays higher adsorption energies for intermediates than Erythrite. This study demonstrates that the chemical environment induces a different distortion in the cobalt octahedra between the two cobalt sites, thereby modifying their behavior[2]. In conclusion, Erythrite and Pakhomovskyite exhibit intrinsic catalytic activity modulated by the anions within their structures.

Acknowledgment: Thanks to Centro de Investigación en Ciencia e Ingeniería de Materiales (CICIMA), Universidad de Costa Rica for the support.

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Recuperación de iones litio desde soluciones acuosas de magnesio usando adsorbentes biobasados de lignina

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Para satisfacer la creciente demanda futura de litio, se han desarrollado diversas tecnologías de recuperación, que a menudo resultan en la pérdida de litio cuando hay altas concentraciones de magnesio (Mg)[1]. El método de adsorción se considera una opción prometedora para la separación de iones a gran escala con alta eficiencia[2,3]. Sin embargo, los adsorbentes selectivos para litio utilizados tienen limitaciones prácticas. En este contexto, se propone el desarrollo de materiales adsorbentes a base de lignina[4], con el objetivo de reducir la relación de concentración de Mg/Li. Esto se lograría mediante la captación de Mg, lo que potencialmente permitiría la recuperación indirecta de litio. En primer lugar, se modificó lignina con sulfito de sodio (se usó 50, 100 y 150% con respecto a los gramos de lignina) para la obtención de lignina sulfonada (LS). El grado de modificación se determinó por titulación potenciométrica y análisis elemental, y se obtuvieron valores de 11.69, 12.08 y 13.64 mmol/g de LS, con diferentes porcentajes de azufre en el material. Se confirmó la estructura molecular de LS mediante espectroscopía infrarroja por transformada de Fourier (FT-IR) y análisis termogravimétrico (TGA), que revelaron las señales características de los grupos sulfonatos y su degradación térmica. Posteriormente, se sintetizaron materiales adsorbentes biobasados mediante polimerización radicalaria utilizando acrilato de potasio 3-sulfopropilo, N,N-metilen-bis-acrilamida y persulfato de amonio. Estos adsorbentes se caracterizaron mediante FT-IR, TGA y se determinó su punto de carga cero para verificar su formación y carga superficial, respectivamente. Finalmente, se llevó a cabo un estudio preliminar sobre la retención de iones de magnesio en presencia de iones de litio mediante el método batch, logrando retener aproximadamente un 50% de magnesio en soluciones acuosas con diferentes relaciones de concentración Mg/Li (2/1 y 1/1), lo que permitió reducir la concentración de magnesio en el medio.

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Syntheses an characterization of new homo dimers lanthanides complexes bridged by 2,2-bipyrimidine [Ln(TTA)$_3$(μ-bpm)Ln(TTA)$_3$], (Ln= Nd, Dy o Yb)

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Lanthanides luminescent properties, particularly in the near-infrared (NIR) range, make them attractive for various applications, such as biomarkers. Their specific narrow bands and stable wavelengths due to f-f transitions enhance detectability, and NIR luminescence offers deep tissue penetration and reduced health risks. This study focuses on Neodymium (Nd), Dysprosium (Dy), and Ytterbium (Yb) as lanthanides with NIR luminescence. 2,2-bipyrimidine was selected as a bridging ligand, given its small size and two coordination centers, enabling both homo and hetero dimer possibilities.

This study comprises experimental research involving the synthesis and analysis of complexes, as well as a theoretical investigation of their properties.

Six complexes were prepared starting with Ln(TTA)$_3$H$_2$O (Ln = Nd, Dy, and Yb), (TTA= 2-Thenoyltrifluoroacetone). Synthesis: Ln(NO$_3$)$_3$ · XH$_2$O was mixed with TTA in a 1:3 ratios in EtOH at 65°C for 1 hour. Yields 79% Nd(TTA)$_3$H$_2$O, 65% Dy(TTA)$_3$H$_2$O, and 69% Yb(TTA)$_3$H$_2$O.

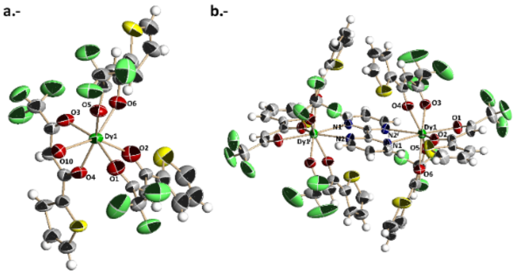

Figura 1. Structures of **a.- [Dy(TTA)$_3$(H$_2$O)]** and **b.- [Dy(TTA)$_3$(μ-bpm)Dy(TTA)$_3$]**.

The three homo-dimer species [Ln(TTA)$_3$(μ-bpm)Ln(TTA)$_3$] were synthesized by mixing Ln(TTA)H2O with 2,2-bipyrimidine in a 2:1 ratio in EtOH under stirring for 2 hours at 65°C. Yields were 79% [Nd(TTA)$_3$(μ-bpm)Ln(TTA)$_3$], 65% [Dy(TTA)$_3$(μ-bpm)Ln(TTA)$_3$], and 69% [Yb(TTA)$_3$(μ-bpm)Ln(TTA)$_3$].

Crystalline structure where obtained for every species and utilized for single-point DFT calculations with ORCA v4.2.1, using the B3LYP functional paired with the SARC2-ZORA-QZV basis set for lanthanides and zora-def2-tzvp for all other atoms. TDDFT was carried at gas face.

The experimental results confirm the successful synthesis of the compounds with high purity and reaction yields. NIR luminescent bands were detected for Nd and Yb species, with the TTA acting as antennae. The theoretical calculations have good with the experimental data and help us to have a better understanding of the nature of the electronic transitions.

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DOCKING MOLECULAR, SÍNTESIS Y CARACTERIZACIÓN DE NUEVOS ANALOGOS DE BRASINOESTEROIDES DE TIPO 22,23-BISNORCOLANOS CON C-22 BENZOILADOS.

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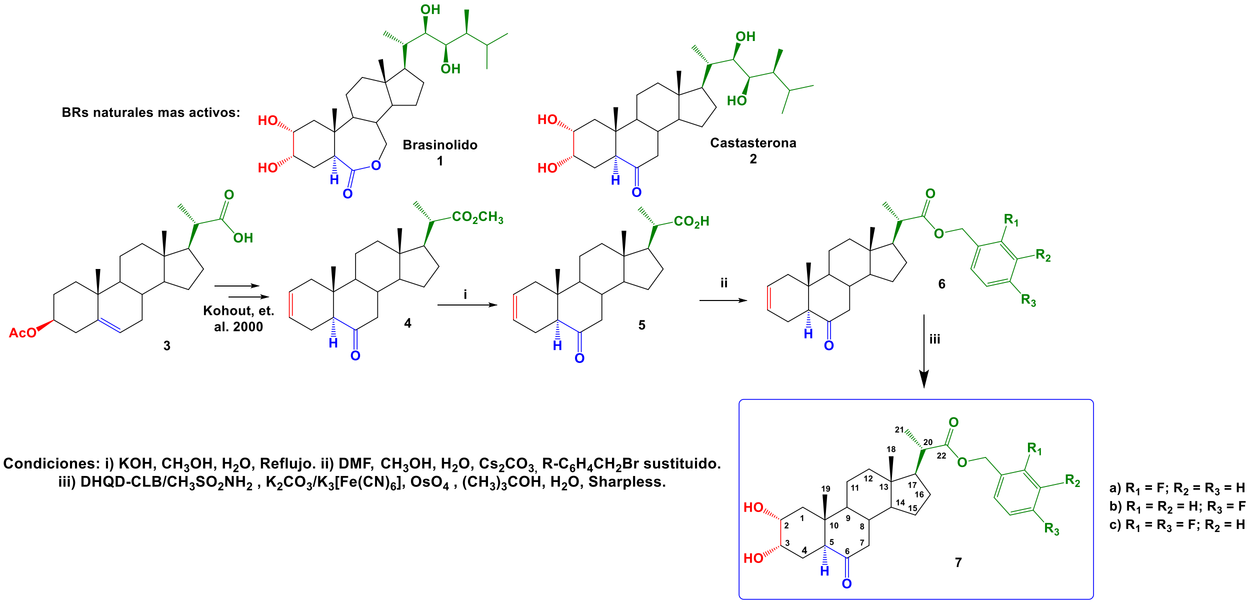
Los Brasinoesteroides (BRs) son fitohormonas que estimulan el crecimiento vegetal y las protegen de estreses bióticos y abióticos. Los compuestos naturales que presentan mayor actividad **1** y **2** definen ciertas características estructurales y funciones orgánicas necesarias para obtener buenos niveles de actividad. Además, dado su bajo contenido en fuentes naturales, la síntesis es la principal fuente de obtención [1]. En este trabajo se presenta el estudio computacional por Docking Molecular, la síntesis y caracterización de una nueva familia de análogos de BRs que cumplen con funciones orgánicas en el esqueleto esteroidal de tipo 5α-colestano, similar a Castasterona (**2**). La síntesis de los nuevos análogos se realizó según el Esquema descrito en la Figura 1 [1-4]. Para los nuevos análogos de la serie **7a-c** se determinó su punto de fusión, además fueron caracterizados por técnicas espectroscópicas de IR y RMN.



Condiciones: i) KOH, CH_3OH, H_2O, Reflujo. ii) DMF, CH_3OH, H_2O, Cs_2CO_3, R-$C_6H_4CH_2Br$ sustituido. iii) DHQD-CLB/$CH_3SO_2NH_2$, K_2CO_3/$K_3[Fe(CN)_6]$, OsO_4, $(CH_3)_3COH$, H_2O, Sharpless.

a) R_1 = F; R_2 = R_3 = H
b) R_1 = R_2 = H; R_3 = F
c) R_1 = R_3 = F; R_2 = H

Figura 1: Brasinoesteroides naturales más activos **1** y **2** y Esquema de síntesis de los nuevos análogos **7a-c**.

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D-MBIS non-bonded force field parameters improve density and vaporization enthalpy predictions of organic liquids.

