XVII

2019 ESOR

European Symposium on Organic Reactivity

September 8–13, 2019, Dubrovnik, Croatia

BOOK OF ABSTRACTS

University of Zagreb, Faculty of Science,
Department of Chemistry

Croatian Chemical Society

Inter-University Centre - Dubrovnik

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Dear Participants,

On behalf of the Organising Committee, we welcome you to the **17th European Symposium on Organic Reactivity (ESOR 2019).** The symposium is organised by the Department of Chemistry (Faculty of Science, University of Zagreb), the Croatian Chemical Society, and in cooperation with Inter-University Centre Dubrovnik.

The meeting will be held in the beautiful Croatian city of Dubrovnik on the Adriatic coast between 8 and 13 September 2019.

The ESOR series has a long and proud history, with meetings being held in Paris (1987), Padova, Italy (1989), Göteborg, Sweden (1991), Newcastle, UK (1993), Santiago de Compostela, Spain (1995), Louvain la Neuve, Belgium (1997), Ulm, Germany (1999), Cavtat (Dubrovnik), Croatia (2001), Oslo, Norway (2003), Rome, Italy (2005), Faro, Portugal (2007), Haifa, Israel, (2009), Tartu, Estonia (2011), Prague, Czech Republic (2013), Kiel, Germany (2015), and Durham, UK (2017).

The meeting will cover all areas of Physical Organic Chemistry, including all aspects of mechanism, structure and binding in organic systems. This also encompasses a wider range of areas from biology to materials using both theoretical and experimental approaches.

There will be a mixture of plenary and invited lectures plus submitted oral and poster presentations.

We very much look forward to welcoming you to Dubrovnik!

Hrvoj Vančik
Local Organising Committee

International Standing Committee of ESOR Conferences

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PLENARY LECTURERS

Josef Michl (University of Colorado, USA)

Porphene – a Regular Heterocyclic Two-dimensional Polymer

Henry Dube (Ludwig-Maximilians-Universität München, DE)

From Indigoid Photoswitches To Molecular Machines

Eric Vauthey (University of Geneva, CH)

Photoinduced Symmetry-breaking Charge-transfer

Massimo Bietti (Università "Tor Vergata", IT)

Reactivity and Selectivity Patterns in Hydrogen Atom Transfer from Aliphatic C-H Bonds

Stefan Grimme (University Bonn, DE)

New Tight-binding Quantum Chemistry Methods for the Exploration of Chemical Space

Leonard J. Prins (University of Padova, IT)

Energy Consumption in Chemical-fuel Driven Self-assembly

Sason S. Shaik (Hebrew University, IL)

Oriented External Electric Fields as Effectors in Chemistry

Johan Åquist (Uppsala University, SE)

Entropy and Enzyme Adaptation

Lyle Isaacs (University of Maryland, US)

Cucurbit[n]uril Molecular Containers: from Basic Science to Biomedical Applications

Harry L. Anderson (University of Oxford, UK)

Global Aromaticity at the Nanoscale

INVITED LECTURERS

Jirí Kaleta (Institute of Organic Chemistry and Biochemistry, CAS, CZ)

Regular 2-D Assemblies of Molecular Machines

J. Chris Slootweg (University of Amsterdam, NL)

Circular Chemistry, Steric Attraction and Photoinduced Single-electron Transfer: New Adventures in Main-group Chemistry

F. Matthias Bickelhaupt (Vrije Universiteit Amsterdam, NL)

Chemical Reactivity

Amnon Stanger (Technion – Israel Institute of Technology, IL)

Surprises in NICS Studies and a New NICS-based Criterion for Aromaticity

Yitzhak Apeloig (Technion – Israel Institute of Technology, IL)

Isomerization Mechanisms Around E=E’ (E,E’=C,Si,Ge) Bonds- Double Bonds, Anions, Radicals. Experiment and Theory

Nikola Basarić (Ruđer Bošković Institute, HR)

Photochemical Elimination of Nitrogen from Diazirines and Diazo Compounds

Ruth M. Gschwind (University of Regensburg, DE)

NMR in Catalysis and Photocatalysis Pushing the Frontiers

Davor Margetić (Ruđer Bošković Institute, HR)

Guanidine-carboxylate Bonding Motif in Self-assembly of Aromatic Donor-acceptor Systems

Marcin Stępień (Uniwersytet Wrocławski, PL)

Open-shell Nanographenoids

SCHEDULE

SUNDAY, 8 SEPTEMBER

14:00-20:00	**Registration**	
17:30	**Introduction, Hrvoj Vančik**	
18:00	**PL-1**	**Opening Lecture, Josef Michl (University of Colorado, USA)** *Porphene – a Regular Heterocyclic Two-dimensional Polymer*
19:00	**Welcome Party, IUC**	

MONDAY, 9 SEPTEMBER

9:00 – 9:50	**PL-2**	**Henry Dube (Ludwig-Maximilians-Universität München, DE)** *From Indigoid Photoswitches To Molecular Machines*
9:50 – 10:20	**IN-1**	**Jirí Kaleta (Institute of Organic Chemistry and Biochemistry of the CAS, CZ)** *Regular 2-D Assemblies of Molecular Machines*
10:20 – 10:40	**OP-1**	**Michael Schmittel (University of Siegen, DE)** *Multicomponent Catalytic Machinery: How the Machine Speed Impacts Catalytic Activity*
10:40 – 11:10	**Coffee Break**	
11:10 – 11:30	**OP-2**	**Henrik Ottosson (Uppsala University, SE)** *Exploring Photoreactions Potentially Triggered by Excited State Antiaromaticity Relief*
11:30 – 11:50	**OP-3**	**Moisés Canle (Universidade da A Coruña, ES)** *Short-lived Intermediates Derived from Sym-triazines: Structure, Thermodynamic Properties and Reactivity*
11:50 – 12:10	**OP-4**	**Shigeru Yamago (Kyoto University, JP)** *Synthesis and Properties of Novel Cyclic π-conjugated Molecules*
12:30 – 14:00	**Lunch Break**	
14:00 – 14:50	**PL-3**	**Eric Vauthey (University of Geneva, CH)** *Photoinduced Symmetry-breaking Charge-transfer*
14:50 – 15:20	**IN-2**	**J. Chris Slootweg (University of Amsterdam, NL)** *Circular Chemistry, Steric Attraction and Photoinduced Single-electron Transfer: New Adventures in Main-group Chemistry*
15:20 – 15:40	**OP-5**	**Eva Blokker (Vrije Universiteit Amsterdam, NL)** *Hydride Affinities of Cationic Main Group-element Hydrides*
15:40 – 16:10	**Coffee Break**	
16:10 – 16:30	**OP-6**	**Trevor Hamlin (Vrije Universiteit Amsterdam, NL)** *1,3-dipolar Cyloaddition Reactivity of Alkynes*
16:30 – 16:50	**OP-7**	**Uta Wille (The University of Melbourne, AU)** *Decoding the Mechanism of Environmental Polymer Degradation: a Mass Spectrometric Approach*
16:50 – 17:10	**OP-8**	**Hendrik Zipse (Ludwig-Maximilians-Universität München, DE)** *Molecule-induced Radical Formation With Peroxides*
17:10 – 17:30	**OP-9**	**Götz Bucher (University of Glasgow, UK)** *Bay Quinones – Electronic Properties and Stability*

TUESDAY, 10 SEPTEMBER

9:00 – 9:50	**PL-4**	**Massimo Bietti (Università "Tor Vergata", IT)** *Reactivity and Selectivity Patterns in Hydrogen Atom Transfer from Aliphatic C-H Bonds*
9:50 – 10:40	**PL-5**	**Stefan Grimme (University Bonn, DE)** *New Tight-binding Quantum Chemistry Methods for the Exploration of Chemical Space*
10:40 – 11:10	**Coffee Break**	
11:10 – 12:00	**PL-6**	**Leonard J. Prins (University of Padova, IT)** *Energy Consumption in Chemical-fuel Driven Self-assembly*
12:00 – 12:30	**IN-3**	**F. Matthias Bickelhaupt (Vrije Universiteit Amsterdam, NL)** *Chemical Reactivity*
13:30	**CONFERENCE TRIP**	

WEDNESDAY, 11 SEPTEMBER

9:30 – 10:20	**PL-7**	**Sason S. Shaik (Hebrew University, IL)** *Oriented External Electric Fields as Effectors in Chemistry*
10:20 – 10:50	**IN-4**	**Amnon Stanger (Technion – Israel Institute of Technology, IL)** *Surprises in NICS Studies and a New NICS-based Criterion for Aromaticity*
10:50 – 11:10	**OP-10**	**Hans-Ullrich Siehl (Ulm University, DE)** *1,3-H-shift – a New Route to Static Bicyclobutonium Ions Further Answers to the Conundrum of the Structure of $C_4H_7^+$ Cations*
11:10 – 11:40	**Coffee Break**	
11:40 – 12:00	**OP-11**	**Sujan K. Sarkar (Hiroshima University, JP)** *Heavy Atom Tunneling, Matrix Effect, and Wavelength Effect in the Photoreaction of 2,3-diazabicyclo[2.2.1]hept-2-ene*
12:00 – 12:20	**OP-12**	**Neil Griffin (Syngenta, UK)** *Applying Physical Organic Processes To Formulation Chemical Stability*
12:30 – 14:00	**Lunch Break**	
14:00 – 14:30	**IN-5**	**Yitzhak Apeloig (Technion – Israel Institute of Technology, IL)** *Isomerization Mechanisms Around E=E′ (E,E′=C,Si,Ge) Bonds- Double Bonds, Anions, Radicals. Experiment and Theory*
14:30 – 15:00	**IN-6**	**Nikola Basarić (Ruđer Bošković Institute, HR)** *Photochemical Elimination of Nitrogen from Diazirines and Diazo Compounds*
15:00 – 15:15	**In Memory of Prof. Brian G. Gowenlock (H. Vančik)**	
15:15 – 15:30	**Coffee Break**	
16:00 – 18:30	**POSTER SESSION**	
20:00	**CONFERENCE DINNER**	

THURSDAY, 12 SEPTEMBER		
9:00 – 9:50	**PL-8**	**Johan Åquist (Uppsala University, SE)** *Entropy and Enzyme Adaptation*
9:50 – 10:20	**IN-7**	**Ruth M. Gschwind (University of Regensburg, DE)** *NMR in Catalysis and Photocatalysis Pushing the Frontiers*
10:20 – 10:40	**OP-13**	**David R. W. Hodgson (Durham University, UK)** *Chemo-enzymatic Preparation of Nucleoside Triphosphates from Diphosphates Using Feedstock Chemicals*
10:40 – 11:10	**Coffee Break**	
11:10 – 11:30	**OP-14**	**Marina Šekutor (Ruđer Bošković Institute, HR)** *Application of Adamantyl Aminoguanidines in Functional Self-assembled Nanovesicles*
11:30 – 11:50	**OP-15**	**Veronika V. Semionova (Voevodsky Institute of Chemical Kinetics and Combustion, RAS, RU)** *Supramolecular Compounds Formed by Organic Photochromes and Metal-organic Coordination Polymer*
11:50 – 12:10	**OP-16**	**Benita Barton (Nelson Mandela University, ZA)** *Host Behaviour of N,N′-bis(9-phenyl-9-thioxanthenyl)ethylenediamine in the Presence of Aromatic and Aliphatic Five-membered Heterocyclic Guest Compounds*
12:30 – 14:00	**Lunch Break**	
14:00 – 14:50	**PL-9**	**Lyle Isaacs (University of Maryland, US)** *Cucurbit[n]uril Molecular Containers: from Basic Science to Biomedical Applications*
14:50 – 15:20	**IN-8**	**Davor Margetić (Ruđer Bošković Institute, HR)** *Guanidine-carboxylate Bonding Motif in Self-assembly of Aromatic Donor-acceptor Systems*
15:20 – 15:50	**Coffee Break**	
15:50 – 16:10	**OP-17**	**Maria L. S. Cristiano (University of Algarve, PT)** *Substituent Effects On the Photochemistry of 5-aminotetrazoles*
16:10 – 16:30	**OP-18**	**Armin R. Ofial (Ludwig-Maximilians-Universität München, DE)** *Reactivities of Electrophilic Alkynes and Allenes*
16:30 – 16:50	**OP-19**	**Bagrat A. Shainyan (A. E. Favorsky Irkutsk Institute of Chemistry, RU)** *Silacyclohexanes: Conformational Preferences in Gas and Solution*
16:50 – 17:10	**OP-20**	**Robert J. Mayer (Ludwig-Maximilians-Universität München, DE)** *Ambident Reactivity of Phenolate Anions Revisited: a Quantitative Approach To Phenolate Reactivities*

FRIDAY, 13 SEPTEMBER		
9:00 – 9:50	**PL-10**	**Harry L. Anderson (University of Oxford, UK)** *Global Aromaticity at the Nanoscale*
9:50 – 10:20	**IN-9**	**Marcin Stępień (Uniwersytet Wrocławski, PL)** *Open-shell Nanographenoids*
10:20 – 10:40	**OP-22**	**Ian Williams (University of Bath, UK)** *Computational Simulation of Energy Landscapes and Isotope Effects for Glycosidic Reactivity*
10:40 – 11:00	**OP-23**	**Kazuhide Nakata (Hosei University, JP)** *Computational Study of Substituent Effects on Gas-phase Stabilities of 1-phenylcyclobutane-1,3-diyliums*
11:00 – 11:20	**OP-24**	**Tatiana Nekipelova (Emanuel Institute of Biochemical Physics, RAS, RU)** *Structure–reactivity Correlation in the Reaction of Mixed Phosphonium-iodonium Ylides With Acetylenes*
11:20 – 11:40	**OP-25**	**Rebecca Hawker (University of Sheffield, UK)** *Predicting the Effects of Solvent Mixtures on the Kemp Reactions*
11:40 – 12:00	**OP-26**	**Cedric W. McCleland (Nelson Mandela University, ZA)** *A DFT Comparative Study of Substituent Effects in Radicals, Cations and Radical Cations*
12:00 – 12:20	**OP-27**	**Eduardo Humeres (Universidade Federal de Santa Catarina, BR)** *Mechanism of Reduction of Air Pollutants on Carbons: Sulfur Dioxide and Ozone*
12:20	**Closing Ceremony**	

LEGEND:

PLENARY LECTURES*	**INVITED LECTURES**	**ORAL PRESENTATIONS**

* Plenary lectures will be held at the nearby auditorium of the **University of Dubrovnik.**

CONTENTS

PLENARY LECTURES

INVITED LECTURES

ORAL PRESENTATIONS

POSTER PRESENTATIONS

PLENARY LECTURES

PL-1

PORPHENE – A REGULAR HETEROCYCLIC TWO-DIMENSIONAL POLYMER

Thomas F. Magnera,[a] Josef Michl[a,b,*]

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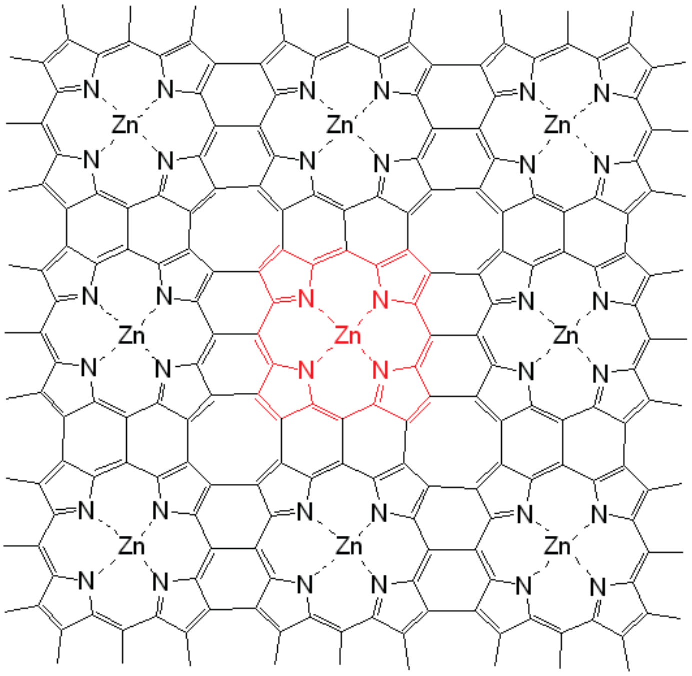
Surface-constrained oxidative coupling of zinc porphyrin on an aqueous subphase containing a strong oxidant yields a bilayer of porphene in the form of sheets up to 0.1 mm across, which can be transferred to various solid substrates. The structure of this fully conjugated two-dimensional polymer with fourfold symmetry was proven by diffraction on the aqueous surface using a synchrotron grazing incidence X-ray beam. It was examined also by non-contact atomic force microscopy after transfer to highly ordered pyrolytic graphite. It is analogous to that of graphene, but is composed of fused free-base porphyrin rings instead of fused benzene rings. The absence of Zn ions has been demonstrated by X-ray photoelectron spectroscopy. Investigations of porphene formation mechanism and its spectroscopic, structural, electrical, chemical, and mechanical properties, as well as exfoliation to single sheets and construction of twisted multilayer sheets using bidentate ligands, are currently underway. The ability of the porphyrin macrocycle to bind many different kinds of metal cations carrying two, one, or no additional ligands promises that porphene has the potential for being not be a single polymer but rather, a large family of two-dimensional polymers with tunable properties. Here, porphene differs from graphene in that its functionalization does not require taking any of its π-electron centers out of conjugation, and merely involves insertion of metal ions into its macrocycles and attachment of arbitrary ligands. It is therefore expected that it will be at least as versatile as graphene.



FROM INDIGOID PHOTOSWITCHES TO MOLECULAR MACHINES

Henry Dube

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Indigoid chormophores are a class of emerging photoswitches[1,2] possessing many advantages compared to the most commonly used photoswitch motives. Despite their high potential as versatile and efficient molecular triggering unit, they have been largely overlooked by the chemistry, biology, or material science communities.

In the recent years, we have explored the interesting and somewhat unusual photophysical properties of different indigoid photoswitches such as hemithioindigo, hemiindigo, or indigo itself in depth and developed a thorough mechanistic understanding of their light induced motions and behavior in the excited state.[3,4] This fundamental knowledge allows us to tailor photoswitches with specific property profiles using strategic substitutions in combination with predictable environmental influences.

We further use indigoid chromophores to build responsive supramolecular systems with unprecedented properties[5] and next generation molecular machines.[6,7] Our main goal is to develop smart molecular entities, which can conveniently be implemented into more complex architectures to manipulate matter at the molecular scale with the highest possible precision. Key issues that we address are a complete control over the mechanics of molecular motions and the interactions between different molecular entities[8] using nondestructive visible light.

Keywords: Photoswitches, Molecular Machines, Photochemistry

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PL-3

PHOTOINDUCED SYMMETRY-BREAKING CHARGE-TRANSFER

Eric Vauthey

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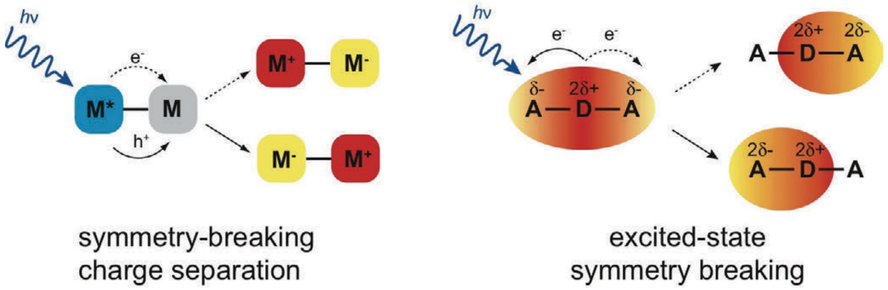
A substantial number of symmetric molecular systems, including the reaction centre of photosynthetic bacteria, undergo photoinduced charge transfer along one among several energetically equivalent pathways, resulting in a breaking of their symmetry.[1] Some of our efforts toward a better understanding of the origin and dynamics of these processes will be presented.



Photoinduced charge separation between two identical sub-units will be illustrated by studies on bichromophoric molecules. They reveal the importance of the environment for the direction of the charge separation and of the distance between the sub-units for the extent of asymmetry in charge distribution.

Most symmetric quadrupolar and octupolar D-(π-A)$_{2,3}$ or A-(π-D)$_{2,3}$ molecules behave like their dipolar D-π-A analogue once in the electronic excited state. This was ascribed to excited-state symmetry breaking, where electronic excitation, originally distributed evenly over the molecule, localises on a single D-π-A branch.[2] We will show how this process can be directly visualised using time-resolved IR spectroscopy.[3] The influence of various parameters, such as solute-solvent interactions and structural disorder on the symmetry breaking will be discussed.[3,4]

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PL-4

REACTIVITY AND SELECTIVITY PATTERNS IN HYDROGEN ATOM TRANSFER FROM ALIPHATIC C–H BONDS

Michela Salamone, Teo Martin, Marco Galeotti, Massimo Bietti*

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Site-selective aliphatic C−H bond functionalization represents an important goal of modern synthetic chemistry. By avoiding substrate prefunctionalization associated to traditional functional group manipulation and interconversion, direct functionalization provides access to transformation of high synthetic potential that can offer advantages both in terms of decreased waste generation and reaction step economy.

Among the available methodologies, those based on hydrogen atom transfer (HAT) have attracted considerable interest and accordingly, the factors that govern reactivity and site-selectivity in these processes have been discussed in detail.[1] These include bond strengths, electronic, steric and stereoelectronic effects, conjugation and hyperconjugation, and, with cyclohexane derivatives, torsional effects. Medium effects have also emerged as a powerful tool that has been successfully employed to dramatically alter both reactivity and site-selectivity in HAT based C−H functionalization procedures.[2]

Within this framework, we have been interested in the study of HAT reactions from aliphatic C−H bonds, with the main objective of obtaining quantitative kinetic information on the role of structural and medium effects on the reactivity and selectivity patterns. This goal has been achieved through time-resolved kinetic studies on the reactions of an alkoxyl radical such as cumyloxyl ($PhC(CH_3)_2O^\bullet$) with a variety of substrates, accompanied by product studies on C−H bond oxidation of selected substrates with hydrogen peroxide catalyzed by iron and manganese complexes.[3] The results of these studies will be discussed.