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One way to model the thermodynamic behavior of chemical systems is through computational chemistry. Computational chemistry focuses on describing chemical interactions as accurate and efficiently as possible. One approach of doing this is performing molecular dynamics simulations to reproduce thermodynamic properties of chemical compounds in condensed phase. As it is not affordable to simulate complex systems for long time periods using quantum chemistry, approximations are made which describe forces between atoms classically with specific interaction potentials. One of these force fields is OpenForceField[1]. It describes these interactions defining chemical environments called SMIRKS. This description allows an automated parameter assignment for each contributing force by software packages as OpenFF Evaluator[2], which performs computer simulations to predict thermodynamic properties as density or vaporization enthalpy of a compound using a specific OpenFF force field model. The force field parameters can also be further optimized with the Minimal Basis Iterative Stockholder method (D-MBIS)[3] deriving systematically environment-specific atomic partial charges and dispersion/repulsion Lennard-Jones parameters per molecule. This work compares the original OpenFF force field with two different combinations of MBIS-derived non-covalent parameters for 49 diverse organic compounds. Our results show that the environment-specific atomic partial charges and Lennard-Jones parameters improve predictions for estimated thermodynamic properties as density and enthalpy of vaporization.

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Graphene-supported MB_{36} clusters (M=Fe, Co, Ni) as single-atom catalyst for the oxygen reduction reaction: A DFT study

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The search for non-precious metal cathode catalysts for the oxygen reduction reaction (ORR) that replace Pt and Pt-based catalysts in fuel cells and metal-air batteries, is one of the main challenges toward the largescale commercialization of renewable-energy technologies based on hydrogen. Recently, ORR catalysts with single-metal-atom site have attracted widespread attentions, particularly Fe-N-C to exhibit SAC characteristics for ORR competitive with the industrial standard Pt-based catalyst in alkaline environment [1,2].

In this work we study the ORR catalytic activity of graphene-supported 36-atom boron clusters doped with transition metals (MB_{36}, with M=Fe, Co, Ni). The equilibrium structural and electronic properties were obtained by spin-polarized density functional theory (DFT) calculations using the Vienna Ab Initio Simulation Package (VASP)[3], including dispersion-corrected van der Waals interactions, within the SCAN+rVV10 approach [4]. In addition, the stability of the MB_{36} on graphene were tested by ab-initio molecular dynamic simulations at 300 K. Our results show that all clusters are highly stable on graphene, preserving its structure at room temperature during 5 ps of simulation time. The ORR activity of MB_{36} was studied by calculating the adsorption and dissociation energies after the interaction of O_2 and OOH molecules with the metal center. Minimum energy path for the molecular dissociation were obtained by the CI-NEB method.

The dissociation barrier is found of 0.72 eV, which is lower than that previously calculated on Fe-N-C single-atom catalysts [5]. For the case of OOH, we find that after interacting at the Fe center of FeB_{36}, it spontaneously dissociates leaving one O atom attached to Fe, while the OH radical is rapidly expelled. Whereas, for CoB_{36} and NiB_{36}, the same reactions occur after overcoming energy barriers of 0.54 and 1.02 eV, respectively. Therefore, we conclude that the graphene-supported FeB_{36} cluster shows better ORR activity than other single-atom catalysts like Fe-N-C and also on Pt(111).

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Exploring the Structural and Energetic Aspects of Ubiquitin Specific Protease 7 (USP7) Catalytic Mechanisms through Hybrid QM/MM Simulations

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Background: USP7, a prominent member of the Deubiquitinase (DUB) family, plays a pivotal role in cellular processes,[1] including apoptosis, [2,3] DNA replication, [4] transcription, [5] and immune response. [6] This enzyme's versatility arises from its interactions with various substrates within the ubiquitination pathway, making it a key player in cell signalling. Dysregulation of DUB activity, including USP7, is implicated in multiple pathologies, notably cancer.

Methods: This study employed advanced theoretical methodologies to elucidate the catalytic mechanism of USP7. Our approach integrated homology modeling, classical molecular dynamics simulations using the *ff14SB* Amber force field, protein-protein interaction analysis, and cutting-edge hybrid quantum mechanics/molecular mechanics simulations at the *DFTB3/ff14SB* level of theory using the adaptive string method.

Results: Our research unveiled crucial insights into the catalytic mechanism of USP7, shedding light on its dynamic behaviour during interactions with its substrate. These findings provide a foundational understanding of USP7's enzymatic function and its relevance in cellular processes. Additionally, they offer opportunities for the targeted design of specific USP7 inhibitors.

Conclusion: Our work focused on unravelling the catalytic mechanism of USP7 using theoretical methodologies. By deciphering the structural dynamics of USP7 during its interactions with the substrate Ub-Rho, we contributed to the fundamental understanding of this enzyme's function. Furthermore, our findings opened the door to the development of highly selective USP7 inhibitors, holding promise for cancer therapy. This research underscores the significance of theoretical approaches in dissecting complex biochemical mechanisms.

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Síntesis y caracterización de nuevos análogos de brasinoesteroides de tipo 23,24-Bisnorcolánocos con grupos benzoatos en la posición C-22 de la cadena lateral.

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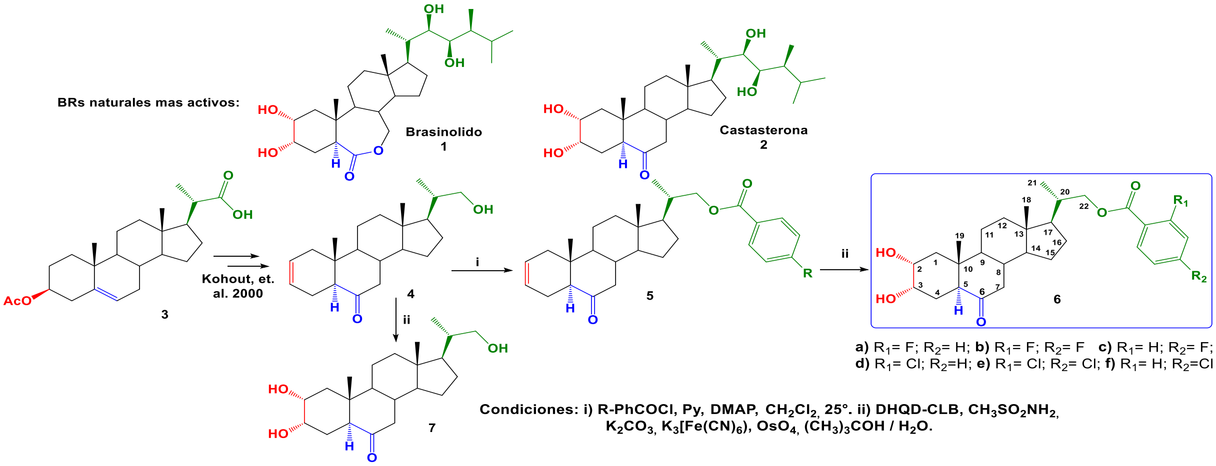
Los Brasinoesteroides (BRs) son un grupo de hormonas vegetales que se desempeñan esencialmente en el crecimiento y desarrollo de las plantas [1]. Los BRs con mayor actividad biológica es el Brasinólido (**1**), se caracteriza por poseer una estructura de lactona esteroidal polihidroxilada. Por otra parte, la Castasterona (**2**) se diferencia del Brasinólido al no tener el grupo lactona, dado que presenta en la posición C-6 un grupo cetona. En este trabajo se presenta la síntesis y caracterización de siete nuevos análogos de BRs, compuestos **6a-f**, y **7** (Figura 1), estos poseen un grupo benzoato (con diferentes sustituyentes) en la posición C-22 de la cadena lateral. En este trabajo, se presenta la determinación estructural por técnicas espectroscópicas de IR y RMN de los análogos finales **6a-f** y **7**.



a) R_1= F; R_2= H; **b)** R_1= F; R_2= F **c)** R_1= H; R_2= F;
d) R_1= Cl; R_2=H; **e)** R_1= Cl; R_2= Cl; **f)** R_1= H; R_2=Cl

Condiciones: i) R-PhCOCl, Py, DMAP, CH_2Cl_2, 25°. ii) DHQD-CLB, $CH_3SO_2NH_2$, K_2CO_3, $K_3[Fe(CN)_6]$, OsO_4, $(CH_3)_3COH$ / H_2O.

Figura 1: Brasinoesteroides de origen natural **1, 2** y esquema de síntesis para nueva serie de análogos de BRs **6a-f** y **7**.

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Preparación de materiales adsorbentes de nanocristales de celulosa con potencial aplicación en la eliminación de antibióticos de agua

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En este estudio, se aborda la problemática de la presencia de antibióticos en el entorno, que contribuye al surgimiento de patógenos resistentes y mutaciones genéticas[1,2]. Los métodos convencionales para eliminar estos contaminantes en el agua muestran limitaciones al lograr únicamente una eliminación parcial[3]. Por lo que, en este estudio, se propone la adsorción. Para ello, se sintetizaron adsorbentes poliméricos a base de biomasa con el potencial de eliminar antibióticos del agua. En primer lugar, se produjeron nanocristales de celulosa (CNC) mediante hidrólisis ácida. Estos CNC fueron sometidos a una oxidación controlada con 2,2,6,6-tetrametilpiperidina-1-oxilo (TEMPO), lo que introduce grupos carboxílicos en su estructura en dos niveles de modificación, (bajo (CL) y alto (CH)). El grado de modificación se determinó mediante titulación conductimétrica, con valores de 200 y 677 mmol/Kg$_{CNC}$ para CNC-CL y CNC-CH, respectivamente. Además, los CNC-carboxilados(CNC-C) se caracterizaron mediante espectroscopia infrarroja de transformada de Fourier, lo que evidencia las señales características de los CNC y la incorporación de grupos carboxílicos en su estructura. Mediante análisis termogravimétrico se confirmó que una mayor cantidad de grupos carboxilato disminuye la estabilidad térmica. Los CNC-C obtenidos se incorporaron en una matriz polimérica mediante polimerización radicalaria, creando redes semi-interpenetradas (semi-IPN) utilizando dos monómeros en paralelo. Se llevaron a cabo análisis estructurales y térmicos de las redes semi-IPN para verificar la formación y evaluar el efecto de la incorporación de CNC-C en las semi-IPN. Finalmente, se investigó la capacidad de hidratación y se realizó un estudio preliminar en la eliminación de la amoxicilina mediante el método de lotes, obteniendo eficiencias de retención de hasta 70%.