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PL-5

NEW TIGHT-BINDING QUANTUM CHEMISTRY METHODS FOR THE EXPLORATION OF CHEMICAL SPACE

Stefan Grimme

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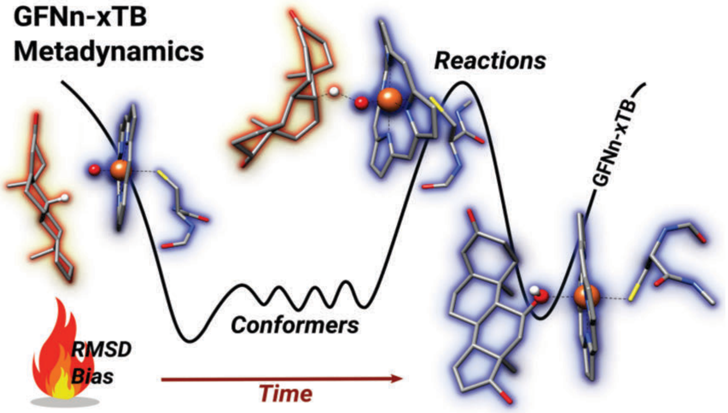
The GFN-xTB family of semi-empirical tight-binding methods, which are variants of the well-known DFTB approaches, is introduced. The methods follow a global and element-specific parameters only strategy and are consistently parameterized for all elements through radon. Their original purpose and main target for the parameter optimization has been the computation of molecular geometries, vibrational frequencies, and non-covalent interactions. Very recently, the original GFN-xTB has been extended by including multipole electrostatic as well as one-center exchange-correlation terms leading to higher accuracy (at lower empiricism) specifically for non-covalent interactions and conformational energies.[1] A new, much faster (speedup of 3-5) first-order form employing classical electrostatics is briefly described (GFN0-xTB). The most sophisticated GFN2-xTB approach which furthermore employs density dependent D4 dispersion, is effectively used in the framework of meta-dynamics (MTD) to globally explore chemical compound, conformer, and reaction space.[2] The biasing potential given as a sum of Gaussian functions is expressed with the RMSD in Cartesian space as a metric for the collective variables. For typical conformational search problems of organic drug molecules, the new MTD(RMSD) algorithm yields lower energy structures and more complete conformer ensembles at reduced computational effort. Because TB methods (when combined with the Fermi-smearing technique) can also describe difficult electronic situations at least qualitatively correct, chemical reaction space exploration in a virtual nanoreactor also for transition metal containing systems is routinely possible.



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ENERGY CONSUMPTION IN CHEMICAL-FUEL DRIVEN SELF-ASSEMBLY

Leonard J. Prins

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Nature extensively exploits high-energy transient self-assembly structures that are able to perform work through a dissipative process. Often, self-assembly relies on the use of molecules as fuel that is consumed to drive thermodynamically unfavourable reactions away from equilibrium. Implementing this kind of non-equilibrium self-assembly process in synthetic systems is bound to profoundly impact the fields of chemistry, materials science and synthetic biology, leading to innovative dissipative structures able to convert and store chemical energy.

Here, we present a conceptual insight in the design of chemical-fuel driven processes and illustrate experimental approaches.

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PL-7

ORIENTED EXTERNAL ELECTRIC FIELDS AS EFFECTORS IN CHEMISTRY

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The talk will discuss the wide-ranging potential of using **oriented external-electric-fields (OEEFs) as new effectors of chemical change**.[1–5] Generally speaking, an OEEF along the direction of electron reorganization from reactants to products, will catalyze/inhibit at will nonpolar reactions, while orientations of the OEEF off the "reaction axis" will control selectivity patterns and chiral discrimination.[1,3] The field's direction will similarly affect bonds, molecular structures and aggregation.[5]

I shall discuss OEEF effects, using a selection from the following topics: (a) Control of bond length and strength, and molecular structures,[1,5] (b) control, at will, of non-redox chemical reactions by catalyzing or inhibiting them through a flip of the field's direction, (c) control of regioselectivity (e.g., C=C vs. C-H activation by oxoiron reagents (e.g., P450 like), *exo*/*endo* selectivity in Diels-Alder reactions), (d) control of spin-state selectivity, (e) control of reaction mechanisms, (f) the dilemma of electric fields in enzymes,[5] and (g) control of chiral discrimination and enantioselectivity.[3]

Some future prospects may be discussed as well: (a) the ability of OEEF to act as tweezers that orient the reactants in space and catalyzes their reactions, (b) the role of OEEFs in self-assembly.

As shall be described, there are by now **a variety of experimental techniques** to implement the OEEF idea,[2,5] including **scalable options**.[2b] The field is rapidly expanding. As experimental techniques mature further, chemical transformations may become an exercise in zapping oriented molecules with OEEFs

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ENTROPY AND ENZYME ADAPTATION

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The speed of chemical reactions in water and in enzymes varies with temperature, depending on how the free energy of activation is partitioned into enthalpy and entropy. In enzymes, this partitioning is also optimized as a consequence of the organism's adaptation to the environment. We will show how the temperature dependence of chemical reaction rates can be obtained from brute force computer simulations. Such calculations shed new light on entropic effects in enzyme catalysis and on how protein structures have evolved in differently adapted species.

PL-9

CUCURBIT[*n*]URIL MOLECULAR CONTAINERS: FROM BASIC SCIENCE TO BIOMEDICAL APPLICATIONS

Lyle Isaacs

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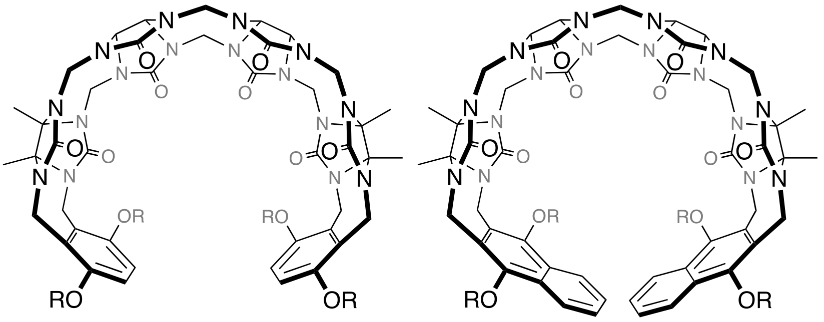
In this talk I will present our recent work on the preparation and use of macrocyclic and acyclic CB[n] (**1** and **2**) in biologically relevant applications. For example, I will discuss the use of acyclic CB[n] as a solubilizing excipient for insoluble drugs,[1] as a reversal agent for neuromuscular block as well as hyperlocomotion induced by drugs of abuse (e.g. methamphetamine),[2] the preparation of metal organic polyhedra that are either covalently or non-covalently functionalized with CB[n],[3] and new acyclic CB[n] featuring triptycene sidewalls.[4]



1 R = $(CH_2)_3SO_3Na$ **2** R = $(CH_2)_3SO_3Na$

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PL-10

GLOBAL AROMATICITY AT THE NANOSCALE

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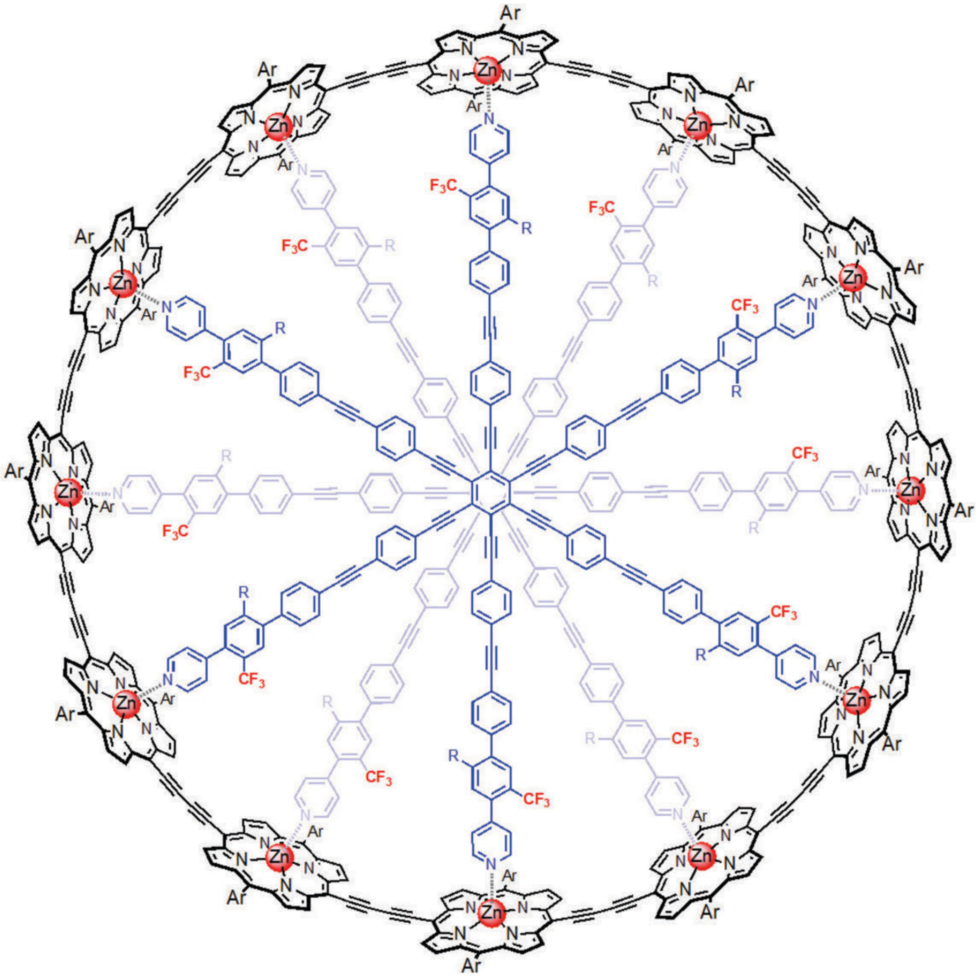
Aromaticity was once thought to be limited to molecules with less than 22 π-electrons. We have discovered that global aromatic ring currents can lead to charge delocalization in large porphyrin nanorings[1] and that the Hückel $4n + 2$ rule is obeyed in the cations of these macrocycles with up to 162 π-electrons ($n = 40$).[2] Recent result on aromatic nanorings, such as the complex shown below, will be presented.



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INVITED LECTURES

IN-1

REGULAR 2-D ASSEMBLIES OF MOLECULAR MACHINES

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Controlled attachment of various molecular machines (motors, rotors, and switches) to flat surfaces is an attractive and promising route towards new generation of regular 2-D materials. Organization of individual molecules into regular arrays (Figure 1) should amplify their function and lead thus to the new types of smart materials with potential application for example in nanoelectronics. Several approaches leading to such systems built on solid-gas[1,2] and liquid-gas[3,4] interphases will be discussed.

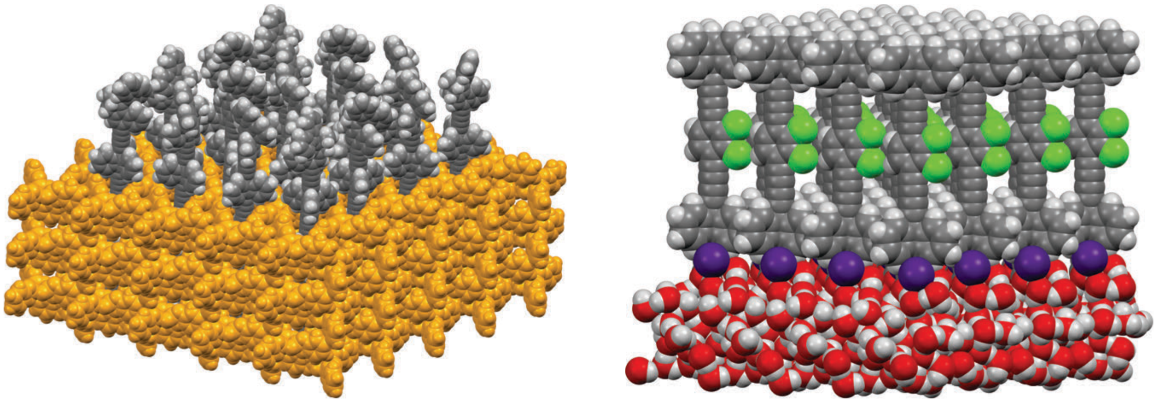

Figure 1: Regular array of molecular motors (left) and rotors (right).

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IN-2

CIRCULAR CHEMISTRY, STERIC ATTRACTION AND PHOTOINDUCED SINGLE-ELECTRON TRANSFER: NEW ADVENTURES IN MAIN-GROUP CHEMISTRY

J. Chris Slootweg

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In this lecture, I will introduce Circular Chemistry as a new concept,[1] discuss the 12 principles of circular chemistry and highlight these important concepts with appealing examples aiming at making chemical processes and production cycles truly circular.

After this holistic view on chemistry, I will focus on our bottom-up approach using the complete physical organic chemistry toolbox and highlight our new adventures in main-group chemistry for the activation and functionalization of small molecules using steric attraction and photoinduced single-electron transfer.

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IN-3

CHEMICAL REACTIVITY

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The aim of this talk is to convey a way of understanding the factors that determine bonding and reactivity in the framework of quantitative Kohn-Sham molecular orbital theory. Herein, a central role is reserved for how chemical bonding in transition states works and how it decides the course of chemical reactions. To this end, I will first discuss the activation strain model (ASM) which creates a causal relationship between, on one hand, reactivity trends and, on the other hand, electronic and structural properties of reactants as well as the nature of the chemical transformation (see Figure 1). The ASM covers not only the interaction between reactants but also the energy needed to distort them as they proceed along the reaction coordinate. A typical activation strain diagram (ASD) can be found in the illustration, showing the strain associated with distortion of reactants as well as the interaction between the ever more distorted reactants for a metal-mediated bond-activation reaction. Examples of ASM applications in this talk may, depending on the available time, comprise examples from homogeneous catalysis (bond activation), organic chemistry (S_N2, E2 and pericyclic reactions, including dual activation of aromatic Diels-Alder additions) as well as biochemistry (models for DNA replication).

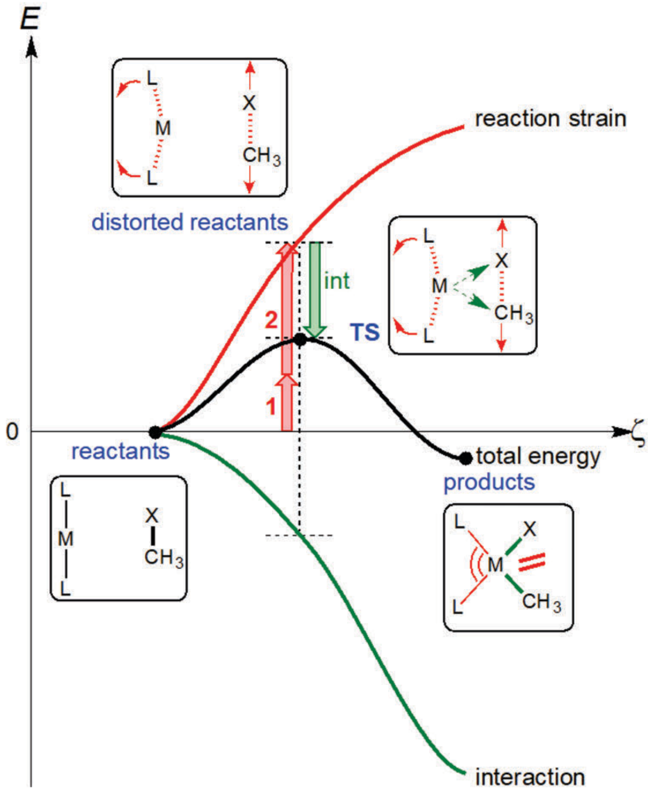

Figure 1. Schematic activation strain diagram (ASD) for bond activation via oxidative addition.

SURPRISES IN NICS STUDIES AND A NEW NICS-BASED CRITERION FOR AROMATICITY

Amnon Stanger

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All the different NICS methods (for example, NICS(r), NICS(r)$_{zz}$, etc., where r is the distance from the molecular plane) are calculated at and above the geometric center of the molecule. The rational behind this is that the induced magnetic field by the π electrons induced current (under an external magnetic field) is the strongest along the line that originates at the center and perpendicular to the molecular plane. However, a careful study, using a two-dimensional grid of BQs, suggests that at (relatively) short distances from the molecular plane the maximal induced magnetic field is off-center. Only at larger distances (1.4–2.2 Å, depending on the specific system), the maximal induced field is above the geometrical center of the system.

The paper discusses the possible reasons for these findings and suggests a new aromaticity criterion - $\int$NICS$_{\pi,zz}$, which is based on the pure π-induced ring current.

IN-5

ISOMERIZATION MECHANISMS AROUND E=E' (E,E'=C,SI,GE) BONDS-DOUBLE BONDS, ANIONS, RADICALS. EXPERIMENT AND THEORY

Lieby Zborovsky, Arseni Kostenko, Daniel Pinchuk, D. Bravo-Zhivotovskii, Yitzhak Apeloig

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The mechanism of isomerization around C=C bonds has been studied extensively both experimentally and theoretically and appears in every organic chemistry textbook.

In contrast, relatively little is known about the isomerization mechanisms around E=E' bonds- where E,E'=Si,Ge - carbon's heavier congeners.

In this lecture we discuss isomerization mechanisms around E=E' (E,E'=C,Si,Ge) bonds in silenes and germenes (RR'C=ERR', E=Si,Ge), and in silenyl anions ($RR'C{=}SiR^-$) and radicals, recently synthesized in our group.[1,2] The experimental and computational studies reveal interesting differences between the isomerization mechanisms of alkenes and vinyl anions and radicals *versus* their heavier silicon and germanium congeners.

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IN-6

PHOTOCHEMICAL ELIMINATION OF NITROGEN FROM DIAZIRINES AND DIAZO COMPOUNDS

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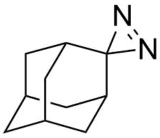
Elimination of nitrogen from diazo compounds and diazirines that delivers carbenes is a well known reaction, which can be initiated thermally or photochemically.[1] Prompted by our interest in the synthesis of polycyclic strained molecules,[2] we studied photoelimination of nitrogen from adamantane **1** and pentacycloundecane (PCU) diazirine derivative **2**. Combined preparative irradiations, spectroscopic study and computations for **1** and **2** indicated that photoproducts were formed *via* singlet and triplet carbenes, even though singlet carbenes are more stable then the triplets. Complexation of diazirines with macrocyclic host molecules changed the distribution of singlet and triplet photoproducts.[3] Furthermore, upon irradiation of **2** in CH_3OH we isolated some products with rearranged PCU skeleton, which indicated that carbenes undergo protonation in CH_3OH, and not O-H bond insertion, changing the paradigm for the mechanism of the reaction of carbenes with alcohols.

Combined experimental and theoretical investigation of photoelimination of nitrogen from diazo compounds **3** and **4** unraveled hitherto undisclosed pathway involving higher excited singlet states. Fluorescence takes place from S_2, whereas the photoelimination of nitrogen upon excitation to S_2 proceeds more efficiently then upon excitation to S_1, due to efficient deactivation to S_0 *via* a conical intersection.[4] The discovery of anti-Kasha photochemical pathways is interesting due to its fundamental value, as well as for potential applications, since the photoreaction can be tuned by appropriate choice of light wavelength.



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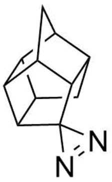

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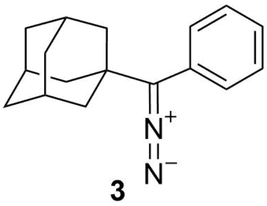

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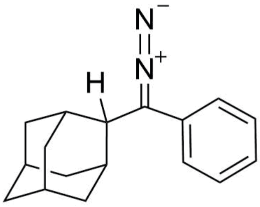

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IN-7

NMR IN CATALYSIS AND PHOTOCATALYSIS PUSHING THE FRONTIERS

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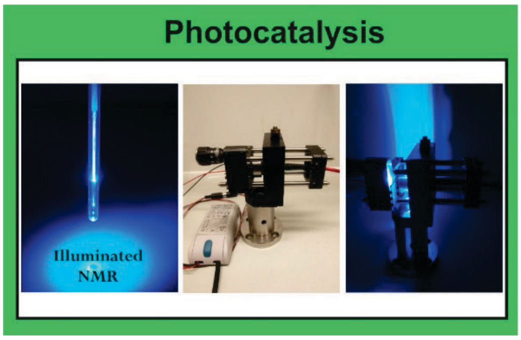
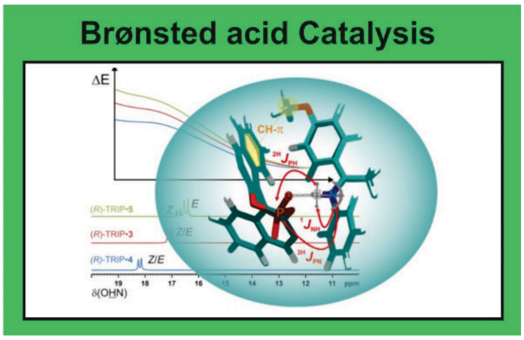
The detection and characterization of intermediates in catalytic reactions is crucial for the rational optimization of reaction conditions. However, in many rapidly expanding fields of asymmetric catalysis, mechanistic studies as well as structural investigations on intermediates or intermolecular interactions are scarce. In this talk I will present techniques and methods to extend the application of NMR in catalysis and photocatalysis and explain their impact on examples. First our LED based NMR illumination device[1] will be introduced together with the new triple combination illumination/NMR/UV[2] and an NMR access to intermediates below the detection limit.[3] These methods allow for new insights into one- versus two-electron processes usually inaccessible to UV/Vis,[4] the inclusion of radical species into NMR reaction profiles,[2] the structure elucidation of thermally labile photoswitches[2] and the sequencing of tiny intermediates.[5] Last, the extension of the NMR time scale to µs is demonstrated using relaxation dispersion methods. In a catalyst substrate complex taken from Brønsted acid catalysis even the switching of a single hydrogen bond can be detected experimentally.[6]





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IN-8

GUANIDINE-CARBOXYLATE BONDING MOTIF IN SELF-ASSEMBLY OF AROMATIC DONOR-ACCEPTOR SYSTEMS

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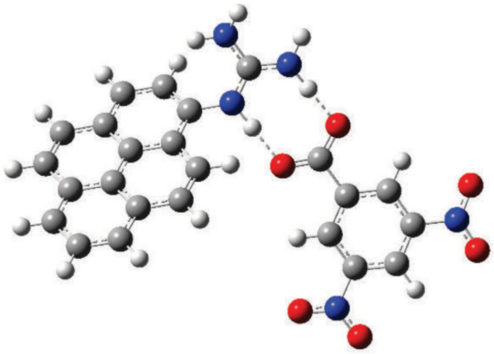
Guanidine-carboxylate hydrogen bonding motif[1] was exploited in self-assembly of aromatic electron donor-acceptor (D-A) pairs. These artificial systems are models for study of photo-induced electron transfer processes through guanidine-carboxylate bonds in more complex natural photosynthetic systems.[2] As typical electron donor systems, aromatic monosubstituted guanidines such as 1-pyrenylguanidine and 5-(4-phenyl guanidinyl)-10,15,20-triphenyl porphyrin were prepared. Synthetic procedure for conversion of aromatic amines to guanidines by *N,N′*-di-Boc-1H-pyrazole-1-carboxamidine guanylation reagent was developed. Synthesis of aromatic guanidinium chromophores was optimized by using environmentally more friendly high-speed vibration milling technique.[3,4] The fundamental physico-chemical properties of supramolecular D-A assemblies obtained via guanidine-carboxylate salt bridges were studied spectroscopically. Molecular modelling (DFT method) was employed in design of D-A systems and study of their molecular and electronic structures.



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IN-9

OPEN-SHELL NANOGRAPHENOIDS

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The interest in open shell aromatic molecules is motivated by the fundamental aspects of their electronic structure, posing considerable challenges to synthetic, physical, and theoretical chemists, and by their unique properties, with emerging applications in materials science.[1–3] Modern strategies of creating biradicaloid molecules typically combine quinoidal, aromatic, and antiaromatic substructures in ways that stabilize open-shell configurations and high-spin states. Our own research on two-dimensionally fused aromatics containing hetero- and carbocyclic ring systems[4–8] has provided access to novel π-conjugated frameworks that can be tailored into radicals and oligoradicaloids. In this contribution we will discuss our recent synthetic advances and describe the spectroscopic and supramolecular features of these systems. In particular, we will discuss an air-stable tetraradicaloid macrocycle, which is simultaneously active as an anion receptor and a redox switch, and can function as a unique "diiodine splitter."[9] We will also present the first example of an azacoronene-derived radical and its giant σ-dimer.

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ORAL PRESENTATIONS

OP-1

MULTICOMPONENT CATALYTIC MACHINERY: HOW THE MACHINE SPEED IMPACTS CATALYTIC ACTIVITY

Indrajit Paul,[a] Pronay Biswas,[a] Suchismita Saha,[a] Abir Goswami,[a] Michael Schmittel[a],*

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While nature has built and optimized rotating catalysts (e.g. ATP synthase) over millions of years with the purpose to improve catalytic conversion for instance by eliminating product inhibition, abiotic examples using analogous nanomechanical action in catalysis have been lacking. Recently, we have developed examples of multicomponent machinery that operate by two distinct novel mechanisms. The first machinery operates by dynamic allosteric effect that leads to an increasing liberation of catalyst into solution the higher the rate of machine motion.[1] In the second example, product inhibition is increasingly reduced at augmented machine speed.[2] The complete mechanism of action in both catalytic machinery has been clarified by a variety of physical organic methods, including VT-NMR to determine the machine speed, evaluation of the catalytic rate at zero conversion (v_0), binding constants, speciation analysis and product liberation studies.

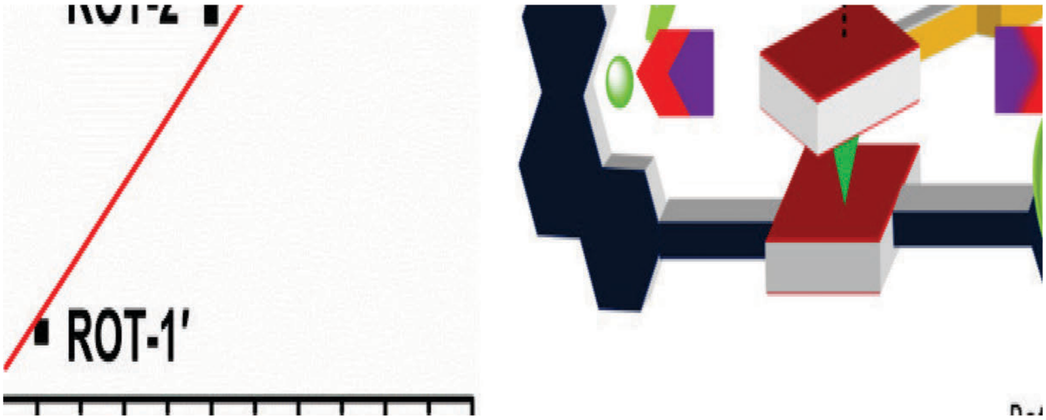

Figure 1. Cartoon representation of the multicomponent catalytic machinery that increases conversion due to reduction of product inhibition at higher machine speed.

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OP-2

EXPLORING PHOTOREACTIONS POTENTIALLY TRIGGERED BY EXCITED STATE ANTIAROMATICITY RELIEF

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Baird's rule tells that the electron counts for aromaticity and antiaromaticity in the first ππ* triplet excited state (T_1) of simple annulenes are opposite to those in the ground state (S_0),[1] and it has been shown that the rule also extends to the lowest singlet excited state (S_1).[2,3] Motivated by this aromaticity/antiaromaticity switch we earlier labelled benzene as a molecular "Dr. Jekyll and Mr. Hyde".[4] Now, to what extent is photoreactivity of S_0 state aromatic molecules triggered by relief of excited state antiaromaticity?

We recently showed in a combined experimental and computational study of cyclopropyl (cPr) substituted annulenes that the aptitude for cPr ring-opening in the T_1 state is strongly linked to the number of π-electrons of the annulene.[5] T_1 state antiaromaticity in 6π-electron (hetero)cycles lowers the activation energy for cPr ring-opening by 3–8 kcal/mol when compared to cases with the cPr group attached to π-conjugated, yet, T_1 nonaromatic cycles. We will now present results revealing to what extent excited state antiaromaticity relief triggeres various photoreactions that progress in the S_1 state instead of the T_1 state. Particular focus will be given to the photorearrangement of benzene to benzvalene and the photochemical formation of substituted bicyclo[3.1.0]hex-2-enes in protic nucleophilic media. In this context, we will also discuss the potential involvement of structures influenced by excited state homoaromaticity.[6]

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OP-3

SHORT-LIVED INTERMEDIATES DERIVED FROM *SYM*-TRIAZINES: STRUCTURE, THERMODYNAMIC PROPERTIES AND REACTIVITY

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Sym-triazines show extended π-electron delocalization ranging over adjacent substituents in positions 2, 4 and 6. *Sym*-Triazines are widely used as systemic herbicides (inhibit photosynthesis), and as dyes (their planarity being determinant to their dying properties). Melamine {1,3,5-Triazine-2,4,6-triamine} has potential as a supramolecular synthon, due to both its ease to establish extended hydrogen bond networks. We have previously studied different aspects of *sym*-triazines chemistry.[1–3]

We report on the neutral and singly charged radical species derived from *sym*-triazine (**1**): 2,4-diamino-(1,3,5)-triazine (**2**), atrazine {N-ethyl-N'-isopropyl-6-chloro-1,3,5-triazine} (**3**), atraton {N-ethyl-N'-isopropyl-6-methoxy-1,3,5-triazine} (**4**) and ametryne {N-ethyl-N'-isopropyl-6-methylthio-1,3,5-triazine} (**5**). From laser flash photolysis and pulse radiolysis experiments, we report on the spectra of radical cations and radical anions, and of the lowest triplet state, their ionization threshold, the reduction potential for the radical cation ($E^{o}(T^{\bullet +}/T)$), and radical anion ($E^{o}(T/T^{\bullet -})$), the pKa of the radical anion, as well as kinetic information and linear free energy relationships showing inductive and steric effects for one-e^- oxidation and one-e^- reduction. From DFT, we report optimised geometries of neutral and singly charged radicals, and show that the triazine ring and exo -NR_2 groups in (**1**)–(**5**) tend to be planar in radical cations, whilst for radical anions only (**5**) shows an important conformational change in the exo groups. We also report computed vertical and adiabatic ionization potentials (VIP, AIP) and electron affinities (EA) for (**1**)–(**5**). Reduction potentials of the radical cations ($E0(T^{\bullet +}/T)$), and radical anions ($E0(T/T^{\bullet -})$) have been computed, as well as pKa's for the radical anions.

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OP-4

SYNTHESIS AND PROPERTIES OF NOVEL CYCLIC π-CONJUGATED MOLECULES

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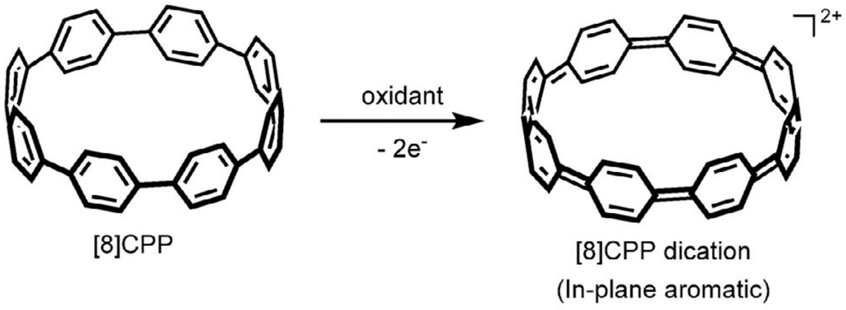
Cyclic π-conjugated molecules have attracted significant attention due to their unique molecular structures, distinct properties, and potential application in materials science and technology. In particular, cycloparaphenylenes (CPPs), which possess the simplest cyclic structural unit of armchair carbon nanotubes have received considerable attention because of their availability by bottom-up organic synthesis.[1] In this presentation, I will report on our endeavor for synthesizing novel cyclic π-conjugated molecules[2] and their physical properties, in particular, generation and properties of the oxidized foam of CPPs and their derivatives (Scheme 1).[3]



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

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OP-5

HYDRIDE AFFINITIES OF CATIONIC MAIN GROUP-ELEMENT HYDRIDES

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The hydride ion, H^-, is the simplest Lewis base and it plays an important role in numerous chemical and biological processes.[1–3] The thermodynamic quantity that characterizes the stability and reactivity for these processes is the hydride affinity (HA), which is defined as the enthalpy change associated with the heterolytic dissociation of the complex between the hydride ion and the Lewis acid (here XH_{n-1}^+):

$$XH_n \rightarrow XH_{n-1}^+ + H^- \qquad \Delta H = \mathrm{HA} \qquad (1)$$

We have systematically computed the HAs in gas phase of archetypical anionic bases across the periodic table using relativistic density functional theory (DFT) at ZORA-BP86/QZ4P [4]. We established a consistent set of values of the 298-K hydride affinities of all cationic maingroup-element hydrides (XH_{n-1}^+) in which we have varied the central atom X along groups 14–17 and periods 2–6. The main purpose of this study is to get insight into the underlying physical features behind the periodical HA trends by using Kohn-Sham molecular orbital (MO) theory together with a quantitative bond energy decomposition analysis (EDA).[5] The orbital interaction, or more specifically, the HOMO-LUMO energy gap, nicely determines the trend in hydride affinities across the periodic table.

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OP-6

1,3-DIPOLAR CYLOADDITION REACTIVITY OF ALKYNES

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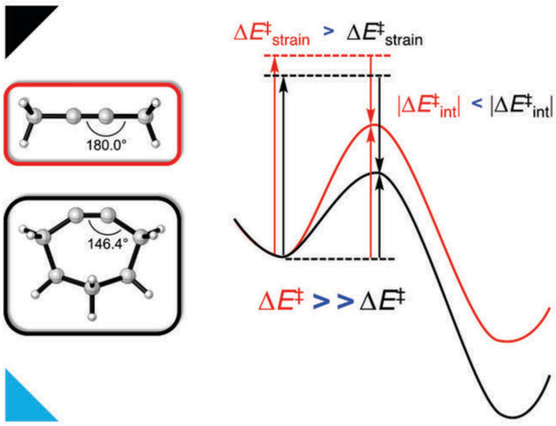

The 1,3-dipolar cycloaddition reactivities of acyclic and cycloalkynes were evaluated using density functional theory (DFT) calculations.[1] Computed activation free energies for the cycloadditions of the acyclic alkyne (2-butyne) are 16-22 kcal mol^{-1} higher in energy than for the cyclic alkynes. The strained, or pre-distorted nature of cycloalkynes is often solely used to rationalize this significant rate enhancement. Activation strain and bonding analyses have revealed, for the first time, that the degree of the geometrical pre-distortion of the cycloalkyne ground state geometries acts to enhance reactivity compared to acyclic alkynes via three distinct mechanisms: not only due to (i) a reduced strain energy; but also to (ii) a smaller HOMO–LUMO gap; and (iii) an enhanced orbital overlap, which both contribute to a more stabilizing orbital interactions.

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OP-7

DECODING THE MECHANISM OF ENVIRONMENTAL POLYMER DEGRADATION: A MASS SPECTROMETRIC APPROACH

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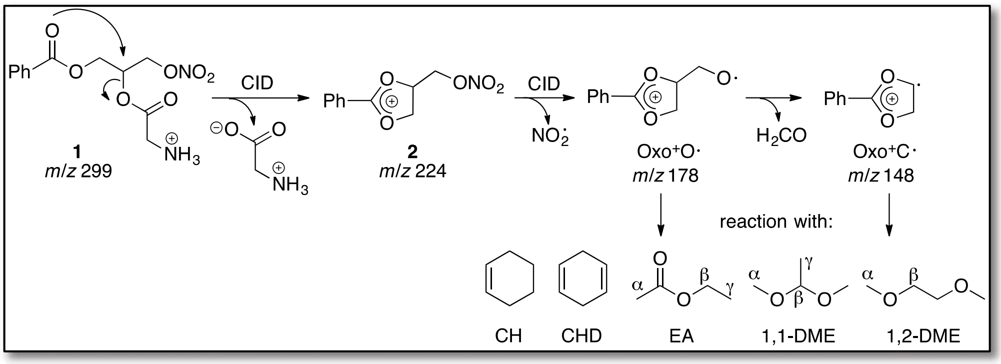
Synthetic polymers are amongst the most widely used materials due to their extremely diverse properties. Unfortunately, exposure of polymers to environmental conditions, in particular UV radiation and humidity, leads to dramatic changes of their properties, resulting in decreased service life and limited usage. The most important degradation pathways in polymers proceed through radical steps. Key-intermediates are polymer-derived peroxyl radicals, $ROO^{\bullet}$, which act as carrier in a radical chain process that propagates damage through hydrogen abstraction from a neighboring polymer strand.

We have recently demonstrated that $ROO^{\bullet}$ reactions with polyester model systems can be explored on the millisecond time scale by mass spectrometry using the distonic radical ion approach.[1] This study revealed clear deficiencies in our understanding of $ROO^{\bullet}$ chemistry and suggests that the current mechanistic model for radical polymer degradation is by far not complete. In particular, the role of *C*- and *O*-centred radicals (other than $ROO^{\bullet}$) in the degradation process requires further investigation.[2] We have designed novel precursors of type **1** to generate distonic radical ions of type $Oxo^{+}O^{\bullet}$ and $Oxo^{+}C^{\bullet}$, which were reacted with a series of small model systems featuring typical substructures in polyesters (alkenes, esters, acetals, amines, etc.). Product and kinetic studies, in combination with computational methods, were employed to elucidate the mechanism of these reactions.[3]



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MOLECULE-INDUCED RADICAL FORMATION WITH PEROXIDES

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O–O Bond homolysis in (hydro)peroxides is commonly believed to represent an important initiation pathway in autoxidation reactions, where the O-centered radicals formed in the homolysis step are subsequently involved in hydrogen abstraction reactions from substrate hydrocarbons. Using quantum chemically calculated and experimentally available thermochemical data we show that a combined "Molecule-Induced Radical Formation (MIRF)" process integrating both reactions into a single elementary step is highly competitive.[1] Moreover, we also show for selected classes of hydrocarbons that reaction barriers for MIRF processes are lower than those for classical O–O bond dissociation reactions.[2,3]

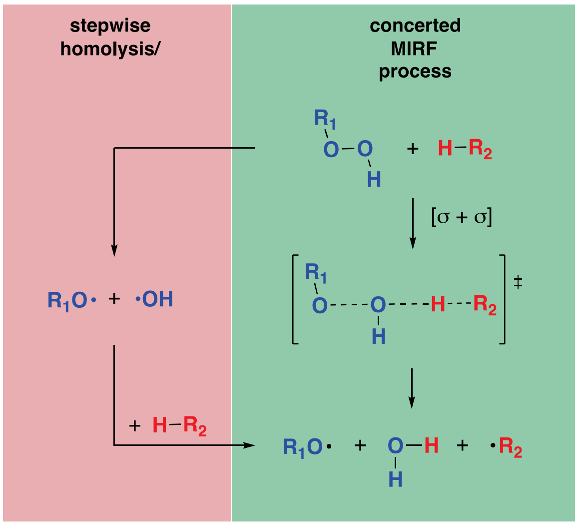

Figure 1: Competition between stepwise O-O bond homolysis and concerted MIRF pathways in the decomposition of peroxides.

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OP-9

BAY QUINONES – ELECTRONIC PROPERTIES AND STABILITY

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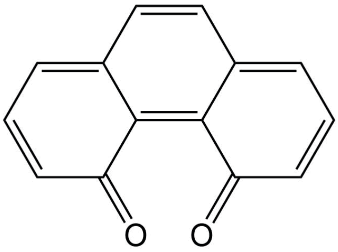
Bay quinones have carbonyl groups pointing into the congested space of a bay region of their hydrocarbon skeleton. The parent bay quinone, phenanthrene-4,5-quinone **1**, has never been synthesized, in spite of several attempts.[1–3] In this contribution, we report on our experiments aimed at generating **1** via low temperature electrochemical synthesis and matrix isolation spectroscopy. We will also report on the electrochemical synthesis of the larger homologue violanthrone-16,17-quinone **2**, and on the results of quantum chemical calculations revealing structure-property relationships in this little-explored class of compounds. Very low-lying, thermally populated triplet excited states were found to be a factor contributing to the very limited stability of **1** and derivatives.



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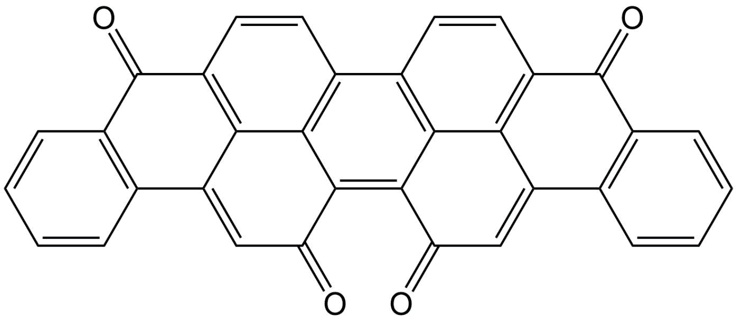

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OP-10

1, 3-H-SHIFT – A NEW ROUTE TO STATIC BICYCLOBUTONIUM IONS FURTHER ANSWERS TO THE CONUNDRUM OF THE STRUCTURE OF $C_4H_7^+$ CATIONS

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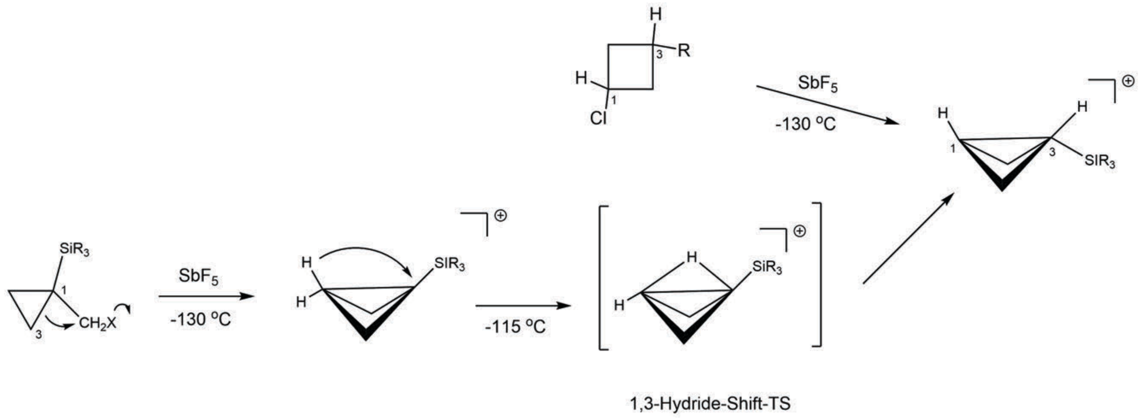
The cyclobutyl/cyclopropylmethyl cation system $(C_4H_7)^+$ has most likely been the focus of more studies than any other carbocation system except the 2-norbornyl cation. Over a timespan of more than half a century practically all the tools of experimental physical organic chemistry and numerous computational methods have been utilized to shed light on the structure and dynamics of these type of carbocations. The current consensus for the parent $C_4H_7^+$ cation seems to be that two isomeric structures each threefold degenerate and of nearly equal stability equilibrate on a very flat potential energy surface. The fast interconversion prevented a straightforward structural assignment in solution.