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Exploration of the Regulation Mechanism of the Enzymatic Activity of NSD2 Histone Methyltransferase

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The Histone Methyltransferases (HMT) are a family of enzymes that catalyse the transfer of one, two or three methyl groups to the N-terminal domain from histones. The nuclear receptor binding set domain (NSD) are a family of enzymes capable of mono and di methylation of the substrate lysine 36 from the N-terminal region from the histone 3 (H3K36me2 and H3K36me), in which the malfunction of NSD2 has been reported to be associated with colon and rectal cancer. (1) NSD2 presents higher preference towards nucleosome-DNA substrates, than non-nucleosomal histone octamer substrates. The latter is related to the fact that the NSD family of enzymes is inactive in their free form by what is defined as an autoinhibitory state. Their activation has been shown to depend on the binding to nucleosomes as shown in **Figure 1**, which triggers the dimethylation of H3K36. It has been found that the allosteric interaction between the NSD2 and the nucleosome entails different methylation states, but the molecular basis behind this regulation mechanism of the enzymatic activity is still unclear. To elucidate the regulation mechanism, we studied the behaviour of NSD2 with molecular dynamics (MD) simulations and quantum mechanical–molecular mechanics (QMMM) calculations of the reaction process in the presence and absence of the nucleosome complex. This allowed to shed light into the regulation of the enzymatic activity, by elucidating the role of the residues from the catalytic machinery involved in the methyl transfer reaction, and how the interaction with the nucleosome regulates the conformational stability of the catalytic site. The understanding of the role of the interaction with the nucleosome in the methylation process will provide insights for the design of structure-based allosteric inhibitors representing a good opportunity in cancer disease treatment. (2)

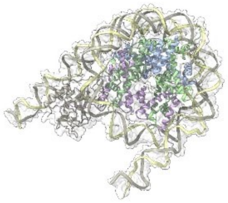

Figure 1. Nuclear receptor binding set domain two (NSD2) bound to nucleosome complex.

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Singlet Oxygen generation and photoinduced carbon monoxide release by Mn - Re Carbonyl Complexes

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New multi-target strategies have been recently developed against microbial resistance like the Antibacterial Photodynamic Therapy (aPDT) or the use of Photoinduced Carbon-Monoxide Releasing Molecules (PhotoCORMs). The combined action of singlet oxygen ($^1O_2$) generation and the photoinduced release of carbon monoxide by tricarbonyl metal complexes is a promising synergic treatment against multi-resistant bacterial infections.[1] In this work, we explore the use of a polydentate ligand (dp = 2,5-bis(1-pyrazolyl)pyrazine) that offers the opportunity to accommodate two metal centers exhibiting both, singlet oxygen generation and carbon monoxide releasing properties in a single molecule. The heterobimetallic [Br(CO)$_3$Re(dp)Mn(CO)$_3$Br] complex was synthesized and photophysically characterized. In addition, CO-release and $^1O_2$ generation quantum yields were evaluated and compared with values obtained for the monometallic [Mn(dp)(CO)$_3$Br] and [Re(dp)(CO)$_3$Br] complexes.

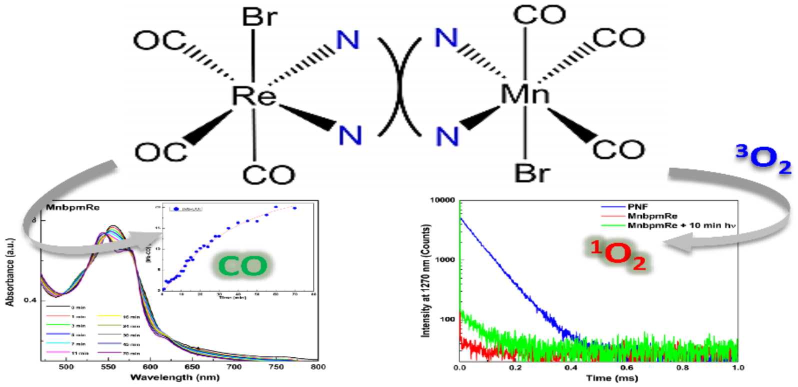

Fig.1. Singlet oxygen ($^1O_2$) generation and release of carbon monoxide upon excitation of tricarbonyl metal complexes.

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Lanthanides (II) Aryloxides: Electronic Structure and Magnetic Properties

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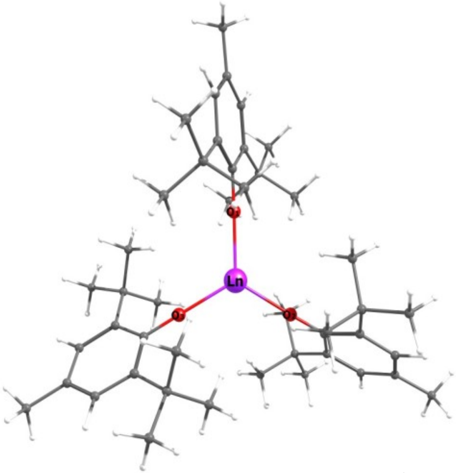

Figure 1. $[Ln(OAr')_3]^-$ structure.[2]

Divalent lanthanides (Ln) offer the opportunity to consider how it would be possible to improve the magnetic properties by increasing the magnetic moment of the ion. This idea has been considered by Long et al. who analyzed the $[LnCp'_3]^-$ series. They proved that the accessibility to the $4f^n5d^1$ configuration does indeed produce higher magnetic moments.[1] In addition, Evans et al. reported the synthesis of new divalent lanthanide complexes of the type $[Ln(OAr')_3]^-$ (Figure 1), (Ln = Gd, Dy, Ho, Er; OAr' = $OC_6H_2{}^tBu_2$ - 2,6 - Me - 4 aryloxide). The SOMOs (single - occupied molecular orbitals) of Gd^{2+}, Er^{2+} and Ho^{2+} have $d_z{}^2$ character, as found previously for $[LnCp'_3]^-$ complexes. Hence, it is possible to achieve stabilization of the $4f^n5d^1$ configuration for this type of compounds with trigonal symmetry.[2] However, this latest study was focused on the electronic structure, leaving aside the magnetic properties. The latter are considered for the work presented below. Experimental geometry synthesized in Ref. 2 (Figure 1) were used for *ab-initio* calculations. CASSCF wavefunctions calculations were carried out with MOLCAS[3] code considering different active spaces. CAS(n,8)SCF, which includes the seven orbitals of the 4f shell and the $5d_z{}^2$ orbital, was considered as the minimum active space followed by a CAS(n,12)SCF where both 4f and 5d shells were completely included (n is the number of f and d electrons). Spin-orbit coupling was introduced by state interactions between the CASSCF wave functions, using the Restricted Active Space State Interaction (RASSI) program. After obtaining the electronic structure, the magnetic properties (effective magnetic moment, *g* factor and magnetic susceptibility) were calculated using the SINGLE-ANISO module of MOLCAS. Results showed a considerable increase in the magnetic moment of the ion when being in this configuration. $[Dy(OAr')_3]^-$ (11.67 μB) and $[Ho(OAr')_3]^-$ (11.64 μB) were the highest values reported in this work.

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Exploring Photodynamic Therapy: Theoretical insights into Porphyrin-Based Photosensitizers and Singlet Oxygen Production

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Photodynamic Therapy (PDT) is an effective cancer treatment and a fascinating research topic, based on the use of photosensitizer (PS), laser, and oxygen. It consists of irradiating the PS (S_0), generating a singlet-excited state (S_1), and switching to its triplet state (T_1) after intersystem crossing. This energy can be dissipated by transferred to O_2 ($^3O_2$), which causes a cytotoxic effect through production of singlet oxygen ($^1O_2$). A "good" PS absorbs between 650 - 800 nm wavelengths and exhibits high singlet oxygen quantum yields. The interaction and the encounter complex formation between $^3O_2$ and PS in their ground and excited states, respectively, plays a key role in this field. More recently, Mahajan et al.[2] reported a complete photophysical characterization of substituted tetra(o-hydroxyphenyl)porphyrin (o-THPP). Accordingly, in this communication we present a theoretical study of a set of 9 molecules considered by Mahajan et al.[1] First, the investigation focuses on the performance of DFT-based methods according to Jacob's ladder on unsubstituted o-THPP, finding that it possesses 4 different atropisomers, differing in the rotation of a hydroxyphenyl group (**Figure 1**) obtaining the $\alpha\alpha\alpha\beta$ atropisomer as majority at both M06-2X and ωB97XD levels combined with Def2TZVP basis set. These DFT-based methods were chosen to study the remaining molecules; again, the $\alpha\alpha\alpha\beta$ atropisomer is observed to be the most stable at S_0. Currently, the triplet states are being calculated. In addition, intrinsic reactivity in both electronic states will be performed using the spin-polarized DFT conceptual framework.[2]

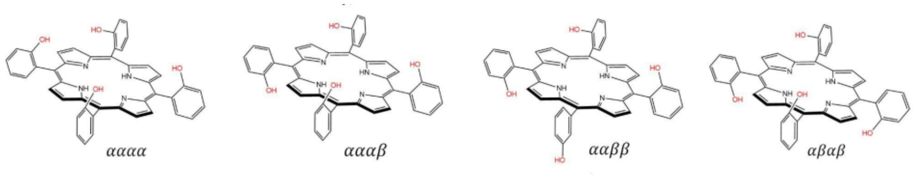

Figure 1: The 4 atropisomers for tetra(o-hydroxyphenyl)porphyrin structural base for the 9 molecules to be studied.

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High-throughput search of new multiferroic materials from first principles

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Multiferroic materials that exhibit and/or couple ferromagnetism and ferroelectricity have become a platform for developing new technologies, and electronic devices. However, to this date, the list of known multiferroic materials remains relatively small. In this work, we present a high-throughput workflow that allows to integrate the Materials Project database [1] and first-principles calculations to search for new multiferroic materials. We use symmetry and chemical arguments to identify several multiferroic candidate families from the Materials Project database. We use Density Functional Theory plus the Hubbard correction (DFT+U) to calculate the electronic, ferroelectric, and magnetic properties of these materials. Furthermore, we study different collinear magnetic arrangements [2] and calculate the electric polarization with the modern theory of polarization [3]. Our preliminary computational results predict 3 materials exhibiting a previously unknown multiferroic phase (ferroelectric and ferromagnetic). We discuss the possibility of coupling between ferromagnetism and ferroelectricity in these materials.