Recently we have shown that **static** substituted bicyclobutonium cations can be generated using appropriate silyl-substituted cyclobutyl precursors.

We now describe a new pathway to generate static 3-silyl substituted bicyclobutonium cations via 1,3-Hydride shift.



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OP-11

HEAVY ATOM TUNNELING, MATRIX EFFECT, AND WAVELENGTH EFFECT IN THE PHOTOREACTION OF 2,3-DIAZABICYCLO[2.2.1]HEPT-2-ENE

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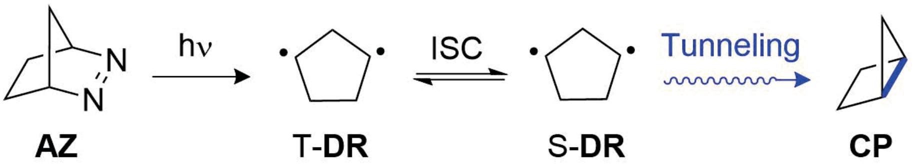
Quantum mechanical tunneling (QMT), recognized as an important phenomenon in chemical reactions, had been studied from mechanistic, kinetic, and theoretical point of view. Hydrogen atom tunneling has been observed in a wide range of chemical reactions in chemistry and biology. Tunneling probability is inversely proportional to the mass of the tunneling particle. Therefore, tunneling reactions involving heavy atoms like carbon (12 times heavier than hydrogen) are rare.

In 1975 and 1979, Buchwalter and Closs directly detected triplet diradical T-**DR** via photolysis of precursor **AZ** and they suggested quantum mechanical tunneling in the decay process of T-**DR**.[1,2] However, the tunneling reaction and product formed after decay of the T-**DR** were not directly characterized. We used low temperature EPR and matrix isolation IR spectroscopy and theoretical calculations to clarify the rate, mechanism, and tunneling process of triplet diradical T-**DR**. Experimental results showed evidence for heavy atom (carbon) tunneling for the formation **CP** from T-**DR** via S-**DR**. The product **CP** formed in the tunneling process was directly characterized using low temperature IR spectroscopy in Ar matrix. We also observed wavelength dependent product distribution in the photolysis of **AZ** at 7 K in Ar matrix. A prominent matrix effect was found as T-**DR** decayed with different rate constants in Ar, glassy 2-methyltetrahydrofuran, and glassy 3-methylpentane matrix.



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OP-12

APPLYING PHYSICAL ORGANIC PROCESSES TO FORMULATION CHEMICAL STABILITY

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Formulation chemical stability is of great importance due to strict criteria, less than a 5% loss in Active Ingredient (AI) after two years at ambient storage is required for regulatory approval even before efficacy considerations are regarded. Whilst simple storage tests can identify where issues lie, supplementary factors such as climate variations in different global positions in the supply chain are often not considered. This talk aims to describe the basic approach taken to increase the understanding of chemical stability in our formulations, by applying Physical Organic principles to model the loss of AI in varying conditions. This ranges from simple solubility and kinetic measurements in the system of interest to more invested approaches such as studying non-aqueous pKa's, photocatalysed decompositions and co-crystals.

The use of case studies to exemplify the approach will detail how whilst we vastly increase the understanding of our formulations, unexpected observations can still occur requiring further investigations to extend our understanding.

OP-13

CHEMO-ENZYMATIC PREPARATION OF NUCLEOSIDE TRIPHOSPHATES FROM DIPHOSPHATES USING FEEDSTOCK CHEMICALS

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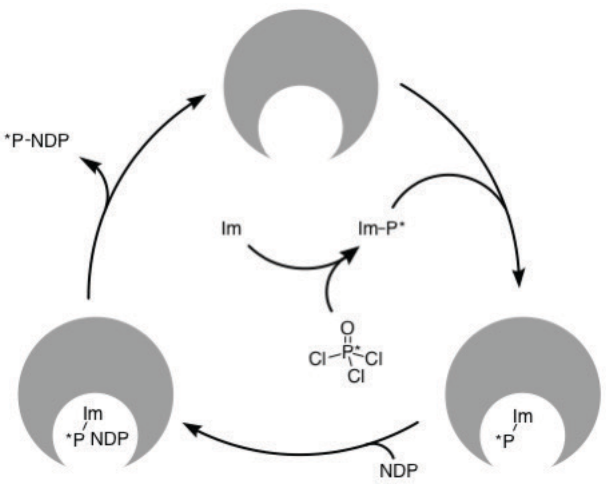

We have used a His→Gly active site mutant of nucleoside diphosphate kinase (NDPK) to prepare nucleoside 5'-triphosphates (NTPs). WT NDPK operates via a ping-pong mechanism where the active site His is phosphorylated by ATP to afford ADP and phosphoryl-enzyme in the 'ping' step. The phosphoryl-enzyme then dispatches the phosphoryl group to a substrate NDP in the 'pong' step. Herschlag and co-workers [1] showed that a His→Gly mutant could successfully *dephosphorylate* ATP using imidazole to 'rescue' the activity that was lost through the mutagenesis of the His residue. In light of the Principle of Microscopic Reversibility, we reasoned that it should be possible to *phosphorylate* NDPs using *N*-phosphoryl-imidazole as the source of the phosphoryl group with His→Gly mutant NDPK as catalyst. We employed our aqueous approach for the phosphorylation of amines to readily and rapidly produce phosphoryl-imidazole from $POCl_3$. We have shown that NTPs are produced rapidly with high conversion levels from these inexpensive precursors. We have shown that mutant NDPK and *N*-phosphoryl-imidazole can be used in combination with another ATP-consuming enzyme, thus illustrating the possibility of using *N*-phosphoryl-imidazole to regenerate (costly) ATP in biocatalytic systems.

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OP-14

APPLICATION OF ADAMANTYL AMINOGUANIDINES IN FUNCTIONAL SELF-ASSEMBLED NANOVESICLES

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Combination of a lipophilic adamantyl subunit and a highly polar guanidine moiety affords adamantyl aminoguanidines, compounds with membrane compatible features capable of binding to complementary molecules possessing phosphate groups.[1] We recently showed that adamantyl aminoguanidines can effectively be incorporated into liposomes and the resulting liposome formulations were capable of recognizing complementary liposomes.[2] We therefore turned out attention to preparing multicomponent self-assembled supramolecular nanovesicles capable of recognition and binding to fluorescently labelled DNA.[3] Our findings suggest that such nanovesicles (Figure 1) could potentially be applied as nonviral gene delivery vectors.

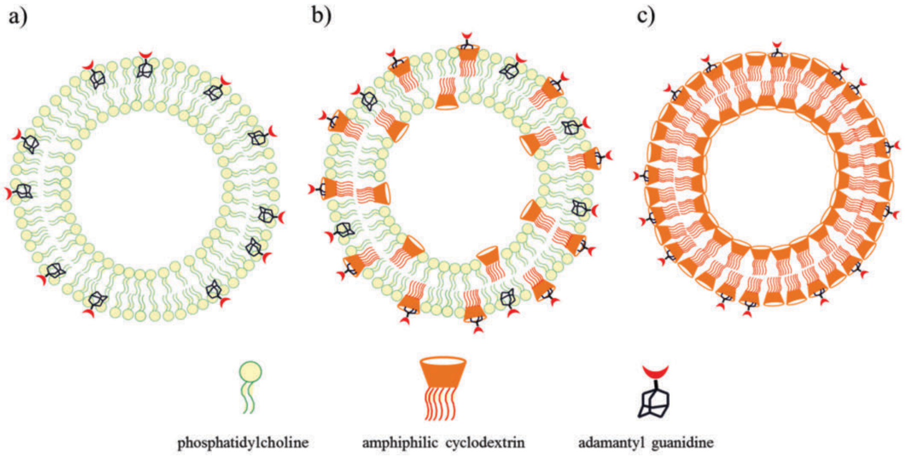

Figure 1. Schematic representation of the prepared functional supramolecular systems consisting of adamantyl aminoguanidines and different liposomes and vesicles.

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OP-15

SUPRAMOLECULAR COMPOUNDS FORMED BY ORGANIC PHOTOCHROMES AND METAL-ORGANIC COORDINATION POLYMER

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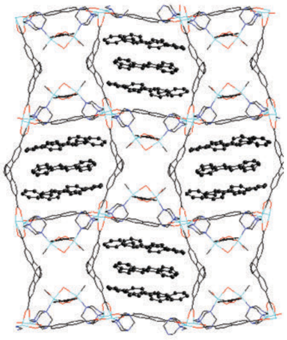

Figure 1. Fragment of Adduct-1 structure. Wire presentation. View along a axis. H atoms are omitted for clarity.

Organic photochromic compounds in the solid state are of great interest for modern microelectronics. In the solid state, photochromes are more stable, since side reactions associated with the solvent lead to photodegradation. Our idea is to incorporate a photochrome into the cavity of a metal-organic framework (MOF). We hope that such systems would have higher quantum yields and would be more resistant to photodegradation.

For the synthesis of hybrid materials we used the MOF $[Zn_4(dmf)(ur)_2(ndc)_4]\cdot 5DMF\cdot H_2O$ (ndc^{2-} is 2,6-naphtalenedicarboxylate, ur is urotropin, and dmf is N,N'-dimethylformamide) with the size of channels 10.5×10.5 Å, and two photochromes - *trans*-stilbene[1] and diarylethene 2,3-bis-(2,5-dimethylthiophen-3-yl-cyclopent-2-en-1-one (DMTC).[2] The composition of Adduct 1 (*trans*-stilbene + MOF) was 1:3 (Figure 1). Adduct 1 exhibits photochemical activity. The composition of Adduct-2 (DMTC + MOF) was 1:1. Adduct 2 exhibited photo chromic reactions typical for diarylethenes.

Therefore, incorporation of organic photochromes into the MOF seems to be a promising approach for creating hybrid materials.

Acknowledgement. The work was supported by the Russian Foundation of Basic research (grant № 18-03-00161).

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OP-16

HOST BEHAVIOUR OF *N,N′*-BIS(9-PHENYL-9-THIOXANTHENYL)ETHYLENEDIAMINE IN THE PRESENCE OF AROMATIC AND ALIPHATIC FIVE-MEMBERED HETEROCYCLIC GUEST COMPOUNDS

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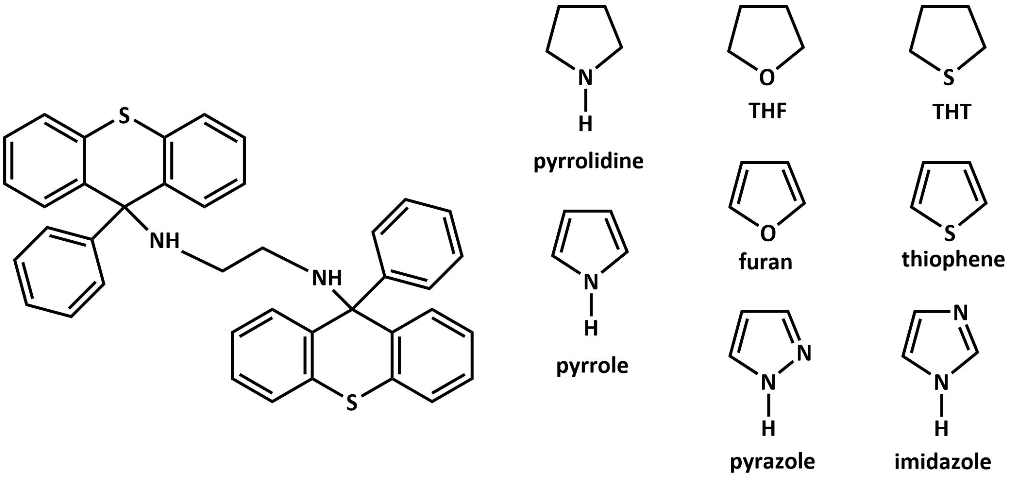
This work describes the host ability of the crystalline compound *N,N′*-bis(9-phenyl-9-thioxanthenyl)-ethylenediamine **1**[1] in the presence of eight five-membered ring heterocyclics, namely saturated tetrahydrofuran (THF), tetrahydrothiophene (THT) and pyrrolidine, and aromatic equivalents furan, thiophene and pyrrole and, additionally, imidazole and pyrazole (Scheme 1).



Scheme 1. Structures of host compound *N,N′*-bis(9-phenyl-9-thioxanthenyl)ethylenediamine **1** and the eight potential five-membered ring guest compounds

Host **1** clathrated all six mono-heteroatomic guests, while complexes were not formed with imidazole and pyrazole. Specifically designed guest/guest competition experiments revealed that **1** preferred the saturated heterocyclics relative to the aromatics, and also the sulfur-containing guests (in both saturated and aromatic series') followed by oxygen and nitrogen (S > O > N). The affinity of the host for the saturated guests was explained by means of a consideration of the applicable host−guest interactions (obtained from single crystal diffraction analyses), where these guests were observed to experience a greater variety and number of these interaction types relative to the aromatic guests. The host selectivity order for the various heteroatoms (S > O > N) was clarified unfailingly when investigating, quantitatively, the percentage of the guest heteroatom−host interactions in each complex by means of Hirshfeld surface analyses. Finally, thermal experiments carried out on all six inclusion compounds provided further illumination for some of the observations made from the competition experiments.

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OP-17

SUBSTITUENT EFFECTS ON THE PHOTOCHEMISTRY OF 5-AMINOTETRAZOLES

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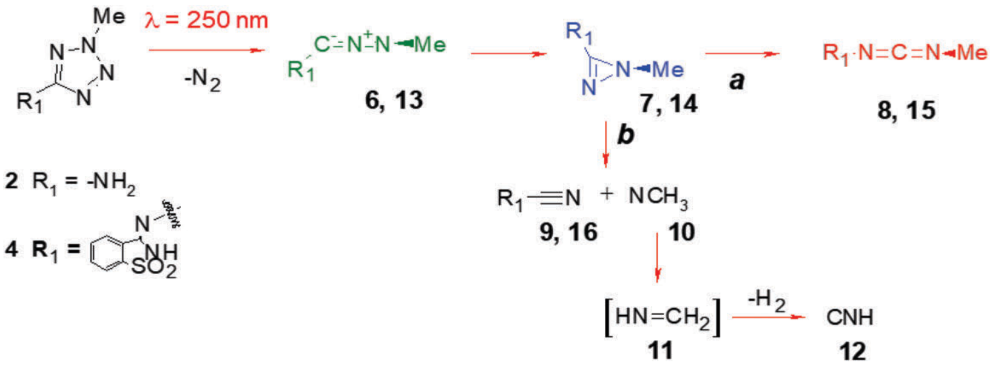
The applications of 2-methyl-(2*H*)-tetrazole-5-amino-saccharinate (**4**; Scheme 1) in catalysis and chelant-based chemotherapy stimulated investigations on its photostability.[1a] The photochemistry of **4** in solid argon (15 K) was compared with those of 2-methyl-(2*H*)-tetrazole-5-amine (**2**) and 1-methyl-(2*H*)-tetrazole-5-amine.[1b] Compounds were subjected to *in situ* narrowband UV-irradiation at different wavelengths. Reactions were followed by infrared spectroscopy, supported by B3LYP/6-311++G(d,p) calculations. Photochemical pathways for **2** and **4** proved similar but photodegradation of **4** was 20x slower, unraveling the photo-stabilizing effect of the saccharyl moiety that extends into the nitrilimine **6**, formed from **4**, and its antiaromatic 1*H*-diazirene isomer **7**, which proved photostable at 290 nm, unlike the 1*H*-diazirene **14**, formed from **2**. Analysis of the photochemistry of **2**/**4** (250 nm), including energy trends calculated for the isomeric $C_2H_5N_3$ species postulated/observed from photolysis and EPR results, enabled a deeper insight into the photodegradation mechanisms of 2,5-substituted tetrazoles. We postulate a pivotal singlet state imidoylnitrene species as common intermediate, which undergoes a Wolff-type isomerization to a stable carbodiimide (**8**, **15**; Scheme 1).[2]



Scheme 1.

Acknowledgements. The authors gratefully acknowledge Fundação para a Ciência e a Tecnologia (FCT) Portugal, QREN-COMPETE-UE and FEDER/COMPETE 2020-EU for financial support (Projects UID/MULTI/04326/2019 – CCMAR; PEst-OE/QUI/UI0313/2014 –CQC; PTDC/EEI-AUT/5442/2014 - INNOVATE; PTDC/QEQ-QFI/3284/2014 – POCI-01-0145-FEDER-016617).

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OP-18

REACTIVITIES OF ELECTROPHILIC ALKYNES AND ALLENES

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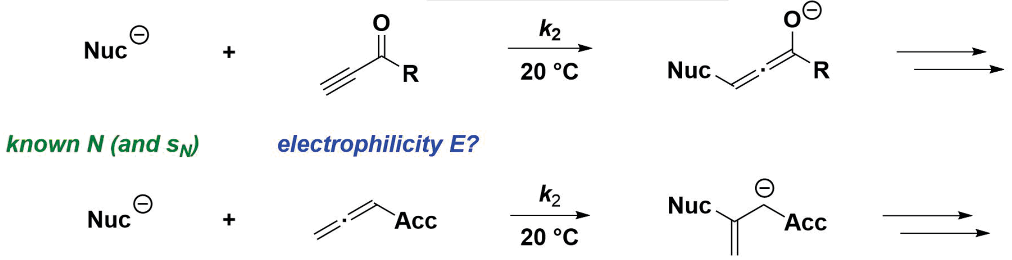
Michael additions belong to the most important C–C-bond-forming reactions in organic chemistry. The electrophilicities of prototypical Michael acceptors, such as alkyl acrylates, acrylonitrile or vinyl ketones, have recently been studied in DMSO by following the kinetics of their reactions with carbon-centered nucleophiles. Analyzing the second-order rate constants for these Michael additions by the correlation equation (1) provided an electrophilicity ranking for classical Michael acceptors.[1]

We have now set out to study the kinetics of the reactions of alkynones, alkyl propiolates, and alkyl allenoates with nucleophiles of known nucleophilicity N (and s_N) to characterize the synthetic potential of Michael acceptors with sp-centered reactive sites. Integration of electron-deficient alkynes and allenes into the Mayr reactivity scales[2,3] allows to compare their electrophilicities E with those of more than 300 structurally diverse electrophiles and provides a semi-quantitative fundament for understanding their prominent role as substrates in nucleophile-catalyzed cycloaddition reactions.[4]

$$\boxed{\lg k(20°\mathrm{C}) = s_N(N + E) \quad (1)}$$



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OP-19

SILACYCLOHEXANES: CONFORMATIONAL PREFERENCES IN GAS AND SOLUTION

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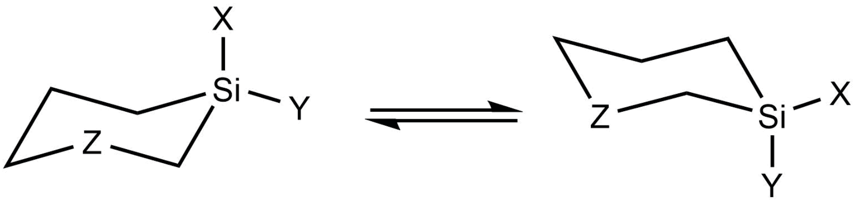
Conformational preferences of silacyclohexanes possessing different substituents at silicon, as well as of their heteroanalogues with N, O, S atoms in the ring will be outlined including recent theoretical and experimental research in gas and solution. The reasons of principal differences between the title compounds and their carbon analogues are established; the main factor is the decisive role of the bulkiness of the substituent at carbon, which can often be neglected for the substituents at silicon, and the dominant role of electrostatic effects in silacyclohexanes, which is a very subordinate effect in cyclohexanes.

Two other discriminating factors are (i) much lower conformational energies (*A*) of the substituents at silicon resulting in appearance or even predominance of the axial conformers and (ii) much lower barriers to ring inversion in silacyclohexanes as compared to those in cyclohexanes, piperidines, tetrahydropyranes or thianes, that makes the title compounds conformationally very flexible. Specific role is played also by stereoelectronic interactions of heteroatoms in the ring with highly polar Si–X bonds, especially for electronegative groups X. All these issues will be discussed in the lecture summarizing research up to 2019.



X, Y = H, Me, Ph, F, Cl, Br, OR, CN;
Z = CH_2, NR, O, S.