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Computational study of the binding orientation and affinity of noncovalent inhibitors of the papain-like protease (PLpro) from SARS-CoV-1 considering the protein flexibility by using molecular dynamics and cross-docking

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The papain-like protease (PLpro) from zoonotic coronaviruses (CoVs) has been identified as a target with an essential role in viral respiratory diseases caused by Severe Acute Respiratory Syndrome-associated coronaviruses (SARS-CoVs). The design of PLpro inhibitors has been proposed as an alternative to developing potential drugs against this disease. In this work, 67 naphthalene-derived compounds as noncovalent PLpro inhibitors were studied using molecular modeling methods. Structural characteristics of the bioactive conformations of these inhibitors and their interactions at the SARS-CoV-1 PLpro binding site were reported here in detail. Firstly, a molecular docking protocol was used to obtain the orientations of the inhibitors. After this, the orientations were compared, and the recurrent interactions between the PLpro residues and ligand chemical groups were described (with LigRMSD and interaction fingerprints methods). In addition, efforts were made to find correlations between docking energy values and experimentally determined binding affinities. For this, the PLpro was sampled by using Gaussian Accelerated Molecular Dynamics (GaMD), generating multiple conformations of the binding site. Diverse protein conformations were selected, and a cross-docking experiment was performed, yielding models of the 67 naphthalene-derived compounds adopting different binding modes. Representative complexes for each ligand were selected to obtain the highest correlation between docking energies and activities. A good correlation (R2 = 0.948) was found when this flexible docking protocol was performed.

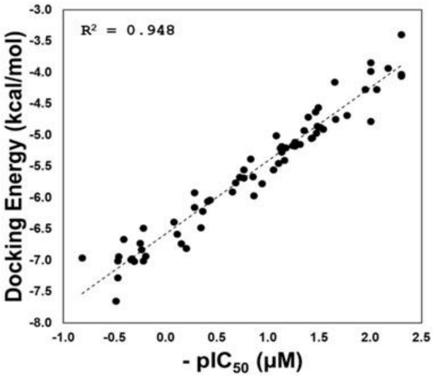

Figure 1. Regression plots of the docking scoring energies versus experimental activities (pIC_{50}).

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Verification of Transmission Selection Rules in Diverse Polycyclic Quinone Conjugates

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The field of single-molecule electronics has gained significant attention due to its potential to revolutionize electronic device miniaturization and introduce novel functionalities.[1] Molecular electronics offers the promise of devices like molecular switches, rectifiers, and thermoelectric devices. A critical aspect in designing such devices is understanding and predicting quantum interference effects.[2, 3]

This study aimed to validate the applicability of various transmission selection rules, including the orbital selection rule (OSR),[4] curly arrow rule (CAR),[5] extended curly arrow rule (ECAR),[5] and counting rule (CR),[6] in the context of polycyclic quinone-based molecular junctions. These rules, which help predict quantum interference effects, were scrutinized as some were found to be less reliable in cross-conjugated systems. The investigation involved assessing electron transport properties and local transmission plots through a combination of Density Functional Theory (DFT) and non-equilibrium Green's function methods.[7]

Additionally, the research explored the influence of molecular structure and electrode connectivity on electronic transport. Comparative analyses of the transmission spectra of phenanthrene, 9,10-phenanthroquinone, 9,10-dihydrophenanthroquinone, pyrene, 4,5-pyrenequinone and 4,5-dihydropyrenequinone shed light on the impact of linear, cross, and broken conjugation on electron transport properties.

In summary, this study provided insights into the behavior of quantum interference effects in molecular junctions and emphasized the importance of considering molecular structure and electrode connectivity when designing molecular electronic devices. These findings contribute to the advancement of future molecular electronics applications.

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Theoretical study of the local magnetic properties in bimetallic complexes of U(V) bridging by oxygen ligands (diamond-shape)

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The uranyl cations (UO_2^+) are of great importance in the design of new Actinide-based single-molecule magnets (Ac-SMMs), been a very active field of research driven by their potential applications in spintronics and high-density information storage. An important aspect of the diamond-shaped coordination is the orientation of metals and the bridging ligand in the same plane of symmetry, allowing overlap between orbitals of both parts due to the degree of covalence, resulting in the amplification of the magnetic interactions between the actinyl ions. Moreover, this model is important because it serves to explain the appearance of an antiferromagnetic ordering through a superexchange pathway.[1] In this work, the local magnetic properties of pentavalent uranyl complexe $(\mu - O_2)[UO(\beta - diketone)_2]_2$ (Figure 1) are theoretically studied using multiconfigurational methods (CASSCF, NEVPT2) necessary to include the strong electron correlation presented in this kind of complexes. Wavefunctions calculations were carried out with ORCA package considering different active spaces. CAS(1,4), which includes the four non-bonding orbitals of the 5f shell, followed by a CAS(7,10), which adds pairs of orbitals with symmetry σ, π in its corresponding bonding and antibonding combinations. Spin-orbit coupling was introduced, in a second step, by state interactions between the CASSCF wave functions in a Quasi-Degenerate Pertubation Theory (QDTP) aproxximation. After obtaining the electronic structure, the magnetic properties (effective magnetic moment, g-tensor and magnetic susceptibility) were calculated using the SINGLE_ANISO module of ORCA code. Finally, to calculate the Magnetic Coupling constant (*J*) we applied the Broken-Symmetry approach (BS) which makes use of an unrestricted or spin-polarized formalism. The findings of this study reveal that magnetic interaction between uranium ions through oxo bridges is crucial in order to develop innovative strategies that can be utilized to investigate magnetic interactions and intermetallic communication in actinides, as well as to develop innovative functional materials involving actinides.

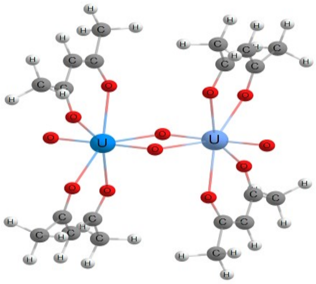

Figure 1: Structure of $(\mu - O_2)[UO(\beta - diketone)_2]_2$.

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Comparación de Glucansucrasas en Streptococcus Mutans a través de Simulaciones de Dinámica Molecular

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La caries dental es un problema de salud pública en Chile, afectando a más del 70% de la población según el Plan Nacional de Salud Bucal 2021-2030.[1] Se conoce que el principal patógeno responsable de las caries dentales es *streptococcus mutans* que secreta tres glucansucrasas (GTF-SI, GTF-I y GTF-S) encargadas de sintetizar glucanos solubles e insolubles favoreciendo la formación de placa dental y la desmineralización de los dientes. Este estudio se centra en la simulación de la enzima glucansucrasa GTF-I, recientemente cristalizada[2] y su comparación con la enzima GTF-SI, cristalizada en 2011 por el grupo de Ito.[3] El principal objetivo es investigar las diferencias en la unión de la sacarosa entre ambas enzimas. Para lograr esto, se realizarán dinámicas moleculares de 300 ns para todos los modelos, utilizando el campo de fuerza de Amber ffSB19. Adicionalmente, se ha incorporado el dominio V a la estructura de GTF-I mediante modelado por homología para evaluar su impacto en la unión con la sacarosa. Se espera que los resultados arrojen diferencias significativas en la afinidad de unión de la sacarosa, lo cual podría tener implicaciones para futuras estrategias de tratamiento de la caries dental. Este estudio contribuirá a una mejor comprensión de los mecanismos moleculares involucrados en la unión de sacarosa y abre nuevas direcciones para futuras investigaciones.

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Triazine-bis-(1,3-phenylamino)Squaraine dyes.
The Synthesis, Spectroscopic and Computational Studies

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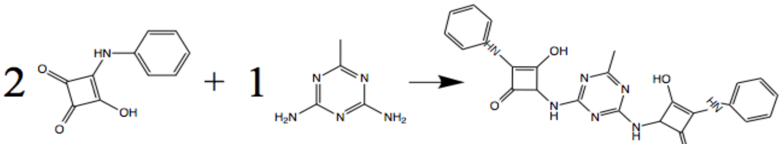
Squaraine derivatives are versatile zwitterionic dyes with applications in solar cells, optical disks and sensors[1-2]. Their distinctive characteristic is their four-member aromatic ring system, which can be modified with substituents such as alkylamino groups, dicyanomethylene or heterocycles[3], obtaining derivatives with different functions and applications such as in materials science. Amongst the heterocyclic substituents that can be incorporated into the four-member aromatic ring system, 1,3,5-triazine can help in the development of dyes with enhanced energy absorption and emission in the near-infrared region[4]. Here we present the synthesis, characterization and theoretical calculations at B3LYP/6-311+G(d,p) level of theory of $\{SQ(Ani)\}_2(MTZ)$ squaraine dye derivative. The ^1H-NMR spectra confirm the presence of the methyl group of the triazine at 2.28 ppm, the amines linked to the MTZ unit between 7.6 to 8.2 ppm, the ring triplets aniline between 7.1-7.3 ppm and carbon doublets between 7.5-7.7 ppm. The solutions of the respective compounds in DMSO at $1x10^{-5}M$ concentration were used to determine their absorption and emissive properties. Our calculations show a good agreement with the experimental results.



SQ(ANI)1 + MTZ (2:1)

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Computational design of potential dual binders: Targeting Tubulin and PD-L1 receptors.

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Tubulin, a globular protein, plays a pivotal role in cellular processes such as cell division, intracellular transport, and maintenance of cell shape. As a critical constituent of microtubules, tubulin provides structural support to cells and facilitates crucial processes like mitosis and cell migration. Given its essential role in cell division, targeting tubulin has been a longstanding strategy for cancer treatment.[1] On the other hand, PD-L1 is an immune checkpoint protein that plays a key function in regulating the immune response. Under normal physiological conditions, PD-L1 binds to its receptor, programmed cell death protein 1 (PD-1), on the surface of immune cells, thereby downregulating immune activation and preventing excessive immune responses. However, cancer cells exploit the PD-L1/PD-1 pathway to evade immune surveillance and suppress antitumor immune responses.[2] The search for dual inhibitors targeting both tubulin and PD-L1 proteins in cancer therapy holds great promise for overcoming the limitations of single-target therapies and achieving synergistic effects, leading to enhanced efficacy.[3]

In this study, deep learning methods, classical molecular dynamics, and binding energy estimations were employed for the exploration of new compounds with potential affinity to the colchicine site of tubulin protein and the PD-L1 receptor. These results are expected to serve as the starting point for the generation and design of new compounds with potential anticancer action.