OP-20

AMBIDENT REACTIVITY OF PHENOLATE ANIONS REVISITED: A QUANTITATIVE APPROACH TO PHENOLATE REACTIVITIES

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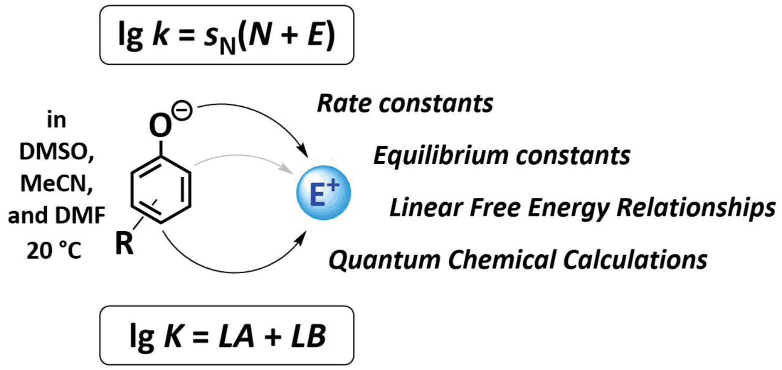
Phenolate ions are ambident nucleophiles, which may react with electrophiles either at oxygen or at carbon. Prompted by the observation that the regioselectivities of their reactions with electrophiles are exactly the opposite to the predictions by the HSAB principle,[1] a comprehensive experimental and computational investigation of phenolate reactivities was performed. By studying rate and equilibrium constants for the reactions of phenolate ions with benzhydrylium ions and related quinone methides in various solvents, the nucleophilicity and Lewis basicity for oxygen-attack as well as the nucleophilicity of carbon attack could be determined. Thus, a series of phenolate ions could be integrated into established reactivity scales.[2]



Except for diffusion limited reactions, O-attack of phenolates is strongly favored under kinetically controlled conditions whereas C-attack is strongly favored under thermodynamically controlled conditions. Product ratios are rationalized by a combination of kinetic and thermodynamic parameters of the phenolates and their electrophilic reaction partners. Furthermore, electrochemical data[3] reveal that the reactions of phenolates with carbocations proceed via polar mechanisms.

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OP-21

COMPUTATIONAL SIMULATION OF ENERGY LANDSCAPES AND ISOTOPE EFFECTS FOR GLYCOSIDIC REACTIVITY

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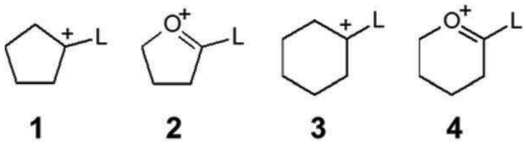
Kinetic isotope effects (KIEs) offer powerful probes for mechanism and transition-state (TS) structure in enzyme-catalyzed reactions, as long as their experimentally determined values and variations can be correctly interpreted. It is common for analyses of TS structure, based upon KIEs for multiple isotopic substitutions, to consider force-constant changes only as functions of molecular geometry. However, work in our group suggests that consideration of the electrostatic environment is also necessary, as force-constant changes can depend on the relative permittivity of the medium. If so, there would be important implications for the interpretation of experimental KIEs in mechanistic enzymology.[1,2]

The use of both implicit (polarized continuum model) and explicit (hybrid QM/MM) treatments of solvation with DFT calculations is considered critically for equilibrium isotope effects upon transfer of some carbocations (cyclopentyl **1**, tetrahydrofuranyl **2**, cyclohexyl **3** and tetrahydropyranyl **4**) from water to cyclohexane, mimicking the change from a polar aqueous environment to an extreme non-polar enzyme active site.



1D scans of potential and free energy for cleavage of the glycosidic bond in 2-(p-nitrophenoxy)tetrahydropyran do not show a TS. A 2D free-energy surface that considers also the distance between C_α and a nucleophilic water indicates a pre-association $D_N{*}A_{Nint}{\ddagger}$ (S_N2 intermediate) mechanism with a TS involving nucleophilic attack upon an ion-pair intermediate, and this is supported by good agreement between the mean values of the calculated and experimental α-D KIEs. This work outlines our efforts to accurately calculate the isotope effects, including the effects of the electrostatic environment on the reactant and transition states, for the hydrolysis of. Both QM and QM/MM molecular dynamics techniques have been used.

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OP-22

COMPUTATIONAL STUDY OF SUBSTITUENT EFFECTS ON GAS-PHASE STABILITIES OF 1-PHENYLCYCLOBUTANE-1,3-DIYLIUMS

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Yukawa-Tsuno equation ($-\Delta E_X = \rho(\sigma^0 + r^+\Delta\bar{\sigma}_R^+)$) (1) has been widely used for over a half century to analyze substituent effects on stabilities of cations of benzene derivatives, which treat the electronic effects of ring substituents dividing into two terms. The σ^0 substituent constant measures the general electronic effect. The $\Delta\bar{\sigma}_R^+$ measures the additional stabilizing capability by the through-resonance effect for *para* –R groups.

In this study, 1-phenylcyclobutane-1,3-diylium (**1**) and its analogs bringing various functional groups at position 3 were chosen, and their substituent effects on gas-phase stabilities were analyzed to reexamine eq. 1. Relative gas-phase stabilities (ΔE_X) of these ring-substituted dications were computationally determined using isodesmic reactions with substituted benzene.

In Figure 1, substituent effects of **1** were compared to those of α,α-dimethylbenzyl cations having 90°-fixed dihedral-angle between the cationic side chain and the benzene ring that have been used as a reference system of σ^0.[1] Plots of *meta* EDGs gave an excellent linear correlation. Plots of *para* –R groups deviated upward from the correlation line, showing the larger degree of the through-resonance effect in **1**. Plots of EWGs also deviated upward from the correlation line. This fact implies that the other kind of stabilizing effect is operating on these derivatives. Examinations of substituent effects of all dicationic systems revealed that the three-term extended Yukawa-Tsuno equation ($-\Delta E_X = \rho(\sigma^0 + r^+\Delta\bar{\sigma}_R^+ + s^+\Delta\bar{\sigma}_s^+)$) is necessary to analyze the substituent effects of these dications.

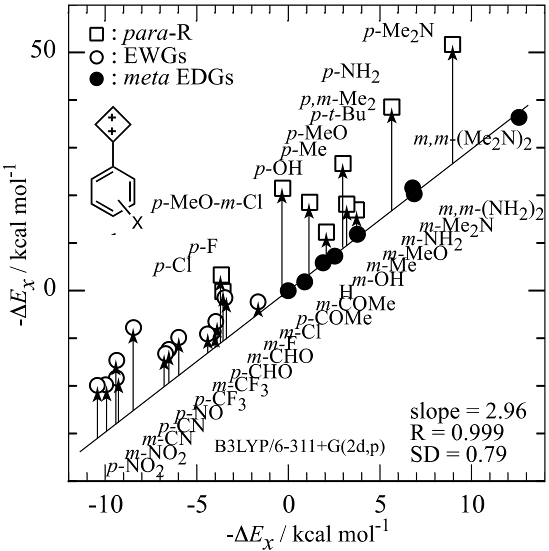

Fig. 1. Comparison of substituent effects.

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OP-23

STRUCTURE–REACTIVITY CORRELATION IN THE REACTION OF MIXED PHOSPHONIUM-IODONIUM YLIDES WITH ACETYLENES

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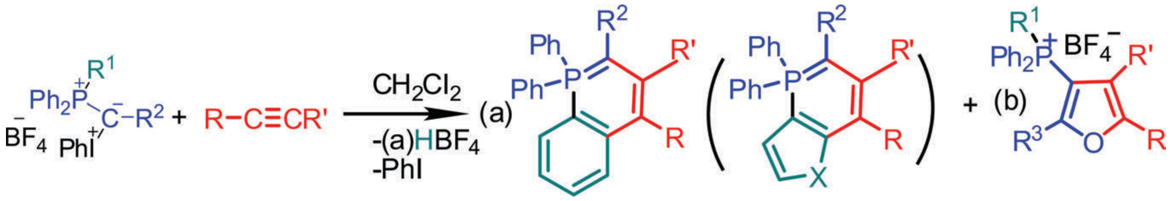
Mixed phosphonium-iodonium ylides **1** (R^1 = Ph or five-membered heterocycle) interact with acetylenes **2** according to Scheme giving either P-containing heterocycles **3** and furan derivatives **4**, when R^2 = C(O)Ph, C(O)OMe and C(O)OEt, or P-containing heterocycles **3**, when R^2 = $PO(OEt)_2$, CN, $S(O)_2(p\text{-}MeC_6H_4)$.[1–3]



1 **2** **3** **4**

In the former case the ratio of the yields for heterocycles **3** and **4** depends on the relationship between the ionizations potential (IP) of an acetylene and the electron affinity of an ylide: for a given ylide the lower IP of the acetylene the higher yield of furan **4**. In both cases the yields of the target heterocycles depend on the ylide structure and the reaction conditions. For certain ylide–acetylene pairs the reaction proceeds only under the action of light, for the others the reaction does not require irradiation. The involvement of radicals in the initiation of the reaction (inhibition with TEMPOL) and in the formation of the products (CIDNP effect) are shown.[4] The mechanism of acid catalysis is established.[5]

In this presentation the reaction mechanism will be discussed with special attention being drawn on the role of the structure of both reactants on the yield of the target heterocycles.

Acknowledgement. This study is supported by the RF State Program no. 1201253303.

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OP-24

PREDICTING THE EFFECTS OF SOLVENT MIXTURES ON THE KEMP REACTIONS

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Reaction rates and selectivity can vary dramatically with choice of solvent.[1] Hence, understanding and being able to predict the effects that solvents have on reactivity is important as it allows for easier solvent choice and gives the ability to select the 'best' solvent for a given purpose. These solvent effects are typically explained using empirical descriptions of polarity, or measures of the interactions of the solvent, though not all effects can be rationalised.[1] Rather less studied are the effects of solvent mixtures, which increases the number of potential solvent choices exponentially.

We have been exploring the solvent-solute interactions that affect the reactivity of the Kemp reactions (Scheme 1)[2,3] using an electrostatic solvent competition model based on supramolecular interactions.[4] The hydrogen-bond donating (α) and accepting ability (β) of the solvents are used to understand and predict the rate constants for the reactions shown below in mixtures of chloroform and alcohols (ethanol and trifluoroethanol).

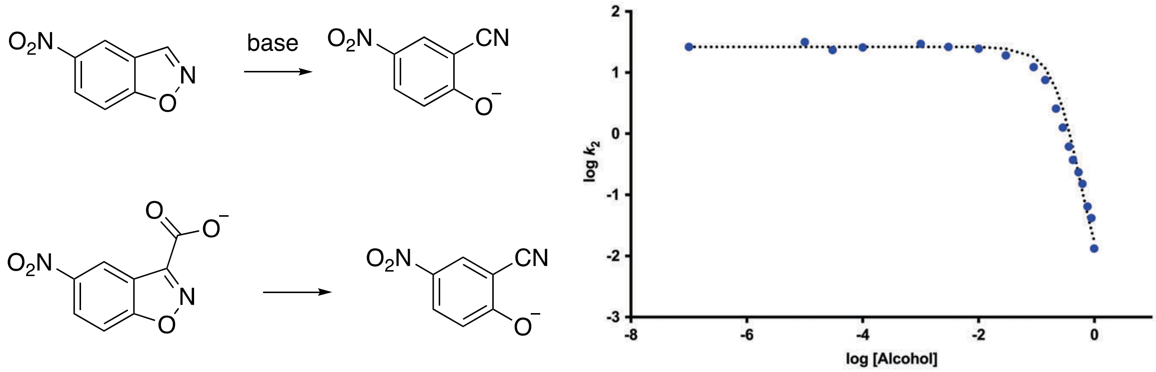

Figure 1. The Kemp elimination of 5-nitro-1,2-benzisoxazole (top-left) and the Kemp decarboxylation of
5-nitro-1,2-benzisoxazole-3-carboxylate (bottom-left), which have been examined in organic solvent mixtures and the dependence of the bimolecular rate constant on the proportion of chloroform and ethanol (right) in the elimination reaction mixture.

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OP-25

A DFT COMPARATIVE STUDY OF SUBSTITUENT EFFECTS IN RADICALS, CATIONS AND RADICAL CATIONS

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In contrast to organic radical centers where both electron donating and withdrawing groups are usually stabilizing, substituent effects are varied in charged intermediates such as cations and anions. Hence it is interesting to consider the effect that substituents exert in open shell systems which are also charged, i.e. radical cations and radical anions.

We describe a DFT computational study where substituent effects in such intermediates as they occur in ethylene and benzene and derivatives are quantified in terms of stabilisation energies obtained through the application of isodesmic equations. Charge and spin distributions in the various species are also examined.

It has previously been shown that cyclisation reactions of alkenyl and aryl alkanols can occur via complementary mechanisms involving either alkoxyl radical or alkenyl and aryl radical cation intermediates.[1] The implications of the current theoretical study for reactivity and regioselectivity in such systems are discussed.

The calculations have employed the global hybrid generalized gradient approximation (GH-GGA) functional, B3LYP, as well as two of the more recent range separated generalised gradient approximation (RSH-GGA) hybrid functionals, ωB97X-D and ωB97X-V, both of which incorporate additional features to account for dispersive interactions.[2] The large 6-311+G(2DF,2P) basis set that contains diffuse and polarization functions for all the elements involved was employed in all calculations.

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OP-26

MECHANISM OF REDUCTION OF AIR POLLUTANTS ON CARBONS: SULFUR DIOXIDE AND OZONE

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Sulfur dioxide, ozone and nitrogen dioxide are air pollutants of the environment that cause acid rain and interfere with human health. The solid-gas kinetics were studied in a flow system with a tubular reactor under differential and steady state conditions. The reduction of XO_2 on carbons proceeds through a common primary mechanism with oxidized and reduced intermediates. The reactivity of the intermediates inserted on carbons (graphite, activated carbon, graphene oxide, carbon nanotubes) modified by SO_2 is selective. Theoretical study of the chemisorption of SO_2 on dehydrogenated pyrene as graphite active site model and computational quantum chemistry calculations, showed that at 900 °C the chemisorption occurs mainly on the diradical zigzag edge through cycloaddition formation of oxidized sulfur intermediates. Tetradehydrogenated-benzo[α]anthracene (TBA) was used as reactive site model of the reduction of SO_2 on graphite. The calculations of the pathways were consistent with the experimental results. Ozonation of graphite showed that the 1,2,3-trioxolane decomposes to an oxyrene, eliminating O_2. Both reactions, the SO_2 and O_3 with graphite, have the same experimental free energy of activation for the decarboxilation reaction. The SO_2 the desulfurization step has a much lower energetic demand than the decarboxylation route. Therefore, the reduction of SO_2 on carbons can occur without increasing the greenhouse effect due to the formation of CO_2.

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POSTER PRESENTATIONS

P-1

KINETIC STUDY ON THE THERMAL *Z-E* ISOMERIZATION OF PHOTOSWITCHABLE N-ACYLHYDRAZONES

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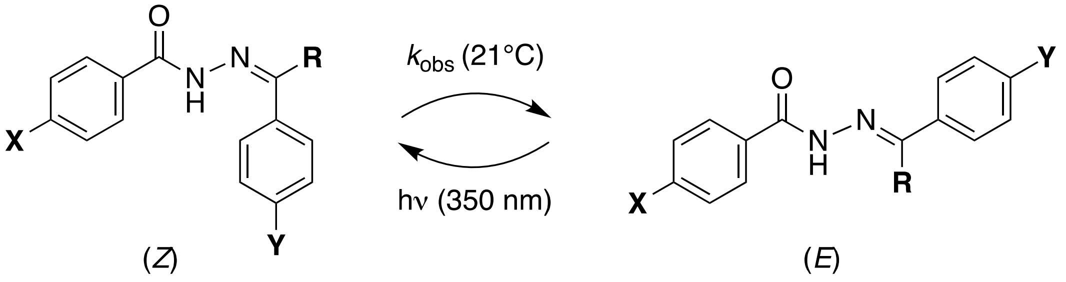
Functional π-conjugated compounds able to undergo reversible changes in double-bond configuration upon exposure to light continue to be the subjects of interest owing to the utility of these materials in the design of biosensors, molecular motors and shuttles, high-density data storage media, and switching elements for microelectronics, for examples.

N-Acylhydrazones, π-conjugated species containing a >N–N=C< moiety, represent a versatile and relatively unexploited class of photochromic material. A thorough understanding of the relationship between their structure, reaction medium and isomerization rates is certainly vital to control and utilize acylhydrazones as photo-responsive materials.

In this contribution, the results of a kinetic study on the thermal *Z*-to-*E* isomerization (in organic solvents) of a series of N-acylhydrazones (Scheme 1) are presented and discussed. Rate constants were measured to assess the effects of varying phenyl ring substituents, imino-C substituents, and solvent polarity.



R = H, CH_3
X, **Y** = OCH_3, H, Br, Cl, CF_3, NO_2

Scheme 1. Structure and isomerization of N-acylhydrazones investigated.

P-2

SIZE-DEPENDENT RATE ACCELERATION IN THE SILYLATION OF SECONDARY ALCOHOLS: THE BIGGER THE FASTER[1]

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The role of attractive dispersion interactions in controlling organic reactions is currently discussed intensely.[2,3] Relative rates for the reaction of secondary alcohols carrying large aromatic moieties with silyl chlorides carrying equally large substituents have therefore been determined by competition experiments in organic solvents. The introduction of big dispersion energy donor (DED) groups in silyl chloride reagents and alcohol substrates enhanced rate constants up to four times (see Figure 1), notably depending on the hydrogen bond donor ability of the solvent. A linear correlation between computed dispersion energy contributions to the stability of the silyl ether products and experimental relative rate constants was found. These results indicate a cooperation between solvophobic effects and DED-groups in the kinetic control of silylation reactions.

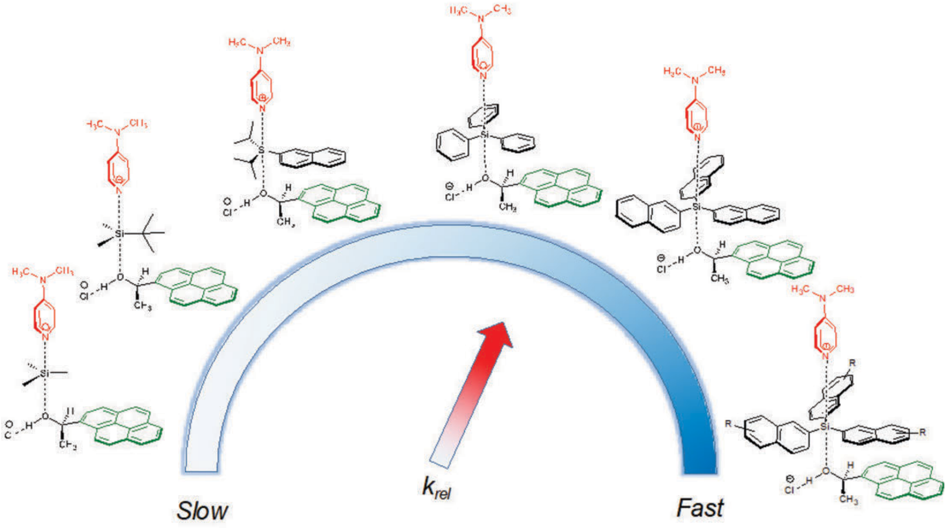

Figure 1: Proposed transition state structures for the silylation reaction in the order of increasing relative reaction rates (left to right).

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P-3

SOLVENTS EFFECTS IN THE FRAGMENTATION OF LIGNOCELLULOSIC BIOMASS

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The replacement of conventional organic solvents (COS) by suitable alternative reaction medium is one of the main concerns nowadays.[1] Alternative green solvents, such as ionic liquids, bio-based and deep eutectic solvents have been proposed as one of the new generations of solvents.

Lignocellulosic biomass is widely recognized as an important renewable resource from which it is possible to produce bioenergy, novel materials, and platform and value-added chemical products. Solvent plays an important role in lignin dissolution, it has been reported that the use of novel and greener solvents in the biomass fractionation process could increase up to 50% the removal of lignin,[2] further allowing for the valorization of fraction such as lignin and hemicelluloses that today are burned for the most part.

This proposal is directed towards developing greener alternative solvents and their aqueous mixtures to solubilize lignocellulosic biomass more efficiently, leading to the isolation of lignin in high yield. Aiming at the optimization of their performance, a systematic study of the structure and composition of the new employed solvents will be carried out. Their efficiency in achieving a cleaner delignification will be evaluated in terms of the yield of recovered lignin and correlated with physical-chemical properties and with solvent parameters (e.g. Kamlet-Taft, Hansen and Hildebrandt solubility parameters, COSMO-RS descriptors), which will provide a rationalization of the observed effects, and become the basis for the design of improved solvents or solvent mixtures.

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SYNTHESIS AND CHARACTERIZATION OF NEW AROMATIC AZODIOXY AND AZO POLYMERS

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Porous organic architectures have attracted much attention in recent years because of their excellent potential in gas storage and separation, catalysis, optoelectronics and sensing. Molecular building blocks of predefined geometry and functionality can associate through covalent bonds into two-dimensional (2D) and three-dimensional (3D) crystalline or amorphous porous materials. Polymerization property of compounds with multiple nitroso groups could be used for design of azodioxy porous materials. Recently, self-polymerization of tetrakis(arylnitroso)porphyrin and compounds with tetrahedrally oriented nitroso groups resulted with formation of 2D and 3D crystalline organic frameworks (COFs), respectively.[1,2] In contrast to aromatic polynitroso compounds, systems with azo functional groups form amorphous covalent organic polymers (COPs) which proved to be beneficial for highly selective gas separations.[3]

In the present work, we prepared new aromatic trinitroso derivative and studied its polymerization features. In addition, we synthesized new azo-linked polymers by Mills reaction of aromatic trinitroso and diamino derivatives and by the coupling of aromatic trinitro and diamino derivatives. Polymers were characterized using IR spectroscopy, powder X-ray diffraction and thermal methods. Trinitroso compound forms crystalline-like *E*-azodioxy polymer in solid state, while azo polymers appear as amorphous solids insoluble in common organic solvent and of very high thermal stability. Azodioxy- and azo-linked polymers were also studied by computational methods. Combination of molecular and quantum-mechanical techniques was used to search a conformational space of the simple model compounds to assess the affinity to form 2D networks and to provide some guidelines for the future design of similar systems.