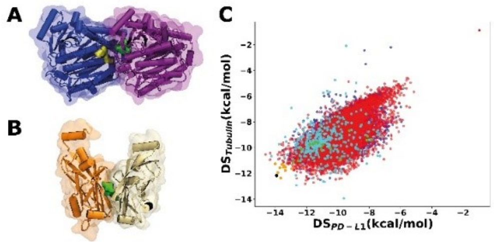

Figure 1. Crystallographic structure of A) Tubulin and B) PD-L1. C) Docking scores obtained for each receptor and the molecules included in this study.

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Spectroscopical studies of Novel Benzylamine, Benzhydrylamine and Triphenylmethylamine 3,5-disustitued Aniline Squaraine Derivatives

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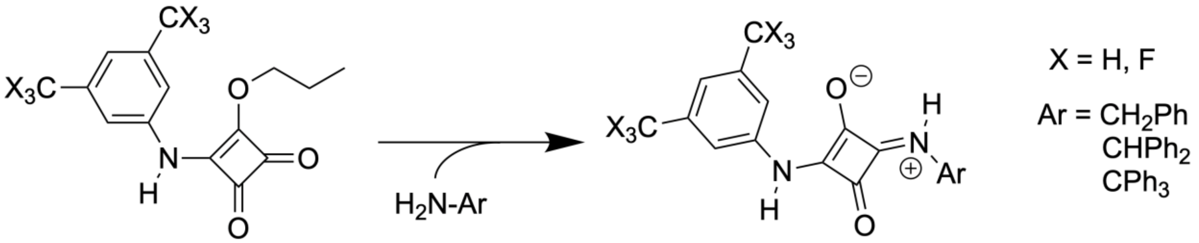
Squaraine (SQ) dyes have recently gained interest as donor materials in organic photovoltaic (OPV) cells due to their interesting properties, such as: direct synthesis, high absorption coefficients, tunable absorption energies, and exceptional photochemical and thermal stability [1,2]. In this context, we have synthetized 3,5-bis-trifluoromethylaniline and 3,5-dimethylaniline squaric acid derivatives as precursors that allow us the creation of various derivatives by including Benzylamine, Benzhydrylamine, or Triphenylmethylamine units. To identify the most stable isomers for these derivatives, and their molecular and electronic structure, computational calculations using the standard B3LYP/6-311+G(d,p) computational methodology were done [3]. The electronic absorption spectra of these dyes were investigated by use of time-dependent density functional theory (TD-DFT) calculations, using the CAM-B3LYP/6-311+G(d,p) density functional-basis sets combination. Bulk solvent effects on the ground and excited states were taken into account by including a Polarizable Continuum Model (PCM). Also, the experimental results are contrasted to validate our computational results.



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Novel derivative of anilino-squaraine dyes and p-phenylenediamine with potential organic photovoltaic applications.

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Solar cells are considered a crucial technology to address environmental problems caused by the use of non-renewable energy, which has encouraged the development of new and diverse chromophores for the development of photovoltaic applications, in order to increase the energy conversion efficiency, performance and durability [1]. In this context, several squaraine derivatives have been used due to their unique optical properties, such as high fluorescence quantum yields and powerful light absorption [2]. However, despite its advantages, its use in organic photovoltaic (OPV) devices and related devices have not yet been widely exploited [3,4].

In this work, the synthesis, characterization and theoretical calculations of a squaraine derivative containing an aniline-squaraine moiety and a p-phenylenediamine spacer, is presented. The molecular and electronic structure was calculated using the B3LYP/6-311+G(d,p) computational methodology [5]. Also, their excitation spectra was calculated using the time-dependent density functional theory (TD-DFT) at CAM-B3LYP/6-311+G(d,p) level.

Acknowledgments: The authors acknowledge the support of the FONDECYT ANID grants 1221904 and 1221676.

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Role of the environment in the antioxidant strength

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Phenolic antioxidants can be found in a variety of natural sources, such as fruits, vegetables and medicinal herbs. These species are capable of neutralizing free radicals, which in high concentrations can cause oxidative stress. When oxidative stress occurs in the cell, it can damage mitochondrial DNA leading to mitochondrial dysfunction, which has been associated with various diseases such as type 2 diabetes, heart failure, and neurodegenerative diseases such as Parkinson's.[1,2] One strategy to combat oxidative stress in mitochondria is to selectively transport antioxidants to this organelle, which is possible by vectorization guided by delocalized lipophilic cations. These are capable of delivering compounds to the mitochondria as they are attracted to the mitochondria due to the high negative potential of the mitochondrial inner membrane, where one that has been successfully tested is the triphenylphosphonium cation (TPP).[3,4] On the other hand, the use of dendrimers for the encapsulation and transport of antioxidants improves their solubility, biocompatibility and pharmacokinetic properties. In this work, we studied the role of the polarity of the environment on the antioxidant capacity of cinnamic acid, p-coumaric acid, and caffeic acid, together with the changes in the mechanism resulting from their conjugation with TPP.

Using computational calculations based on density functional theory (DFT), the oxidation potentials of TPP-conjugated antioxidants in different environments were obtained. The results show that the complexes are inactivated in apolar environments, while in polar environments they are highly activated, thus transporting it in apolar environments and releasing the antioxidants into the mitochondria would increase its efficiency and selectivity. Finally, a detailed explanation is presented to understand the issues underlying the oxidation mechanisms of the different antioxidants presented in different possible environments.

Acknowledgement: This research was funded by FONDECYT 1221898

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Insights into the catalytic mechanism and selectivity of SAM-dependent fluorinase towards carbon-halogen bond formation

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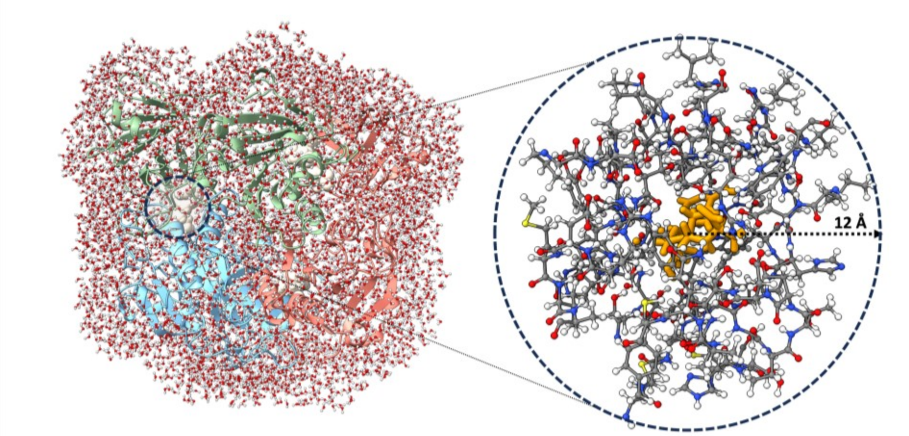
Halogenases are enzymes that incorporate halogens with high regioselectivity into biosynthetic precursors. Fluorinase is a S-adenosyl methionine (SAM)-dependent halogenase capable of catalyzing the carbon-halogen bond by a S_N2 reaction. This enzyme converts SAM into 5’-X-5’–deoxyadenosine (5’-XDA, where X = F and Cl), using the respective halide ion as substrate. [1,2] Fluorinase is highly efficient towards the formation of the C–F bond, and in a lower extent for the generation of the C-Cl bond. No activity towards the formation of the C-Br bond has been found. Here, we present a thorough quantum chemical exploration of the reaction mechanism and selectivity shown by fluorinase for the C–X (X = F, Cl and Br) bond formation. To this end, we combined molecular dynamics simulations, quantum mechanics / molecular mechanics (QM/MM) calculations and quantum chemical cluster models. The full reaction pathway was obtained and characterized by means of physicochemical descriptors to obtain chemical insights about the inner working of the enzyme. Our results reveal that the reaction is dominated by the pullout of the leaving group, although the specific configuration of the halogen coordination in the catalytic site also influences the barrier height and determines the selectivity of the process.



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Correcting the Fukui Potential for Solid-State Reactivity

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Despite the great success of Conceptual Density-Functional Theory in predicting and describing the reactivity of finite systems, its use in solid-state is sparse because of formal and technical problems. *Ab initio* calculations in solid-state frequently use periodic boundary conditions (PBC) and plane-wave basis set. When modelling defects and surfaces, the periodicity is broken and one has to rely on supercells with periodic images. If the system is not neutral, one has to add an homogenous background charge (HBC) distribution to recover neutrality. This is so because the Gauss theorem is not fulfilled by charged distributions with PBC. Yet, this background brings an unphysical term in electrostatic potentials. In this work, we apply different methodologies (Interpolation, Self-Consistent Potential Correction, Exact Coulomb cutoff and *a posteriori* correction) and propose a strategy to easily correct the Fukui potential for qualitative and quantitative purposes for solid-state reactivity. In addition, we show the effect of HBC on the calculation of the Fukui function for a variety of surfaces.

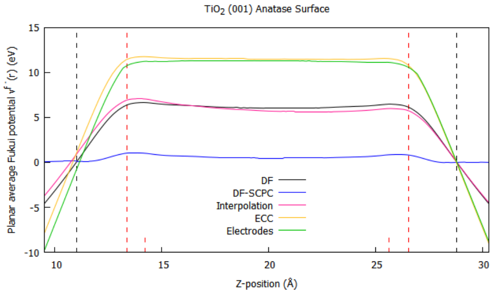

Figure 1: Planar average Fukui potential $v^{f^-}(r)$ of TiO_2 (001) anatase surface obtained with finite differences (DF), finite differences and Self-Consistent Potential Correction (DF-SCPC), Interpolation, Exact Coulomb cutoff (ECC) and *a posteriori* correction (Electrodes). The black dotted lines show the position where the electron density is 10^{-4} bohr^{-3}, while the red dotted lines show the position of the terminal oxygen atoms.

Ab initio Spectroscopic Characterization of $C_2H_4N_2$

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The study of nitrogen-bearing compounds has garnered significant attention due to its role in atmospheric chemistry. Thousands of Nitrogen-bearing molecules exist in the atmosphere such as NOx and secondary products of reactions from this family are known to impact the earth's climate via complex processes. However, N-bearing compounds such as $C_2H_4N_2$ are less studied/known. Here we study novel N-bearing molecules such as $C_2H_4N_2$ with five different isomeric species of potential relevance in atmospheric Chemistry.