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P-5

OPPOSING HOST BEHAVIOUR OF TWO ISOSTRUCTURAL APOHOST MATERIALS IN THE PRESENCE OF SELECTED HETEROCYCLIC GUESTS – CRYSTAL DIFFRACTION AND MOLECULAR MODELLING CONSIDERATIONS

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Research in the field of host-guest chemistry has burgeoned in recent years.[1] Host-guest chemistry is a field of study devoted to investigating the synthesis, properties and applications of new and successful host molecules to form inclusion compounds. Inclusion compounds are “complexes” in which one chemical compound, the host, forms a cage, cavity or channel in which another compound, the guest, is located. The two compounds interact to form one new inclusion compound which does not obey the known definition of a complex, as there are no coordinate covalent/ dative bonds that occur between the guest and the host.[2] There exist many applications for host-guest chemistry, making this a very relevant field of study.[3–10] In this work, we compare the host behaviour of two structurally-related compounds, *N*,*N'*-bis(9-phenyl-9-xanthenyl)ethylenediamine and *N*,*N'*-bis(9-phenyl-9-thioxanthenyl)ethylenediamine which, in the absence of guest, shared the same crystal packing, as observed from diffraction experiments. These hosts also performed similarly when recrystallized individually from heterocyclic guests pyridine, morpholine, piperidine and dioxane, clathrating each one. Surprisingly, however, when each host was recrystallized from an equimolar quaternary mixture of these guests, their selectivities were distinctly opposing: the oxygen analogue demonstrated a significant preference *for* dioxane (68%, with only 8% of pyridine found in the so-formed mixed complex), while the sulfur-containing host discriminated inordinately *against* dioxane (12%) in favour of pyridine (57%). The reasons for the opposing host behaviours were explored comprehensively by employing data from both crystal diffraction experiments and molecular mechanics (at the MMFF94 level), with further refinement at the DFT level. Furthermore, thermal analyses revealed that complexes comprising preferred guests possessed increased thermal stabilities. Finally, the two host materials were also made to compete by dissolving equimolar mixtures of these in each of the heterocyclic guest solvents, and the results of these experiments were related back to their relative selectivity preferences.

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SOLVOLYTIC BEHAVIOUR OF BENZYL HALIDES IN AQUEOUS ETHANOL

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Previous studies on benzyl sulfonates clearly showed that solvolyses of these aromatic primary substrates proceeded through both S_N1 and S_N2 mechanisms, which was indicated by either the break or curvature in a Hammett plot.[1–3] The Hammett treatment of solvolysis rates further indicated that benzyl sulfonates substituted by both strong and weak electron-releasing substituents underwent the monomolecular substitution in aqueous acetone and other solvents of lower nucleophilicity.[1–3] We have determined rate constants for solvolysis of some benzyl halides in 80% ethanol and employed the Hammett correlation analysis to investigate the influence of substituents on the solvolytic behaviour of benzyl derivatives in a media of higher nucleophilicity. Kinetic results confirm the breakdown of the linear relationship, i.e., the change in the mechanism of solvolysis within the series. However, unlike data for hydrolysis in aqueous acetone presented in the previous studies,[1,2] data for solvolysis of alkyl and aryl-substituted benzyl substrates in 80% ethanol do not match the S_N1 line, indicating a strong impact of the solvent nucleophilicity on the mechanistic change in the series. Additional measurements have been carried out to ascertain whether or not the alkyl and aryl-substituted benzyl halides react by the concerted bimolecular mechanism exclusively. Although a simple Hammett analysis suffers from serious flaws,[4,5] it still represents an applicable tool for detecting the change of mechanism in a series of related substrates.

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P-7

ELECTROFUGALITIES AND SOLVOLYTIC BEHAVIOR OF SOME FERROCENYLPHENYLMETHYL CATIONS

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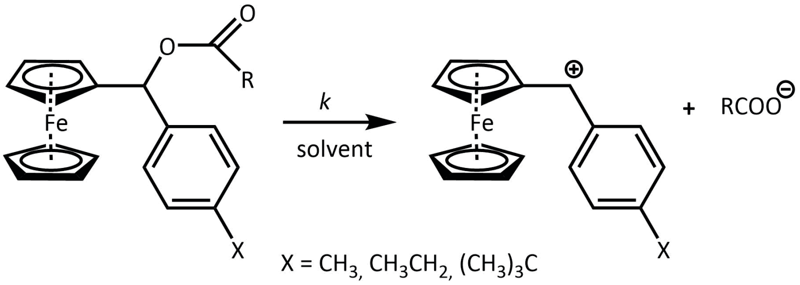
Previous kinetic studies established that the ferrocenyl group in α-position to the reaction center considerably enhances the S_N1 solvolytic reactivity of the ferrocenylphenylmethyl substrate.[1] These investigations have now been extended to determine electrofugalities of new substituted ferrocenylphenylmethyl derivates **1**–**4** (Scheme 1) by applying the linear free energy relationship (LFER) equation: $\log k = s_f (E_f + N_f)$.[2] The carbocation (electrofuge) is characterized here by a single, solvent-independent parameter E_f whereas the couple consisting of the leaving group and the solvent is characterized by the two parameters N_f and s_f. Taking those earlier determined s_f and N_f parameters,[3] the electrofugality parameter E_f of a given electrofuge can be derived from $\log k/s_f$ versus N_f plots.



1 Butyrate, R = $CH_3CH_2CH_2$
2 Isobutyrate, R= $(CH_3)_2CH$
3 Valerate, R = $CH_3CH_2CH_2CH_2$
4 Isovalerate, R = $(CH_3)_2CHCH_2$

Scheme 1. Heterolytic step in solvolysis of ferrocenylphenylmethyl butyrates (1), isobutyrates (2), valerates (3), and isovalerates (4).

Due to ability of the ferrocene moiety to efficiently stabilize positive charge, ferrocenylphenylmethyl cations constitute a group of very powerful electrofuges ($E_f > 1$) in comparison with similar benzhydrylium electrofuges. Furthemore, impact of the phenyl group in ferrocenylphenylmethyl derivatives on stabilization the positive charge is somewhat leveled by the ferrocenyl group, so the rate effect of the alkyl substituents (methyl, ethyl, and *tert*-butyl) on the phenyl ring is suppressed, causing narrow range of E_f parameters.

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[3] unpublished results.

P-8

RADICAL-INDUCED DAMAGE OF PEPTIDES: MECHANISTIC INSIGHTS FROM STUDIES INVOLVING ENVIRONMENTAL OXIDANTS

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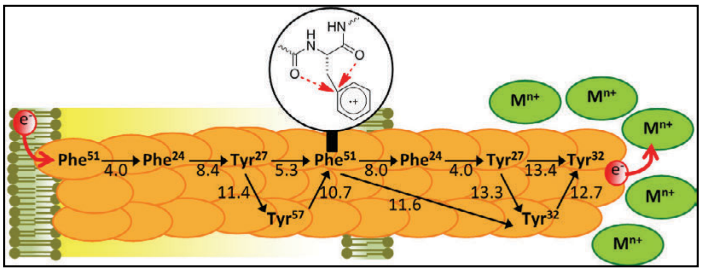
Nature uses proteins as medium for long-distance electron transfer (ET) to carry out redox reactions in distant areas and compartments. These processes are triggered by a multistep charge hopping reaction, using the side chains of Tyr, Trp, Cys and Met as relay amino acids, which have oxidation potentials in peptides of around 1 V vs. NHE. Recently, Lovley and Reguera proposed that Phe acts as a relay amino acid in extracellular electron transfer (EET), where electrons migrate over several hundreds of Å from the respiration site at the inner cell membrane to oxidising metal cations outside the cell.[1] In *Shewanella oneidensis* such EET can use pili, which are aggregates of small proteins that carry Phe and Tyr as possible stepping-stones. However, since the oxidation potential of alkylated phenyl groups is about 2 V vs. NHE, the question arises, whether the oxidation of Phe is influenced by the peptide environment.



Through experimental and computational studies using the environmentally important nitrate radicals ($NO_3^•$) as mode oxidant, we have demonstrated that the developing positive charge during oxidation of the phenyl ring in Phe is efficiently stabilised by adjacent amide groups.[2] As a consequence, Phe cannot only catalyse ET as a relay amino acid but can also be regioselectively and irreversibly oxidised. These processes resemble the peptide backbone effect[3] that turns methionine into a powerful relay amino acid and a target for oxidative stress.[4] On the other hand, oxidation of aliphatic amino acids by $NO_3^•$ occurs without amide neighbouring group facilitation and involves to a significant extent proton-coupled electron transfer (PCET) at the amide N-H bond.[5]

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P-9

4-(DIMETHYLAMINO)DIPHENYLCARBENE: MATRIX ISOLATION STUDIES OF A MAGNETICALLY BISTABLE CARBENE

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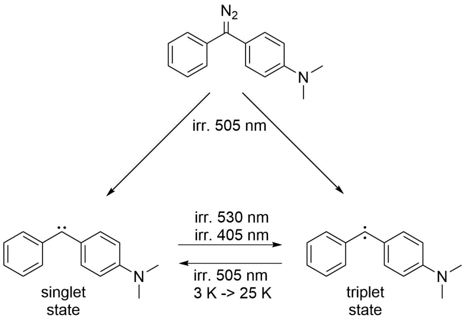
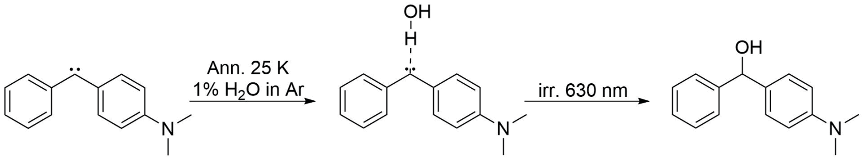
The investigation of reactive intermediates plays a pivotal role in analyzing the mechanistic key steps of reactions.[1] While usually carbenes are formed in either their singlet or triplet state, only few examples of magnetically bistable carbenes were reported for which the singlet and triplet states coexist. These carbenes usually have a very small singlet-triplet energy gap of less than 1 kcal/mol.[2–4]

In this work, 4-(Dimethylamino)diphenylcarbene was successfully generated in an argon matrix at 3 K as a mixture of its singlet and triplet states by photolysis of its diazo precursor. Selective irradiation with visible light led to a partial conversion from the singlet to the triplet state and vice versa. Annealing of the matrix to 25 K resulted in singlet carbene formation. The singlet amount maximum was 92% while the triplet amount maximum of only 42% was obtainable.



Scheme 1. Formation of 4-(dimethylamino)diphenylcarbene by irradiation of its diazo precursor with visible light. The spin state of the carbene can be switched via photochemical or thermal methods.

Additional experiments in a water-doped argon matrix were conducted. Annealing of the matrix to 25 K leads to the softening of the matrix, allowing single water molecules to diffuse through the matrix and interact with the carbene molecules. It was shown that both the singlet and the triplet carbene interact with water to form a hydrogen-bonded singlet-state complex.



Scheme 2: Formation of a water-carbene complex after annealing 4-(dimethylamino)diphenylcarbene in a water-doped argon matrix to 25 K. Subsequent irradiation with visible light led to the conversion to the corresponding alcohol.

The water complex was stable at 3 K and did not undergo any reaction via quantum chemical tunneling.[5] Irradiation with visible light converted the complex to the alcohol (scheme 2).

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P-10

SIZE, SHAPE AND SURFACE STRUCTURE AFFECT INTERACTION OF METALLIC NANOPARTICLES WITH TRANSPORT PROTEINS

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Metallic nanoparticles are currently being used in an increasing number of consumer and medical products, due to particular properties of metals at nanoscale. This necessitates safety assessment for human health including evaluation of fate, transformation and interaction of NPs within biological environment.[1,2]

This study aimed to determine how different physico-chemical properties of silver nanoparticles (AgNPs) affect their behavior and interaction with albumin and α1-acid glycoprotein as non-glycosylated and glycosylated transport proteins from human blood. For this purpose, sixteen types of AgNPs of different shape (spherical, triangular and cubic), size (10 and 50 nm) and surface stabilization were prepared[3] After careful characterization of their size distribution, surface charge, dissolution, and behavior in water, phosphate buffer, and physiological solution, effect of various physical-chemical properties of AgNPs on the binding affinities for these two proteins was evaluated. In addition, changes in the secondary protein structure due to binding to AgNPs surface were evaluated by circular dichroism.

Obtained results demonstrated that the surface charge and nominal diameter of AgNPs both have a significant role in nano-bio interactions. Proteins present in the media bind to the AgNPs surface immediately after their suspension in these media. Binding constants of proteins to AgNPs surface are similar to binding between these proteins and some drugs. Binding of albumin to AgNPs results in a greater and more varied alteration of the protein structure compared to α1-acid glycoprotein.

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P-11

STABILIZATION OF TRIPLET NITRENES IN NAFION POLYMER BEYOND CRYOGENIC CONDITIONS

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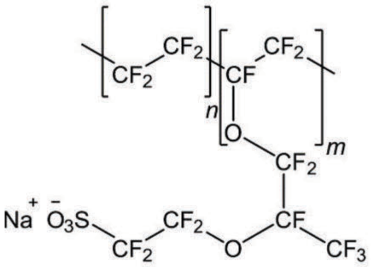
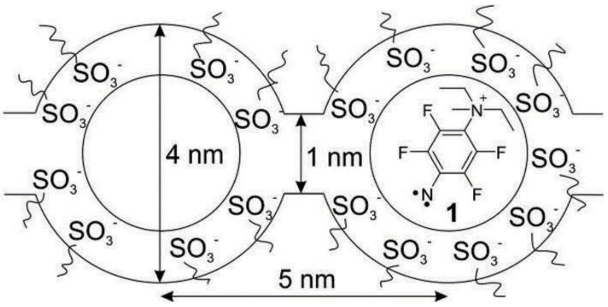
Organic magnets possess properties (e.g. flexibility or transparency) that outcome those of conventional magnets. Triplet nitrenes exhibit strong magnetic properties and are of considerable interest as models for molecular magnets.[1] However, nitrenes are typically very short lived under ambient conditions so are usually trapped in low-temperature matrices.[2,3] Hence, the aim of this work is to generate persistent nitrenes at ambient conditions.





Nafion polymer was chosen as confinement media as its perfluorinated backbone would prevent undesired H-abstraction by nitrenes. Cationic ammonium groups were inserted into azide precursors (2,3,5,6-tetrafluorophenyl, 2,6-bis(pentafluorophenyl)phenyl and 2,6-diphenylphenyl) to facilitate the attachment to Nafion. Irradiation with UV light of cationic azides embedded into Nafion–Na^+ affords the corresponding nitrenes in high yields. Typical byproducts such as azirines or ketenimines were not detected during photolysis or annealing. The stability of the nitrenes was monitored by UV–vis, IR and EPR spectroscopy at different temperatures. Nitrene **1** is fully persistent in Nafion up to 200 K and survived for 30 min at 0 °C. The decay of nitrene **1** was observed to follow second-order kinetics, leading to dimerization as the main deactivation channel. Bulky groups like perflurophenyl extend the lifetime of the nitrene at 0 °C to more than 1 h by hampering its dimerization. Persistent nitrenes at room temperature could be great candidates as building blocks for organic magnets.

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DIRECT OBSERVATION OF HEMITHIOINDIGO-MOTOR UNIDIRECTIONALITY

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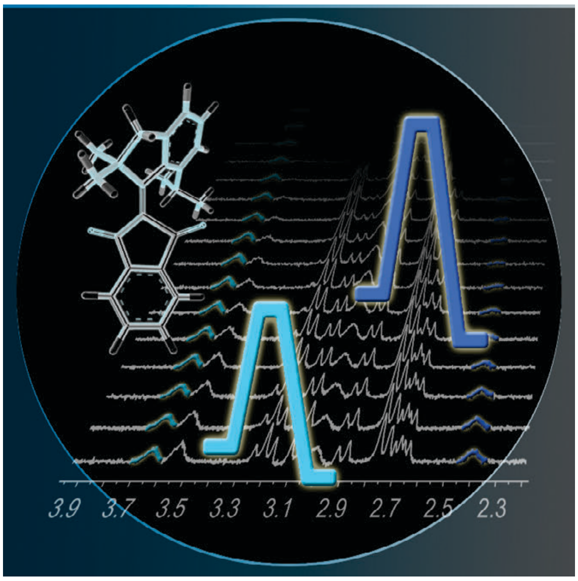

A new class of emerging photoresponsive molecules is Hemithioindigo (HTI). Their prominent advantage; isomerization of the central double bond powered exclusively by non-damaging visible light.[1] A clever design also makes it possible to use HTI-based structures as molecular motors.[2] Their rapid rotations can reach up to 1 kHz at 20 °C, implied enough photoenergy is provided. Although their fast unidirectional motion is eligible for future applications in complex nanomachinery, it however prevented a full analysis of the rotation process up until now.[3]

By developing a new high-yielding synthesis for sterically hindered motor derivatives, we could achieve a considerable slowdown of the rotary motion. This made it possible to directly observe all four of the proposed intermediate states populated throughout rotation for the first time. Using low temperature ^{1}H NMR spectroscopy we were able to follow the exact sequence in which the isomers interconvert and therefore directly prove the complete unidirectionality of the HTI motor system.[4]

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P-13

ACCELERATION OF A TUNNELING REACTION VIA INTERACTION WITH LEWIS ACIDS

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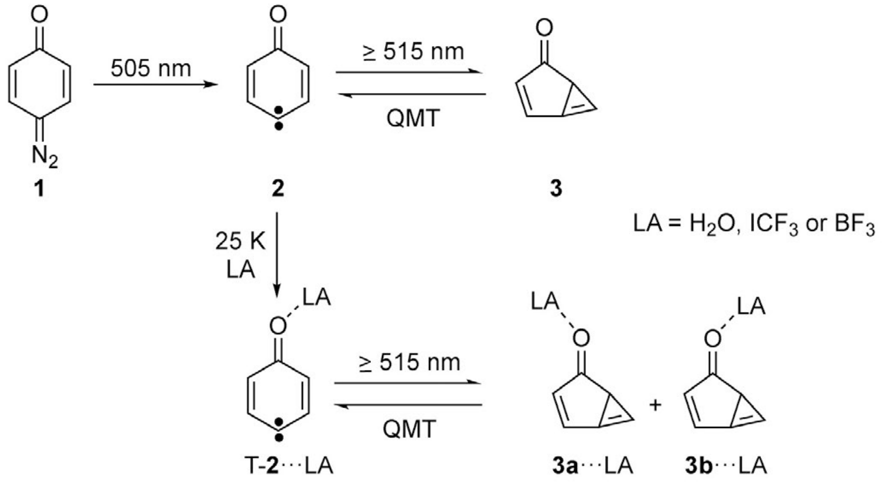
Quantum mechanical tunneling (QMT) is a fundamental phenomenon that is manifested in many chemical reactions. Visible light irradiation of 4-diazocyclohexa-2,5-dien-1-one **1** generates triplet 4-oxocyclohexa-2,5-dienylidene T-**2** in argon matrices at 3 K. Further irradiation of T-**2** produces the highly strained 1H-bicyclo[3.1.0]hexa-3,5-dien-2-one, which is metastable and rearranges back to T-**2** by heavy-atom tunneling.[1–2]

In this work, the interaction of T-**2** and **3** towards three Lewis acids (H_2O, ICF_3 and BF_3) and the influence of complexation on the tunneling ring opening were investigated in argon matrices doped with 0.5–1% of H_2O, ICF_3, and BF_3. Annealing of the matrices to 25 K generates complexes of the carbonylic moiety of T-**2** with the three Lewis acids, while only complexes of **3** with H_2O and ICF_3 were observed. The decay of the complexes of **3** with H_2O and ICF_3 proceed 6 and 10 times faster than the rate reported for the **3**→**2** tunneling rearrangement. Likewise, the ring opening of the complexes **3**-BF_3 proceeds too fast to be observed, indicating that the reaction is accelerated by increasing Lewis acidity of the dopant. Calculations show a decrease in the activation barriers, supporting the experimental observations.



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NATURE OF CHALCOGEN BONDS: A QUANTITATIVE KOHN-SHAM MO INVESTIGATION

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In recent years, the relevance of noncovalent interactions, such as Hydrogen Bonds (HB) and Halogen Bonds (XB), to catalysis, molecular recognition, crystal structure of matter and self-assembly materials has sparked the need to truly understand their nature and underlying bonding mechanism.[1] Towards this end, chemists have attributed the strength of XB to an electrostatic model, coined the "σ-hole"[2] However, quantitative Kohn-Sham molecular orbital (KS-MO) theory has revealed that orbital interactions and Pauli repulsion play an important role in XB and that the electrostatics contribution to these interactions does not follow the expected behavior, as suggested by the "σ-hole" model[3]

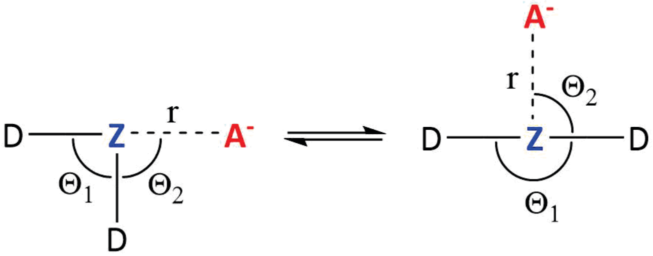

Figure 1. Chalcogen-bonded $D_2Z\cdots A^-$ model complexes (Z = O, S, Se, Te; D, A = F, Cl, Br).

In this work, we have quantum chemically analyzed another, related non-covalent interaction, known as Chalcogen Bonds (ChB), using KS-MO theory and a matching, canonical energy decomposition analysis (EDA). The strength of ChBs is commonly rationalized in terms of the "σ-hole" model. Interestingly, using archetypal model systems, as shown in Figure 1, we have identified the key role of electrostatic attraction, Pauli repulsion and orbital interactions in ChBs. Our work reveals yet another breakdown of the "σ-hole" model by systematically outlining how it is unable to predict and explain the trends in strengths of these noncovalent interactions.

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P-15

TRIPLET STATE ANTIAROMATICITY OF SUBSTITUTED BENZENES: A COMPUTATIONAL INVESTIGATION

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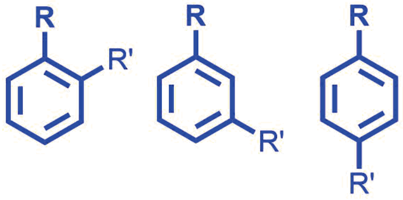
Aromaticity and antiaromaticity are key concepts that define the stability and instability of cyclic π-conjugated molecules.[1] Hitherto, the concepts have been studied and applied extensively to the electronic ground state (S_0) whereas applications to understand properties and processes in excited states are scarce. In 1972, Baird, based on qualitative theory, proposed that the electron counts for aromaticity and antiaromaticity in first ππ* excited triplet state (T_1) is opposite to Hückel's "4*n*+2" rule valid for the S_0 state.[2–3] This excited aromaticity and antiaromaticity concept given by Baird's rule can be used to reinterpret a range of earlier reported photochemical and photophysical phenomena.[4–5]



R = Me, *t*Bu, NH_2, CN, NO_2, OH, F, CF_3, $SiMe_3$, or SiF_3
R' = H, CH_3, CN or NH_2

Whereas benzene is aromatic in its S_0 state, it is antiaromatic in its T_1 and S_1 states. It should now be crucial to determine the effects of substituents on the excited state antiaromaticity of various benzene derivatives. Which substituents are best to alleviate the excited state antiaromaticity of benzene? We focus on the T_1 states of differently substituted benzenes and will present results from quantum chemical calculations of magnetic, geometric and electron density based aromaticity indices.

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P-16

RADICAL CHEMISTRY NEAR BORONIC ESTERS: ELUCIDATING MECHANISM AND REACTIVITY WITH DFT

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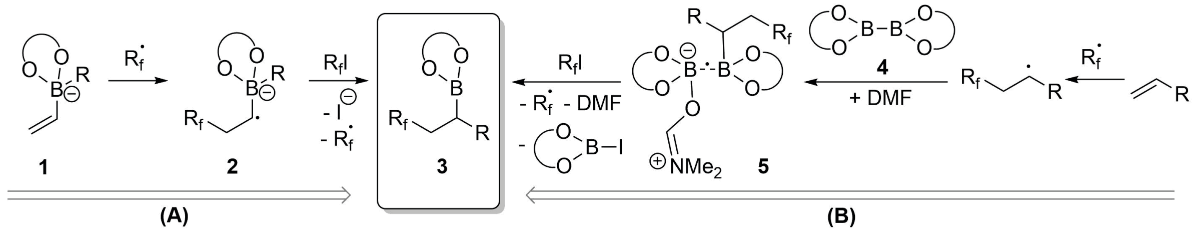
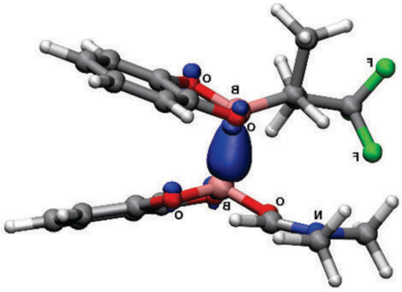
We have developed synthetically useful new radical reactions involving the boronic ester group -B(OR)$_2$. The addition of two alkyl groups (R, R$_f$) to a vinyl group can be achieved starting from vinyl boronic esters in a radical-polar crossover process (**A**).[1] Similar products (**3**) are obtained in the reaction of bis(catecholato)borane **4** with a radical formed by the addition of R$_f$ to substituted alkenes (**B**).[2] Both mechanisms regenerate the initial radicals and the reactions are thus conducted as chain processes. In the absence of an alkene, the reaction of bis(catecholato)borane with a radical allows the metal-free borylation of alkyl and aryl iodides.[3]



We have conducted DFT studies of reaction energies and barriers in the mechanism of these reactions and discuss the reactivity and characteristic properties of radical intermediates **2** and **5**. The latter adduct (**5**) is remarkable as it contains a boron-boron one-electron σ bond and is stabilized by a solvent molecule.[2]



Spin Density (0.02 a.u.) of Radical **5** (PBE0-D3/def2-TZVP)

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P-17

PREDICTING REACTIVITY WITH A SUPRAMOLECULAR ELECTROSTATIC SOLVATION MODEL

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Bulk solvent properties such as polarity and dielectric constant are regularly used in attempts to predict the effect solvents have on reactivity and selectivity. However, these can correlate rather poorly with the observed trends. More detailed methods to predict solvent effects such as the Kamlet-Taft-Abraham equations fare much better but require multiple parameters and their scalars – which need to be determined theoretically or empirically.[1]

A solvent model based on relatively accessible hydrogen bond donor and acceptor parameters has been successful at predicting the binding equilibrium of species in solution.[2] This solvent model bases the strength of the binding on the magnitude of the electrostatic interaction between the solutes and solvents, modelling the processes as a series of competing supramolecular interactions. In this work, we describe our progress in using this electrostatic solvent model to predict the effect solvent has on the rate of two probe reactions: transesterification and nucleophilic attack of a phenolate with triarylmethane dyes. The hydrogen bond donor and acceptor parameters of solvent and reactive species have been used to rationalise and predict the kinetic and thermodynamic behaviour of the probe reactions in a range of pure and mixed solvents.

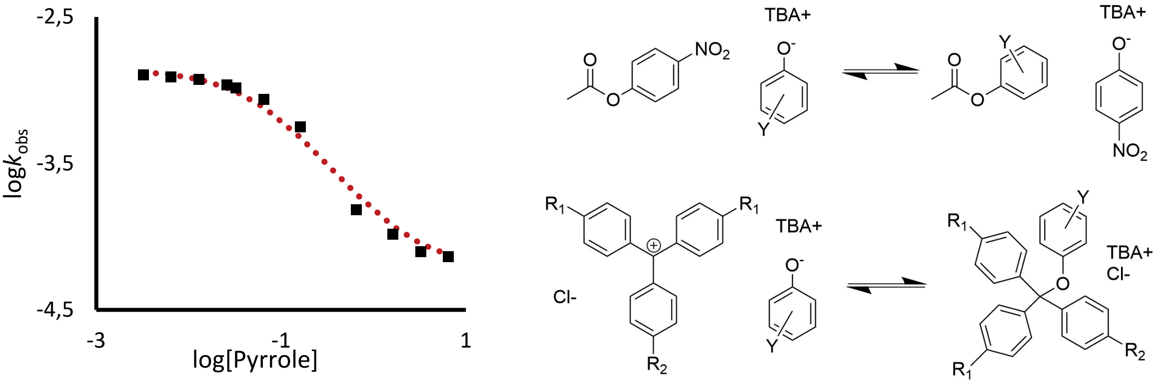

Figure 1. The rate of transesterification of 4-nitrophenylacetate (right-top) and the nucleophilic attack of triarylmethane dyes (right-bottom) have been measured in various binary solvents. The effect on rate has been predicted (left) by determining the proportion of binding between the reactive species and the components of the solvent mixture.

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P-18

BOROHYDRIDE REDUCTION OF 2-HALOCYCLOHEXANONES: DFT ANALYSIS OF REACTIVITY AND STEREOSELECTIVITY

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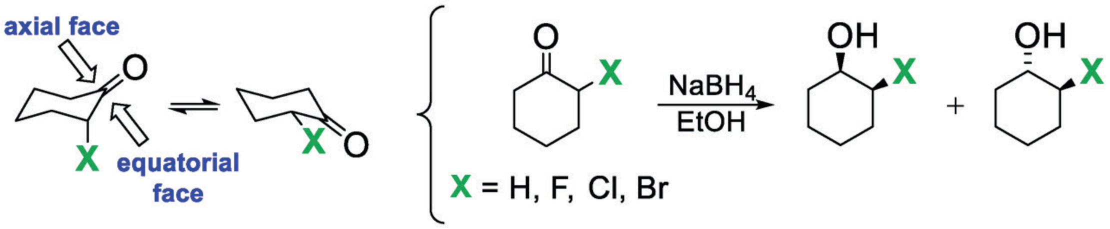
The stereoselective reduction of a carbonyl group is undoubtedly a central reaction in organic chemistry. In the sodium borohydride reduction of 4-*tert*-butylcyclohexanone, for example, the hydride is preferentially added to the axial face of the C=O group to form the equatorial alcohol. According to the Felkin-Anh model, this stereoselectivity can be rationalized based on the stabilization of the transition state by orbital interactions and torsional strain.[1] Herein, we aim at investigating the influence of an α-halogen on the preference for the hydride attack in the 2-halocyclohexanones using state-of-the-art density functional theory (DFT) calculations. Given that the halogen atom may adopt either an axial or equatorial orientation in the cyclohexanone backbone (see the scheme below), we have also investigated how this conformational preference affects the reactivity trends. Therefore, all possible orientations of the hydride attack and the halogen atom have been explored and the trends in reactivity have been quantitatively analyzed using the Activation Strain Model (ASM) along with the matching canonical Energy Decomposition Analysis (EDA).[2]

Acknowledgement. The support of the CAPES, CNPq and FAPEMIG agencies is gratefully acknowledged.



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P-19

ACTIVATION STRAIN ANALYSES OF ARYLIC VERSUS ALIPHATIC C–X BOND ACTIVATION BY PALLADIUM CATALYST

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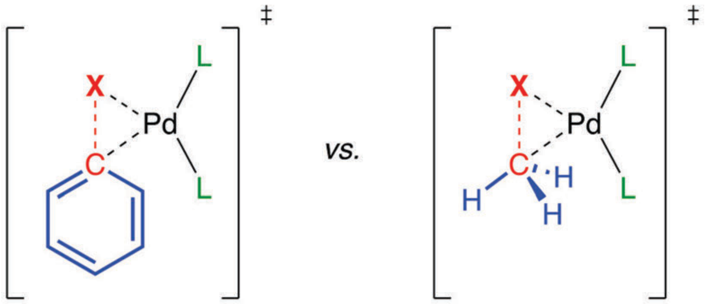
We have quantum chemically explored and analyzed the oxidative insertion of a palladium catalyst into the C–H bond of benzene, C–Cl bond of chlorobenzene and the C–C bond of toluene, using relativistic density functional theory.[1–3] Our study has three objectives. Firstly, we aim at understanding the difference in reactivity between arylic and aliphatic C–X bonds towards palladium catalyst systems. Secondly, we wish to uncover the physical factors behind the selectivity within the series of arylic C–X bonds. Thirdly, we examine how variation of phosphine-type ligands affects the activity of the palladium center towards the various C–X bonds. Our results show that barriers for arylic C–X bond activation are lower than those for the corresponding aliphatic C–X bonds. However, trends along bonds or upon variation of ligands are similar.



X = H, Cl, CH_3; $(L)_2$ = none, PH_3, $(PH_3)_2$, $PH_2C_2H_4PH_2$

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P-20

SIMULATION-BASED EVALUATION OF NON-EQUILIBRIUM SOLVATION FREE ENERGY IN ORGANIC SOLUTION REACTION

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The process in organic solution reaction is essentially accompanied with the geometrical rearrangement of solvation shells. Solution reaction, in general, proceeds with thermal equilibrium of whole system where both solutes and solvents are massively linked and act as a uniform system. The reaction rate can be interpreted within Transition State Theory (TST) framework and the pressure dependence of rate constant in logarithmic form shows a linear relationship. However, when the relaxation timescale gap between chemical reaction and solvent fluctuation become extremely large, the fluctuation-driven relaxation lifetime emerges as a rate-determining step and the pressure dependent reaction rate behavior deviates from TST-predicted linear relationship. Organic reaction kinetics in viscous solvent under high pressure is one of the effective experiment tools to examine how the solvation process is involved in the activation step. Imposing high pressure on viscous solvent intensely increase the viscosity and the chemical equilibrium break down between the initial state and the transition state. So far we experimentally studied several reactions in viscous solvents where the solute-solvent coupling is weak,[1] and strong cases,[2][3] respectively. We found that the observed viscosity dependence of the rate constant can be rationalized by considering the decoupling of the solute coordinate (reaction coordinate) and the solvent coordinate (fluctuation coordinate). Herein, numerical technique[4] combined with MD simulation and solvation theory are applied to evaluate the component of non-equilibrium solvation free energy aiming to elucidate the organic solution reaction mechanism.

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P-21

CALCULATION OF REDOX POTENTIAL IN FERROCENE DERIVATIVES. WHY HYBRID DFT METHODS FAIL?

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A number of studies and library syntheses have been focused on the modulation of the ferrocene (FcH) reduction potential by changing substituents and linkers at the ferrocene core. The tuning of ferrocene redox potential can be assisted and supported by quantum chemical calculations. Different computational methodologies have appeared with the density functional theory (DFT) as the most promising platform for predictions of redox potential in ferrocene derivatives. We applied the selected benchmark method (SMD-B3LYP/6-31G(d)/LanL2TZf level of theory) for series of ferrocenyl derivatives (FcR, where R is Me, F, Br, COOH, OCOMe, CN…) and excellent agreement between calculated and experimental redox potential was obtained. However, for some cases (e.g. R is N_3, Cl, NH_2…) a significant discrepancy between experimental and calculated data was observed. The error (absolute difference from the experimental value) amounts to 1000 mV, which may be converted (by relation $E° = -\Delta G_r / nF$) to the Gibbs free energy equivalent of ca. 100 kJ/mol. This is an unacceptable deviation produced by the benchmarked DFT method. Three variables were assessed to detect a possible origin of the observed failure: functional, basis set, and solvation model. It comes out that the Hartree-Fock exchange fraction (χ) in hybrid DFT methods (e.g. PBE0, BHandH, M06…) is the main source of the error. The higher percentage of exact exchange, the larger is error for calculated redox potential of selected ferrocenes. Most of hybrid DFT methods overestimate the stability of oxidized ferrocene species. Therefore, the calculated value of redox potential for specific $FcR^{1+/0}$ couples is too low, and the ferrocene derivative appears as an extremely strong reducing agent.

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P-22

SOLUBILITY AND SOLVATION PHENOMENON IN WATER ORGANIC MIXTURES AT THE MOLECULAR LEVEL

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The birth of green chemistry has led to increased interest in the use of water as a solvent for chemical reactions in laboratory and in industry for reasons of low cost, safety, and environmental concerns.[1,2] The problem that limits the use of water as a solvent in organic chemistry is poor solubility of many potential reactants. One of the most common technique to overcome this limitation is the use of water miscible organic co-solvents to enhance the solubility of hydrophobic substrates.

In recent years, different approaches have been used to describe solvent effects on solubility of organic compounds and to predict this property for solvent mixtures, proceeding from various empirical or semi-empirical models describing structure of these solutions. These studies have revealed that besides the solvent structure also the solvation of solute molecules by components of the solvent mixture should be considered. This significantly complicates analysis of this phenomenon. Strong structure-making properties of water are well known, but not so well understood and modelled, especially in water-solvent mixtures.[2,3]

Recently we applied molecular dynamics simulations to cast light on the solvation of solutes in different water-organic solvents. We found that the binary solvent effects on solubility are related to the structure of the solvation shell around the solute molecules. Moreover, quantitative relationships between solubilities and solvation structures were found in all investigated systems. These results provide detailde insight into solubility phenomenon and will be discussed in the presentation.

Acknowledgements. This research was financially supported by institutional research funding (IUT20-15) of the Estonian Ministry of Education and Graduate School of Functional materials and technologies receiving funding from the European Regional Development Fund in University of Tartu, Estonia.

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P-23

IRREVERSIBLE INHIBITION OF THE MAO B ENZYME. A COMPUTATIONAL INSIGHT INTO THE INACTIVATION MECHANISM

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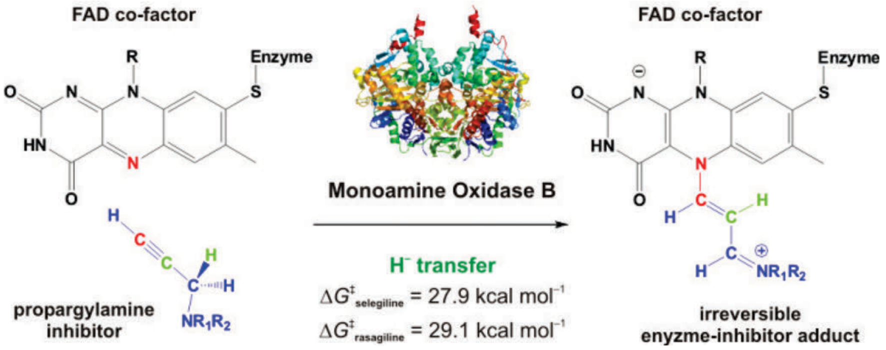
Monoaminooxidases A and B (MAO A and B) are mammalian flavoenzymes responsible for regulating the levels of amine neurotransmitters. These enzymes represent the main pharmacological target in the treatment of depression and neurodegenerative diseases. Two isoforms are present in the human body, MAO A and MAO B, which share about 70% of the identical amino acids in the primary sequence but exhibit significant differences in the substrate selectivity and especially in inhibitory specificity.[1] The focus of this work are selective irreversible MAO B inhibitors, selegiline and rasagiline, widely used in alleviating the symptoms of Parkinson's and Alzheimer's diseases, and their metabolites from the phase one of drug metabolism.

In this work we used molecular dynamics simulations to obtain insight into MAO B interactions with both inhibitors and their metabolites in the active site. It has been shown that Tyr398 and Tyr435 form an aromatic cage responsible for interactions with the aromatic part of an inhibitor. Gln206 is characterized as the active site residue most responsible for accommodating the inhibitors. The binding free energies, obtained using MM-GBSA tools, reveal that tertiary amines bind better than secondary analogues, being consistent with the experimental IC50 values.[2] Analysis of hydrogen bonds and hydrophobic interactions in the enzyme active site shows that hydrophobic interactions are crucial for binding.



Quantum-chemical analysis within the enzyme cluster model suggests a completely new chemical mechanism of MAO inhibition through a 3-step reaction,[4] whereby the first step determines the overall reaction rate in which FAD cleaves the hydride ion from the inhibitor's α-methylene group, being in a complete analogy with the MAO catalytic mechanism.[5] The obtained reaction profiles and the final structure of the inhibited enzyme are consistent with the experimental data.[1,3] The obtained results provide new guidelines for the development of more efficient and more effective MAO B inhibitors for clinical use in the fight against neurodegenerative and psychiatric diseases.

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COMPUTATIONAL INSIGHT INTO THE METAL-FREE CLEAVAGE OF THE CARBON-CARBON TRIPLE BOND IN ALKYNES

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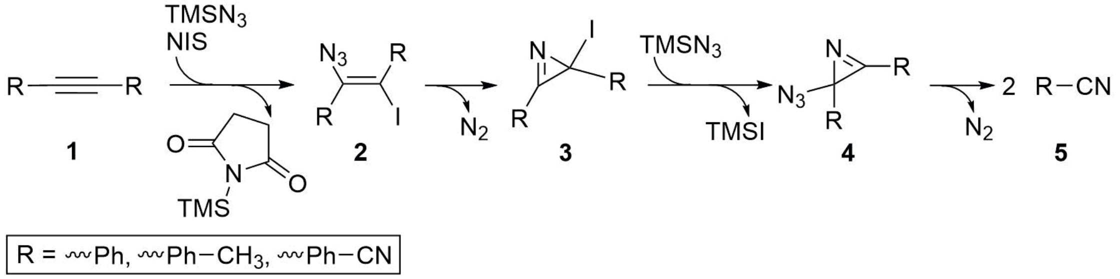
Cleavage of the C-C triple bond is one of the most important processes in modern organic synthesis. Majority of the existing methods rely on the oxidative cleavage with toxic organometallic catalysts under harsh reaction conditions,[1] which makes their application less desirable. Recently, Yanada et al.[2] reported a metal-free cleavage of internal alkynes to nitriles using trimethylsilylazide ($TMSN_3$) as the nitrogen source. Inspired by these experimental advances, in this work, we used DFT computations at M06-2X/6-31+G(d) level of theory to clarify the mechanism of the mentioned reaction.

After inspecting several mechanistic possibilities, our results show that the cleavage of the carbon-carbon triple bond in symmetrical internal alkynes **1** is a downhill process ($\Delta_r G$ between –191.8 and –195.3 kcal mol^{-1}), which occurs in six steps. In the first step, a simultaneous addition of azide from $TMSN_3$ and iodine from *N*-iodosuccinimide (NIS) to the C-C triple bond, leads to the formation of iodo vinyl azide **2**. The intermediate **2** undergoes internal rearrangement to obtain 2-iodo-2*H*-azirine **3**, accompanied by the release of the nitrogen gas under the thermal condition. Addition of $TMSN_3$ to the double bond in **3** with a simultaneous loss of iodine, generates azide azirine **4**. The final cyano compounds **5** are obtained in the last, rate-limiting step ($\Delta G^{\ddagger}$ = 33.5 kcal mol^{-1}) which belongs to the second part of the synthetic route that occurs under temperatures over 70 °C. The computations indicate that alkynes with electron-donating moieties tend to give nitriles easily, which is experimentally confirmed by their higher yields.[2] We believe that obtained results could be of significant value for the future experiments with different reagents and solvents.