To achieve our objective, we conduct *ab-initio* spectroscopic characterization at different theory levels such as MP2, CCSD(T)-F12, with Dunning basis set (aug-cc-pVTZ) and explicitly correlated basis set (F12) (Inostroza et al., 2011). We calculate rovibrational spectroscopic constants which are essential to detect these species using laboratory spectroscopy techniques. Our preliminary results revealed five different isomeric species in different electronic states. Identifying chemical formation pathways is crucial in reproducing molecular species abundances (Franco et al., 2021), we delve into their formation and destruction pathways via the analysis of their intrinsic reaction coordinates. This enables us to construct a likely chemical formation network.

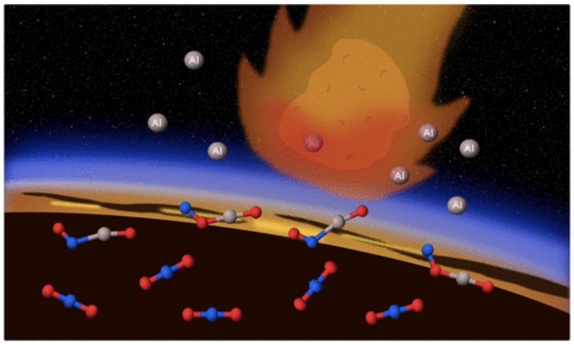

Figure 1. Molecular interactions of different species in earth's atmosphere

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Computational and Experimental Study of Solar Cells Sensitized by Natural Dyes: Buddleja globosa (Matico)

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The study of dye-sensitized solar cells (DSSC) has been widely investigated for a low-cost energy supply and ecological production. The first was created in 1991 by O'Regan and Grätzel,[1] reporting a 7% efficiency in light conversion. Nowadays, the efficiency has achieved up to 14% using porphyrins as dye. In addition, Natural dye as flavonoid and anthocianines has been explored as sensitized with efficiency between 2-3%. For understand the DSSC systems from a chemical viewpoint in 2010, Hagfeldt and Boschloo[2] reported the most outstanding parameters suggesting that the efficiency is directly related with the electron injection (DG_{inj}). In this context, we carry out DFT and TD-DFT[3] (PBE+D, CAM-B3LYP, M11) calculations using Gaussian 16 and VASP, for the essential components of the matic plant (verbacoside, rutine, luteolin, and gallic acid) and their interactions with a model of anatase (101) TiO_2 involving $(TiO_2)_{48}$. Thus, (a) Verbascoside@TiO_2, (b) Luteolin 7-O-glucoside@TiO_2 and (c) Gallic acid@TiO_2 were modeled in bidentate coordination mode. Our results showed a DG_{inj} of -2.79 and -1.74 eV for the verbascoside and gallic acid, respectively, which suggest that this component present a higher electron transfer to the semiconductor. Based on the theoretical studies, we realized *in situ* the matic-based solar cell (d) obtaining a fill factor of 0.035 and an efficiency of 0.013%.

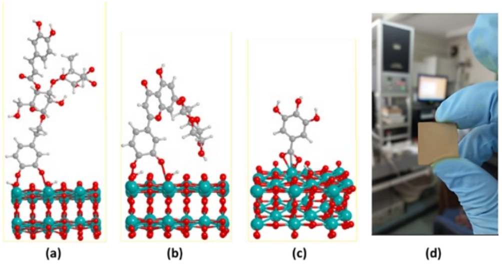

Figure 1. Interaction system (a) Verbascoside@TiO_2, (b) Luteolin 7-O-glucoside@TiO_2 (c) Gallic acid@TiO_2 and (d) matico-based solar cell.

Based on the theoretical studies, we realized *in situ* the matic-based solar cell (d) obtaining a fill factor of 0.035 and an efficiency of 0.013%.

Acknowledgement: Fondecyt de Iniciación 11200264

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Evaluation of the Binding Stability of Rhenium Complexes with Shiff Bases

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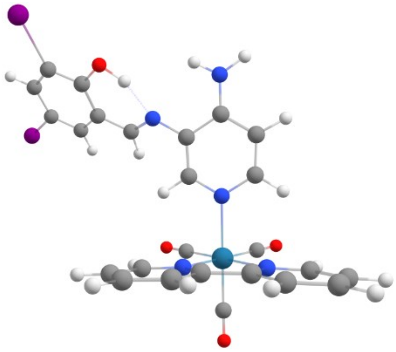
Rhenium(I) tricarbonyl complexes have been described as suitable fluorophores, particularly for biological applications. The fac-$[Re(CO)_3 (N,N)L]^{(0;1+)}$ complexes, where N,N is a substituted dinitrogenated ligand and L the ancillary ligand [a Pyridine Schiff Bases (PSB) harbouring an intramolecular hydrogen bond (IHB)],[1] have presented promissory results concerning their use as fluorophores, especially for walled cells (i.e., bacteria and fungi)[2]. In this work, we present a relativistic theoretical analysis of interaction between fac-$[Re(CO)_3$ (N,N)] with a group of PSB in order to predict the stability of these complexes. Once this process was completed, the Amsterdam Density Functional (ADF) package was employed to apply the energy decomposition analysis (EDA)[3] proposed by Morokuma−Ziegler at BP86/TZ2P level of theory.[4] This analysis allows to explore the nature of the interactions produced between the complex and the base through the separation of the total interaction energy in different terms: $\Delta E_{int} = \Delta E_{Pauli} + \Delta E_{elec} + \Delta E_{Orb} + \Delta E_{disp}$ .These four components describe the Pauli repulsion, electrostatic interaction, orbital mixing, and dispersion energy, respectively. This analysis shows that the interaction energy is favorable in the sense that it guarantees the stability of the bonding between Rhenium and Schiff Bases, with 33% of the overall electrostatic contribution being associated with an ionic interaction and 65-67% of the orbital contribution being associated with a covalent interaction, with the objective of further analysis based on the Natural Orbitals of Chemical Valence (NOCV) to find out which are the orbitals of the metal and ligand that are involved in the covalent character. It is relevant to do this study because it guarantees the stability of these complexes for the biological applications we are trying to make.



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Strategies for understanding the dynamics of peptide-membrane interactions

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Antimicrobial Peptides (AMPs) are short peptides (10-30 amino acids) with diverse structures and a positive charge (+2 to +11). They interact with negatively charged phospholipids like phosphatidylglycerol and cardiolipin in bacterial membranes. Additionally, hydrophobic interactions facilitate the adoption of a helical secondary structure by AMPs when they interact with these membranes [1]. In our study, we have focused on evaluating the orientation and dynamics of these peptides within phospholipid membranes to confirm the changes in the secondary structure conformation of the AMP. To achieve this, we employed classical molecular dynamics simulations and compared our computational models with experimental spectroscopic measurements, specifically circular dichroism, and Electron Paramagnetic Resonance (EPR) spectroscopy. The bacterial membrane model used was composed of a 70-30% molar concentration mixture of palmitoyloleoyl PE (POPE), and palmitoyloleoyl PG (POPG), constructed with CHARMM-GUI Membrane Builder web interface, while the AMP model was CM15 Ac-KWKLFKKIGAVLKVL-NH_2. Classical molecular dynamics was carried out with the CHARMM36 force field using the NAMD software, studying the peptide's stability in water and in lipid membrane environments mimicking large lipid/peptide ratios. Our results show that positively charged residues play an important role in maintaining the helicoidal peptide structure into the POPE:POPG bilayer by hydrogen bond with polar phosphate groups. These results agree with experimental circular dichroism. This strategy also provided information on the spatial orientation of the peptides and a significant penetration of this AMP. To confirm the location and environment properties of internal amino acids residues measured in the peptide by EPR of nitroxide, we have modeled a non-paramagnetic model of the nitroxide, permitting to support the spectroscopic information. These findings support AMPs as potential antibacterial agents with significant membrane-disrupting abilities. Our work aids in understanding and utilizing AMPs to combat bacterial resistance.

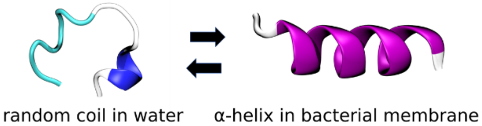

Figure 1. Structure of AMP in presence of water and membrane.

Acknowledgments: This work has been supported by FONDECYT Grant N° 1231468 and 1211143.

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An experimental/theoretical approach for the rational design of new f complexes with potential medical and technological applications

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In recent decades, the synthesis of new lanthanide (III) complexes has become a hot area because of their potential use as materials for biological immunoassays, lasers, cathode ray tubes, lighting systems, electroluminescent devices, sensors, dosimeters, imaging agents, display applications, decoration purposes, light-emitting diodes (LEDs) and photodynamic therapy (PDT). The fascinating optical properties of Ln (III) is due to their unique spectroscopic properties attributed to the characteristic f-f transitions in their inner 4f shell. So, offering desirable spectroscopic properties that addresses various limitations of organic fluorophores. In this work, we have designed and synthesized a series of heteroleptic ternary coordinatively saturated Eu(III) complexes [Eu(R-phen)(BTA)$_3$] and characterized by various physicochemical studies. The introduction the N,N-donor and β-diketonate ligands produce an increase of the luminescence. The triplet level of β-diketonate ligand is lower than the phenanthroline derivative. Therefore, in this case, these kinds of ligands produce a better energy transfer to the resonant level of lanthanide ion. A multiconfigurational ab initio method along with scalar relativistic time-dependent DFT were employed to accurately elucidate the excited state energy transfer pathways and the corresponding electronic states involved in lanthanide complexes. In this work, new f complexes were design and synthetized using the methodology previously mentioned. The experimental results validated the theoretical considerations obtained.[1]

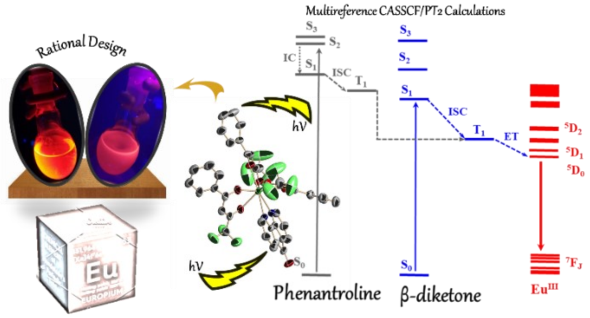

Figure 1: Rational design of lanthanide complexes

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Ozone Conversion and Cloud Condensation Nuclei Precursors Formation in the Troposphere: A Computational Study of the 1,3-Dipolar Cycloaddition

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Human activity-driven degradation and depletion of vegetation resources have led to an increase in greenhouse gases (GHGs) in the atmosphere, contributing to the ongoing climate crisis[1]. This crisis has been particularly evident in Chile, characterized by a lack of precipitation in the last decade. It is well known that, under stressful conditions, vegetation releases Biogenic Volatile Organic Compounds (BVOCs), which are unsaturated compounds capable of reacting with tropospheric O_3 (a significant GHG) through a process known as ozonolysis[2]. The resulting compounds, referred to as Secondary Organic Aerosols (SOAs), have the potential to serve as precursors of cloud condensation nuclei (CCN), playing a role in cloud formation and, consequently, influencing precipitation patterns[3]. Our research is primarily focused on investigating a novel pathway for the formation of SOAs with a high hygroscopic nature. This pathway involves the direct participation of tropospheric O_3 and one of the major BVOCs emitted by native trees in central-southern Chile, linalool. Our research involves investigating the formation and stability of Criegee Intermediates (CIs) and conducting an in-depth analysis of 1,3-dipolar cycloaddition reactions with varying starting material orientations, thereby increasing the diversity of the compounds formed. We aim to assess the significance of these compounds in regulating atmospheric pollutants and their capacity to act as CCN precursor. To conduct this study, we have employed theoretical and computational chemistry based on DFT (Density Functional Theory). These approaches allow us to model and analyse the chemical transformations taking place in the troposphere and establish the mechanisms of the involved reactions, obtaining energy parameters, rate constants and compare them with those previously reported reactions in the troposphere. Finally, we assess the potential of the resulting products to act as CCN by studying their nucleation stability in the presence of various gases found in the troposphere, using classical molecular dynamics simulations.

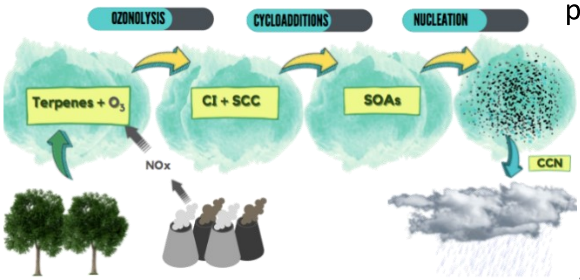

Fig1. Illustration of the chemical processes (involving terpenes) taking place in the troposphere

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Unraveling the intricate reaction mechanisms of the most efficient CO_2-fixing enzyme: a computational study

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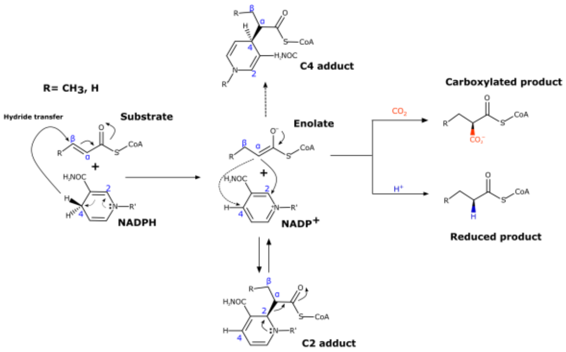
Crotonyl-CoA carboxylase/reductase (CCR) is a highly efficient CO2-fixing enzyme, recognized for its pivotal role in advancing artificial CO_2-fixation cycles [1]. Its primary reaction mechanism involves hydride transfer and carboxylation steps. In the absence of CO_2, a side reaction can occur, leading to the formation of a reduced side product. Interestingly, CCR can also adopt an alternative reaction mechanism, forming a covalent adduct between $NADP^+$ and the enolate intermediate known as the C2 adduct [2], which is reactive and can form the carboxylated product. Furthermore, by mutating a threonine residue near the active site, it is possible to promote the formation of another covalent adduct (C4 adduct, Fig. 1), which acts as an enzyme inhibitor [3]. Consequently, following the initial hydride transfer, the enolate can follow different mechanistic routes as illustrated in Fig. 1.

Figure 1.



To gain a comprehensive understanding of this enzyme's intricate reaction mechanisms, this study employed a range of computational methods, encompassing quantum chemical calculations, molecular dynamics simulations, enhanced-sampling techniques, and QM/MM simulations. Our results provide a detailed molecular description of the reaction mechanisms explaining enzymatic efficiency and reactivity differences for the formed adducts. CCR serves as an excellent model for exploring how enzymes handle multiple reaction pathways where dead-end products need to be avoided, which constitutes a clear example of negative catalysis.

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Beyond Bell-Evans-Polanyi Principle: Exploring Flexibility in Chemical Transformations

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A central focus of attention in physical chemistry has been the search for models and principles that allow a deeper understanding of the transformation of matter from reactants to products passing through a transition state. Among these, the Bell-Evans-Polanyi Principle (BEP)1 is a valuable interpretative tool, which establishes a relationship between the barrier height (ΔE^‡), the thermodynamic driving force (ΔE^o), and the intrinsic barrier (ΔE_0^‡), as follows:

$$\Delta E^{\ddagger} = \beta \Delta E^{o} + \Delta E_{0}^{\ddagger} \qquad (1)$$

Although this model shows remarkable robustness in its ability to represent and predict these thermodynamic properties, it is not fulfilled showing significant deviations from the expected trends. In this context, our research group has studied the effect of (a)synchronicity among primitive processes in BEP diagrams2, in light of Reaction Force (F(ξ))3 and Reaction Force Constant (κ(ξ))4 framework. While F(ξ) allows dividing of potential energy profile into regions of reactants, transition, and products, the fine structure of κ(ξ) along the transition allows elucidating whether the primitive processes take place synchronously or asynchronously. On this basis, a BEP-type equation was proposed that introduces some degree of flexibility by accounting for various aspects (synchronicity, reorganization energy, shapes of reaction profiles, among others) through the parameter γ≡(∂ΔE_act/∂ΔE_0^‡)_(ΔE^o) as stated in eq. (2).2

$$\Delta E^{\ddagger} = \beta \Delta E^{o} + \gamma \Delta E_{0}^{\ddagger} \qquad (2)$$

From this perspective, using the F(ξ) and κ(ξ) framework, hydrogen atom abstraction reactions (HAT) are being explored. Bimodal trends have been observed in the BEP diagrams5, where it has been established that saturated and unsaturated substrates follow different trend lines, justified in the first place by Bernasconi's Principle of Nonperfect Synchronization6. Our preliminary results show distinctive patterns in the fine structure of κ(ξ), indicative of a plausible mechanistic difference, supporting the bimodal trend.

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Estudio Comparativo a Partir de Cálculos de Primeros Principios de la Estructura Electrónica de la Ferrita de Bismuto y Cromita de Itrio

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Los multiferroicos han despertado un gran interés debido a su capacidad de combinar dos o más propiedades ferroicas en una sola fase cristalina. Además, estos materiales tienen diversas aplicaciones en campos como la piezoelectrónica, las memorias magnetoelectrónicas y la espintrónica. Se realizaron cálculos de primeros principios de la estructura electrónica de la ferrita de bismuto con fase hexagonal R3c y de la Cromita de Itrio con fase ortorrómbica Pnma. Se utilizaron arreglos antiferromagnéticos de tipo A, C y G para la cromita de itrio y de tipo A y G para la ferrita de bismuto. Se empleó la teoría del funcional de densidad el método de aproximación de densidad local y seudopotenciales ultrasuaves. Se utilizó el parámetro de Hubbard debido a la presencia de electrones fuertemente correlacionados en el orbital **d** presentes en los metales de transición. El parámetro de Hubbard se calculó con el método de respuesta lineal y se obtuvieron los valores de 2.43 eV para el hierro y 1.13 eV para el cromo. Para la ferrita de bismuto se obtuvo un gap de energía de 1.4 eV para el arreglo antiferromagnético tipo A y 1.8 eV para el arreglo tipo G. Para la cromita de itrio se obtuvo un gap de energía de 1.3 eV para el arreglo antiferromagnético tipo A, 1.32 eV para el arreglo tipo C y 1.6 eV para el arreglo tipo G. Se observa que los gaps de energía de la Cromita de Itrio son mas pequeños que los presentados en la Ferrira de Bismuto. Lo cual puede indicar que tendría un mejor desempeño en aplicaciones tecnológicas donde esta característica sea relevante, por ejemplo, en piezoelectricidad. También se puede observar que en ambos casos el arreglo antiferromagnético de tipo A presenta el gap de energía mas pequeño en cada material. Sin embargo, se debe considerar que el arreglo tipo G es el mas abundante en los procesos de síntesis de estos materiales.

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Dihydrofuran with ozone: Mechanism and atmospheric fate of reaction products

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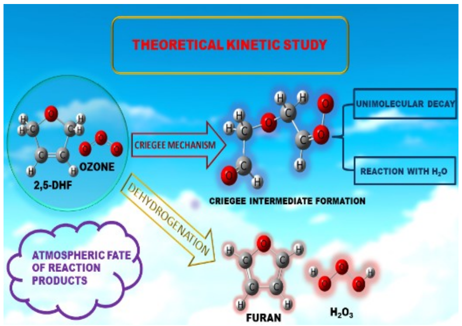
The 2,5-dihydrofuran (2,5-DHF) is an unsaturated heterocyclic molecule used as additive to diesel engines and is employed as a component of second generation biofuels [1]. Therefore, the production and use of this compound could increase its concentration in the troposphere. One of the main loss processes in the atmosphere for unsaturated compounds is the reaction with tropospheric ozone. This reaction can be described by the Criegee mechanism where very reactive birradical species, called Criegee Intermediates (CIs), are formed [2]. They can undergo unimolecular reactions or react with atmospheric species to produce different compounds, some of which could be aerosol precursors, affecting quality of air and contributing to climate change. The two reported experimental rate coefficients of the studied reaction are in good agreement with a value of (1.65±0.31) x 10^{-17}cm^3 molecule^{-1}s^{-1} at 298 K and 1 atm [3,4]. Additionally, an investigation based in matrix isolation technique proposes an alternative pathway to the Criegee mechanism, with the formation of complex furan--H_2O_3 through a dehydrogenation process [5].



In order to analyse the potential atmospheric competition between both processes, we present a theoretical investigation of the energetics and kinetics of the reaction of 2,5-DHF with O_3. The functional M08-HX/6-311++g(3df,3pd) was used to characterise the species and higher levels of theory, like CCSD(T)/aug-cc-pVTZ and DLPNO CCSD(T)/aug-cc-pVTZ, were employed for a reliable estimation of electronic energy. The rate coefficients were derived applying the canonical transition state theory. The results are in excellent agreement with the experimental values, being of 1.74x10^{-17}cm^3 molecule^{-1}s^{-1} at the DLPNO CCSD(T)/aug-cc-pVTZ//M08-HX/6-311++g(3df,3pd) level of theory. The present results suggest that the Criegee mechanism is dominant in tropospheric conditions. In addition, the kinetics of possible unimolecular processes of the generated CI were investigated, and the reaction between CI and H_2O was analysed.

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Aromaticity in the series $E(BeH)_n^{x+}$ (E = B, C, and N, n=5 or 6, x=1 or 2): A different view of the Magnetic Ring Current.

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The concept of double aromaticity was introduced by Schleyer in 1979, using $C_6H_3^+$ cation as a prototypical model. This cation exhibit two cyclic delocalization circuits involving 6π and 2σ electrons.1 This pivotal characterization heralded the synthesis of subsequent systems exhibiting analogous dual aromatic features.2, 3 Double aromaticity extends beyond molecular systems and is relevant in studying atomic clusters. For instance, the Al_4^{2-} dianion was proposed to possess triple aromaticity, involving σ-tangential, σ-radial, and π orbitals.4 However, ring current assessments revealed that Al_4^{2-} displays only σ-aromaticity.5 Moreover, the $E(BeH)_n^{x+}$ (E = B, C, and N, n=5 or 6, x=1 or 2) clusters have been proposed as doubly aromatic systems.6-8 These assignation were based on AdNDP and NICS analysis, although it's acknowledged that NICS values may not be an intrinsic indicator due to their estimation at a single fixed point.9 Consequently, establishing double aromatic behavior has proven challenging, relying on neither the AdNDP orbital shapes nor NICS values. In this study, we explored the aromatic character within the $E(BeH)_n^{x+}$ series using the ring current method implemented in the GIMIC program. Our findings revealed local diatropic currents surrounding the Be-H-Be bonds and a significant diatropic current enveloping the central atom. The latter current could be interpreted as an atomic vortex within the E^{m-} (m = 5, 4 or 3) anion. Furthermore, we assessed the ring currents of monoatomic E^{m-} and were surprised to find that their values closely resembled each other. This suggests that the $E(BeH)_n^{x+}$ series doesn't exhibit the previously postulated double aromaticity. These findings provide a clearer insight into aromaticity in these systems, enhancing our understanding of their electronic structure.

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Theoretical kinetic study of the degradation of 2,6-dichlorobenzamide (BAM) initiated by OH radicals

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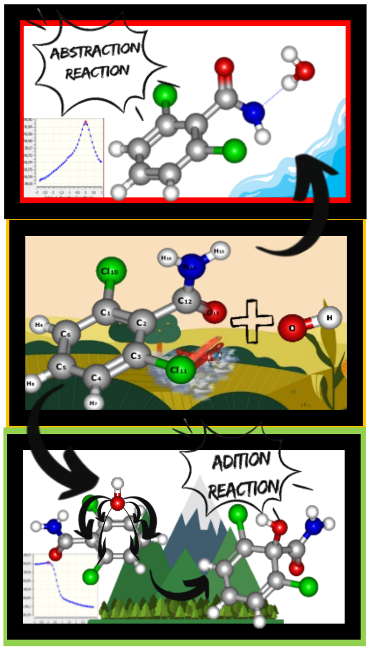
BAM, as a degradation product of the herbicide fluopicolide, can be introduced into the atmosphere and transported to remote places [1]. There, the main degradation way of this by-product could be predominantly by OH radicals reaction [2]. In order to know the atmospheric behavior of BAM and its environmental impact, a kinetic study of the BAM + OH reaction has been proposed. All possible reaction paths, including H-atom abstraction and OH-addition reactions, were considered in the present analysis.



The level of theory BMK/6-311++G(3df,3pd) was employed to determine the molecular and energetics properties of the system. The transition state theory was used to derive the high pressure limit rate coefficients at 298.15 K [3].

The results show that the H-atom abstraction reaction channel presents an electronic barrier higher than those corresponding to OH-addition channels, being more probable paths. A small value of 1.24x10^{-17} cm^3 molecule^{-1} s^{-1} was obtained for the rate coefficient of the H-atom abstraction channel, taking into account the Wigner tunnel effect correction [4]. The rate coefficients for all OH-addition channels were also derived, where the most important channel was the OH-addition to the C atom of the ring bonded to the C atom of the amide group. The corresponding calculated rate coefficient was of 4.31x10^{-14} cm^3 molecule^{-1} s^{-1}. These preliminary results of the degradation of BAM initiated by OH radicals suggest that the OH-addition channels are more favorable than H-atom abstraction channel. The derived rate coefficients are in good agreement with reported values for similar molecules [2].

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Kick-MEP: A Molecular Electrostatic Technique to Explore Potential Energy Surfaces of Fragments

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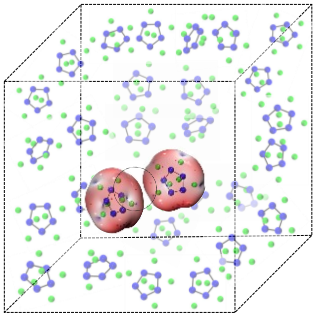
We present a new hybrid approach called Kick-MEP to study interactions between molecular fragments. This method utilizes the Coulombic integral[1] between the electrostatic potentials of stable, small molecule fragments or clusters. The fragments are combined in a stoichiometric ratio to model the larger molecule being analyzed. First, a small subset of candidates is selected randomly from a large pool based on the maximum Coulombic integral value between the electrostatic potentials on each fragment's surface[2,3]. These candidates are then optimized using density functional theory (DFT) calculations and a gradient-based method. We evaluated Kick-MEP for modeling atomic and molecular cluster formation by exploring their electrostatic potentials. In most cases, the global minimum structure was identified with low computational cost. This strategy could provide a good starting population for simulating the formation of larger water and silicon-lithium clusters.



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Quantum Chemical Elucidation of the Luminescence Mechanism in Europium (III) doped UiO-66 Chemosensor Selective to Mercury (II)

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In recent years, the use of chemical methods to detect metal ions has grown due to concerns about environmental pollution and health risks associated with these ions [1]. Ions such as lead, mercury, cadmium and arsenic are toxic and can accumulate in the environment and in living organisms [2]. In this regard, luminescent chemosensors based on Metal Organic Frameworks (MOFs) have emerged as a promising solution for the detection and monitoring of metal ions. Recently, lanthanide doped MOFs (Ln@MOFs) have been synthesized as luminescent chemosensors for metal ions in aqueous media. Among these, Eu^{3+} doped MOFs are expected to be part of effective detector devices [3]. To the best of our knowledge, a few works based on this type of sensors have provided deep insight into the luminescence mechanism and detection principle of this material. In this study, we investigated the luminescence properties and sensing mechanism of a novel UiO-66-type MOF, doped with ions Eu^{3+}, selective for Hg^{2+} ions.[2] From a computational point of view, the study of MOFs represents a challenge, due to the large size of this system.[4] In this study, we have developed a theoretical procedure to elucidate the response of the sensor to Hg^{2+} ions. Our methodology involves a finite model to accurately depict the UiO-66@Eu MOF structure using the well-known and rigorous multiconfigurational *ab initio* methods along with TD-DFT. According to multireference methods, we proposed the following pathway of the lanthanide sensitization mechanism based on the antenna effect: antenna excitation $^1S^* \rightarrow {}^2T^*$, $^2T^* \rightarrow {}^1T^*$ followed by antenna energy transfer $^1T^* \rightarrow$ Eu ($^5D_0$), and that the emission phenomenon takes place from the lanthanide Eu ($^5D_0 \rightarrow {}^7F_J$). Regarding the sensing mechanism, in presence of Hg^{2+}, the energy of the $^1T^*$ state of the antenna is lower than the resonance level $^5D_0$ of the Eu^{3+} ion. For that reason, the energy transfer from the antenna to the Eu^{3+} ion is blocked, resulting in the "Turn-off" of the luminescence. With this in mind, we consider that the proposed accurate methodology is a pioneer in the theoretical elucidation of the sensing mechanism proposed for doped MOFs chemosensors.

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Cellular Automaton-Based Generation of 2D Molecular Arrangements

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Cellular automata (CA) are computational models defined on a grid of cells that evolve based on mathematical rules. This work utilizes CA to generate two-dimensional molecular structures for aromatic systems. The methodology combines CA theory and the Game of Life rules with chemical theory. It extracts information from chemical formulas to assign element states. These states fill a matrix following CA rules based on atomic number, visually representing molecular structures.

CA can effectively explore the potential energy surface and discover new 2D molecular structures like Borazine. By integrating chemical theory into CA rules, the approach serves as a powerful tool for modeling and generating 2D materials. It allows comprehensive exploration of the potential energy landscape to identify novel aromatic systems. This demonstrates the versatility of CA for molecular design and materials discovery.

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Photoinduced CO releasing properties of rhenium(I) and manganese(I) tricarbonyl complexes with P,N-bidentate ligand

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In this work, the photochemical characterization of monometallic complexes with a P,N-bidentate ligand (PN-CH3) was conducted employing a variety of UV-Vis, FTIR, RMN techniques, whose outcomes indicated their possible use as photoinduced carbon monoxide releasing molecules (photoCORMs) [1], [2]. Then, the primary objective of this investigation was to assess the potential of these complexes as photoactivatable carbon monoxide-releasing molecules (photoCORMs). To achieve this goal, a myoglobin assay based on UV/Vis spectroscopy was employed. The results derived from the spectral changes of the myoglobin upon irradiation of the complexes, as depicted in **Figure 1**, provided conclusive evidence of photoinduced carbon monoxide release by the examined manganese complex**.** This significant finding introduces novel prospects in the exploration of photoactivatable compounds for therapeutic applications using controlled CO release.

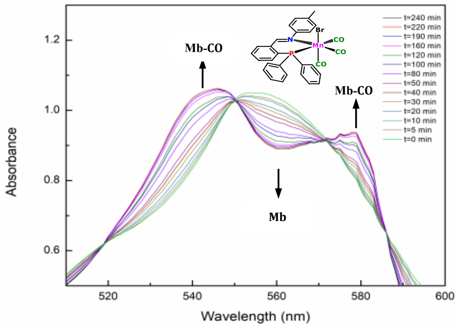

Fig.1. UV-Vis spectral changes of myoglobin as CO is released from irradiated Mn complex.

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