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P-25

BIARYL CROSS-COUPLING INVOLVING ANIONIC REDUCED FORMS OF CYANOARENES IN LIQUID AMMONIA

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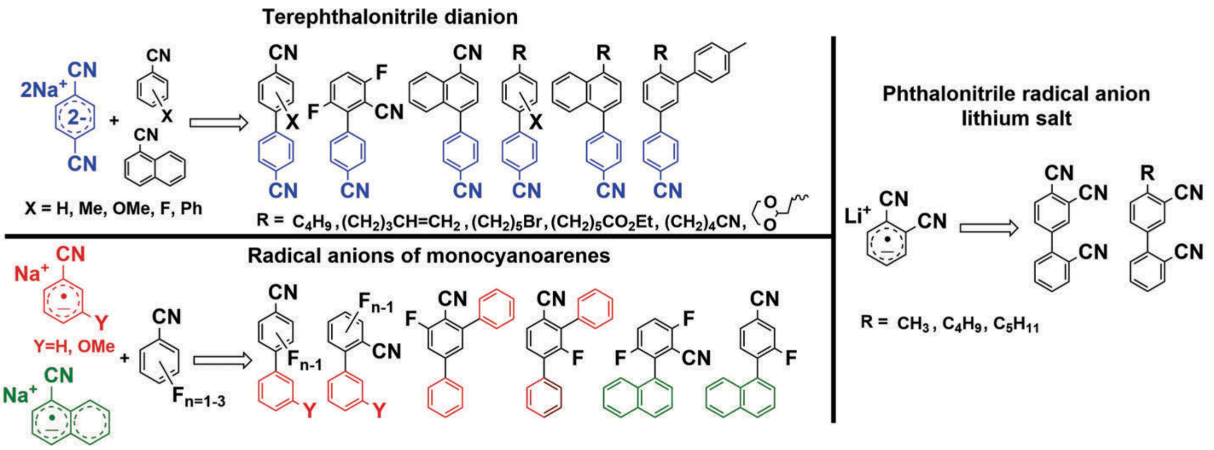
Cyano-substituted biphenyls and terphenyls are universal structural blocks for new materials (LC, OLED, MOF, NLO). A convenient approach to cyanoarenes with desirable aromatic moiety type, a number, and position of substituents is the biaryl cross-coupling involving long-living anionic reduced forms of aromatic nitriles, easily generable by reduction of aromatic nitriles with alkali metal in liquid ammonia. Such forms are terephthalonitrile dianion, radical-anions of benzonitrile, 3-methoxybenzonitrile, and 1-naphthonitrile, which arylates neutral cyanoarenes via S_NH or S_NAr_F. The reaction provides one-pot approaches to di- and monocyanobiphenyls, -terphenyls, naphthylbenzonitriles, their alkylated derivatives with 30–90% yields.[1–3] In addition, earlier found ability of phthalonitrile radical anion lithium salt to undergo dimerization in liquid ammonia allow to obtain 2,3',4'-tricyanobiphenyl and 4'-alkyl-2,3'-dicyanobiphenyls, which used in the synthesis of phthalocyanines and materials with non-linear optical properties.



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P-26

CHEMOSELECTIVITY IN ESTERIFICATION REACTIONS – SIZE MATTERS AFTER ALL[1]

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We studied the reaction of carboxylic acid chlorides with secondary alcohols carrying either flexible alkyl or rigid aryl substituents by a series of competition experiments. Therefore, the main difference between the two alcohols is the surface available for non-covalent interaction. Aliphatic acid chlorides react preferentially with the aryl-substituted alcohols, while acid chlorides derived from aromatic carboxylic acids react with very low selectivity. Catalysis by 9-azajulolidine (TCAP)[2] increases the selectivity strongly, while solvent and temperature effects are only moderate. We found that the size of the alcohol substituents impacts selectivities only for rigid aryl substituents, and also that higher selectivities are found for larger aryl systems up to 1-(1-pyrenyl)ethanol.

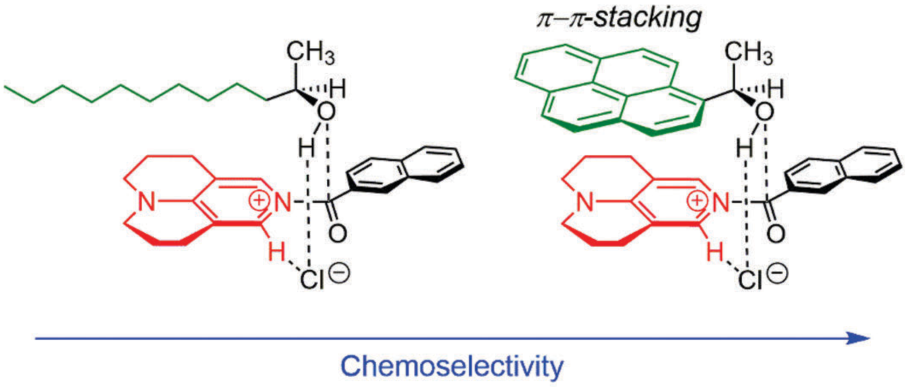

Figure 1. Proposed transition state structures rationalizing size dependent chemoselectivity.

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P-27

SIZE-DEPENDENT INVERSION OF SELECTIVITY IN ESTERIFICATION REACTIONS

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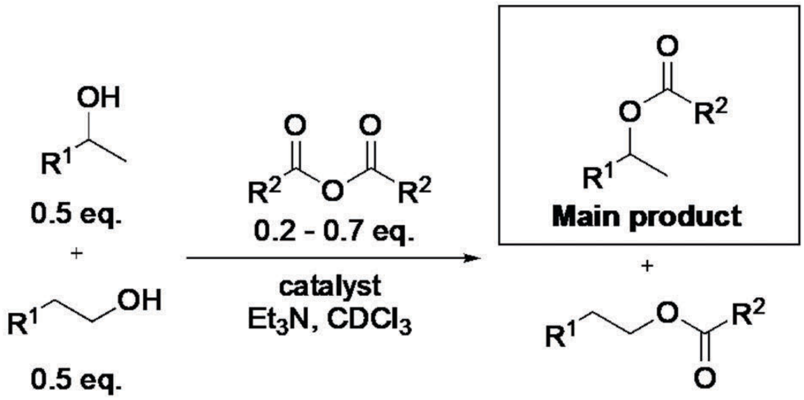
That large dispersion energy donor (DED) groups can influence the relative rates of acylation reactions is already known.[1] Till now the stereoselective protection of hydroxy groups in polyol systems like sugars is a challenge and is only affected by H-bonding between the acylation reagents and sugar surface.[2] Depending on the size of the anhydrides used the formation of the secondary ester can be accelerated over the formation of the corresponding primary alternative. Computational results indicate that kinetics are guided by a dual interaction between the catalyst surface and the sizable groups located at both alcohol and acid anhydride reactants.



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EXPERIMENTAL AND COMPUTATIONAL STUDY OF THE REACTION BETWEEN FERROCENYL LITHIUM AND N-PHENYL PHTHALIMIDE

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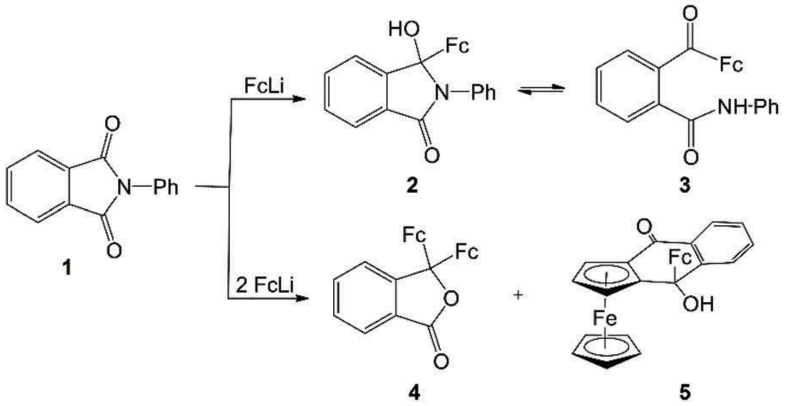
In order to investigate the electronic and structural interactions between organometallic functionalities and heterocycles,[1,2] a reaction between ferrocenyl lithium (FcLi) and N-phenyl phthalimide (**1**) was performed. During the course of this reaction an unusual reactivity was observed. The conversion of one equivalent of FcLi with **1**, resulted in mono-ferrocenyl lactam **2**, which rapidly undergoes ring-chain tautomerism 2⇆3. When two equivalents of FcLi were used, a bis-ferrocenyl lactone **4**, involving a five-membered oxygen bridged heterocycle, was formed. In addition, a tricyclic product **5**, in which one of the ferrocene moieties displays a planar chiral substitution pattern, was isolated.



The compounds **2** – **5** were characterized spectroscopically and electrochemically. The molecular structures in solid state were defined by X-ray diffraction analysis. The involved reaction mechanisms were explored by use of modern density functional techniques.

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P-29

MECHANISM AND STEREOSELECTIVITY OF DECARBOXYLATIVE ELIMINATION OF DIBROMOCARBOXYLIC ACIDS IN DMF

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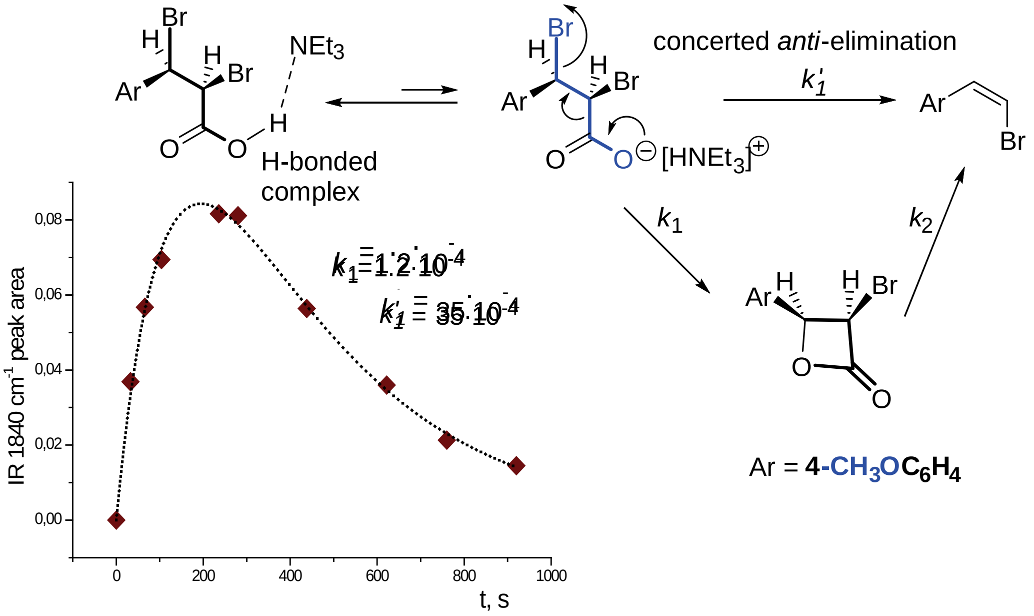
The mechanism of decarboxylative elimination was studied over 60 years ago with inorganic bases in protic solvents.[1] It was proposed that Z-β-bromostyrenes result from concerted *anti*-fragmentation. An alternative mechanism with intermediate β-lactone is also considered in the literature. Nowadays this reaction remains a popular means to prepare β-bromostyrenes but is usually performed with Et_3N in DMF, which strongly improves its Z-selectivity.

We studied the effect of amine base, added water and tetraalkylammonium salts on the rate and Z/E-selectivity of decarboxylative elimination of 2,3-dibromo-3-arylpropanoic acids in DMF. The addition of common ion salt, $[Bu_4N]Br$, did markedly improve the Z-selectivity, while even 1% of water resulted in increased formation of E-isomer. β-Lactones were detected by IR and NMR but kinetic analysis showed that β-lactones are not intermediates, but side products in decarboxylative elimination.



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P-30

HALOGENOPHILIC REACTIONS OF$[Re(CO)_5]^-$ AND $[Mn(CO)_5]^-$ANIONS WITH DIODOACETYLENE PROCUCING SQUARIC ACID ANION COMPLEX

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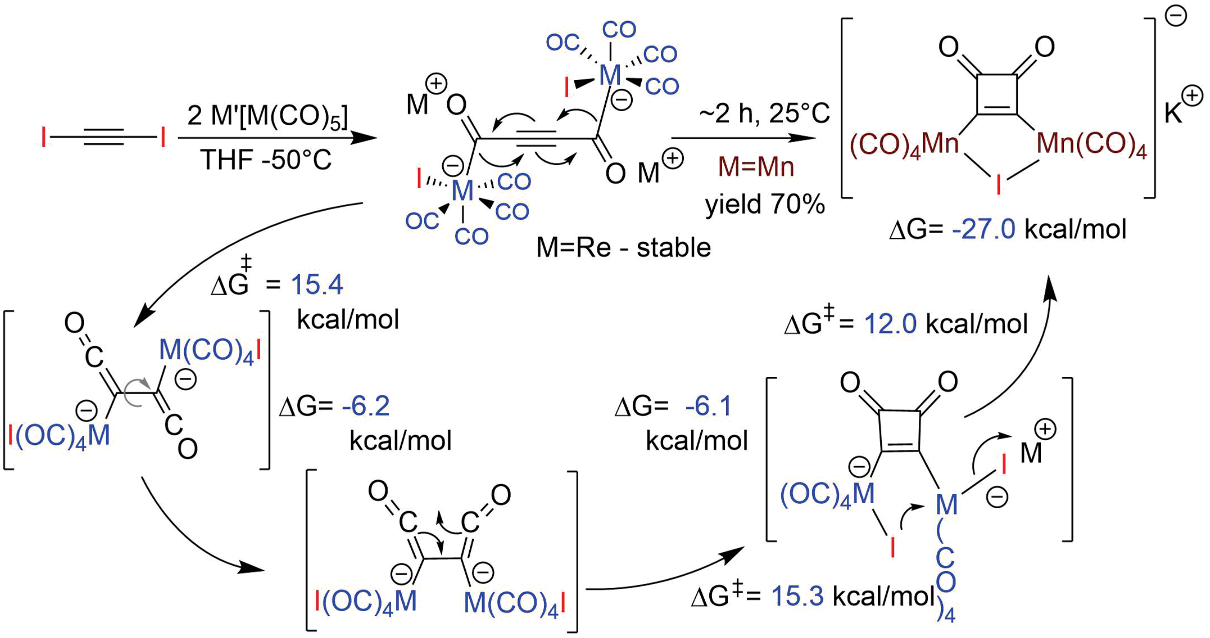
Metal carbonyl anions are excellent halogenophilic agents in the reactions with with various polyfluorinated and non-fluorinated vinyl and aryl halides.[1] However,halogenophilic substitution with carbonylmetallate anions in haloalkynes are far less explored, being limited to Cr, Mo and W-centered anions.[2]

We have studied the reactions of $[Re(CO)_5]^-$ and $[Mn(CO)_5]^-$anions with diiodoacetylene and found that initially they both form the *bis*-iodo-acylmetallate complexes, which proves the halogenophilic pathway of the reactions. Manganese complex rearranges in solution to give a new bis-manganate with a bridging cyclobutenedione ligand, analogous to squaric acid anion. Based on the results of DFT calculation (PBE/3Z) the mechanism of the rearrangement is proposed to include 1,2-shift of $[IMn(CO)_4]$ group and electrocyclization of *bis*-ketene intermediate.



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P-31

ORIENTED EXTERNAL ELECTRIC FIELDS AFFECT RATE AND STEREOSELECTIVITY OF ELECTROCYCLIC REACTIONS. A COMPUTATIONAL DFT STUDY

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Oriented External Electric Fields (OEEFs) can modify kinetics and thermodynamics of chemical reactions. Computational studies showed how OEEFs may affect the rate, the mechanism, the regioselectivity and the stereoselectivity of different organic reactions.[1,2] The experiment of Aragones et al.,[3] based on scanning tunneling microscopy, paved the way for the extensive use of OEEF in the "real world" of catalysis.

In this work we explore the impact of OEEFs on a model system: the conversion reaction of 3-substituted cyclobutene to butadiene, with variable functional groups. In particular, the impact OEEFs on the stereochemical output has been investigated. This electrocyclic reaction is depicted as being concerted and the understanding of its mechanism represents one of the most important and popular results of Woodward-Hoffmann (WH) rules.

OEEFs modify the energy and the geometry of various critical points along the reaction surface. At high OEEFs values, we observed i) strong catalytic effect along the favoured reaction channel or ii) the switch to an alternative reaction channel (Figure 1), depending on the nature of the substituent groups on the cyclobutene ring and on the intensity and orientation of the applied OEEFs.

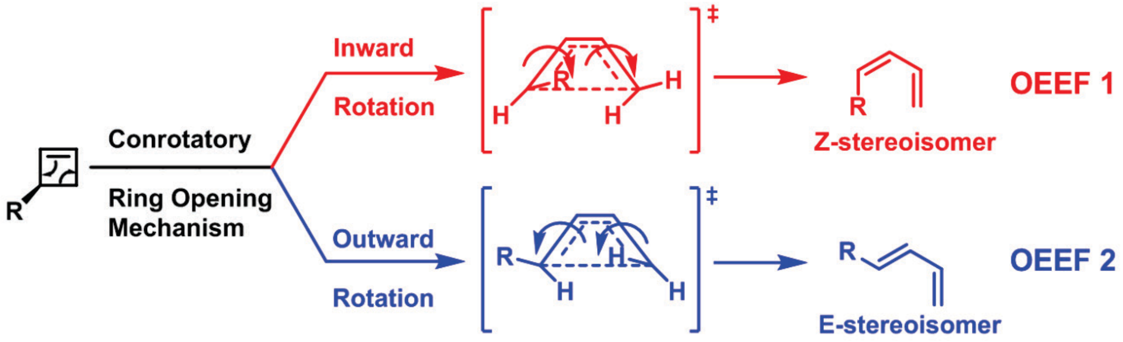

Figure 1. Reaction mechanism is split in two pathways which imply different products. OEEFs define which pathway will be followed.

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P-32

SOLVENT EFFECTS ON THE IN-CAGE REACTIONS IN THE PHOTOSOLVOLYSIS OF 2-OCH$_2$PH-3-OME-NAPHTHALENE

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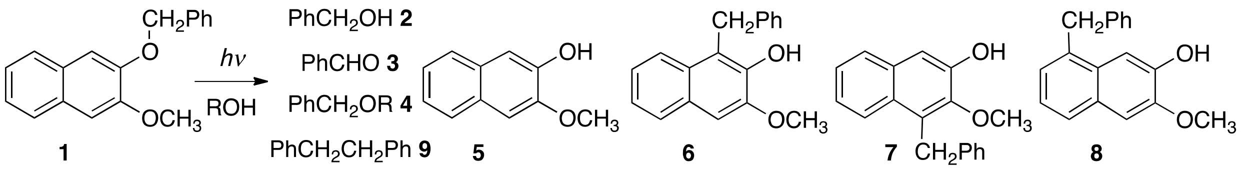
Irradiation of 2-OCH$_2$Ph-3-OMe-naphthalene (**1**) in MeOH exhibits cleavage of benzyl ether bond, resulting benzylalcohol (**2**), benzaldehyde (**3**), benzyl methyl ether (**4**), and 2-OH-3-OMe-naphthalene (**5**) in very low yields. The major products were 2-OH-3-OMe-naphthalenes with benzyl group at 1-, 4-, or 8-position (**6**, **7**, or **8**, respectively), which were resulted from the in-cage recombination of benzyl and naphthoxide moieties derived by the benzyl ether bond cleavage. The evacuation of O_2 from solution reduces the yields of 2 and 3, with minor formation of bibenzyl (**9**) but did not affect the yield of other products. The result indicates **2**, **3**, and **9** were obtained through benzyl radical. The fifty hours irradiation of **1** in benzene solution did not afford any apparent products, suggesting that **6**, **7**, and **8** were obtained by the electrophilic aromatic substitution between benzyl cation and naphthoxide anion within in the solvent cage. Solvent effects on the photosolvolysis products were subjected by using HLPC chromatography (Table 1) to see if out-of-cage reaction could be facilitated by increasing solvent ionizing ability. Photosolvolysis in H_2O, which has the same nucleophilicity and higher ionizing ability compared to MeOH, greatly enhances the yield of out-of-cage product **4** with decrease of **5**. On the other hand, the photosolvolysis in TFE, of which ionizing ability is the same as H_2O but is much less nucleiphilic, exhibited nearly the same yield of **6** with slight increased yields of **7** and **8**.

Table 1. In-Cage Reaction Product Yields in the Photosolvolysis of **1**

Solvent	Irrad	**5**	**6**	**7** + **8**
MeOH	40 min	2.5 %	34.0 %	8.0 %
TFE	30 min	13.1 %	35.2 %	4.9 %
H_2O	4 h	52.4 %	20.9 %	0.0 %



P-33

KINETICS OF RING-OPENING REACTIONS OF ELECTROPHILIC CYCLOPROPANES

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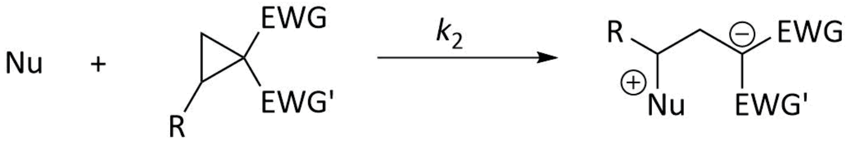
Ring opening of acceptor-substituted cyclopropanes with various nucleophiles is a useful approach to achieve an 1,3-substitution pattern.[1,2] The resulting homologous Michael adducts can often be used for subsequent reactions like cyclizations, depending on the nucleophiles and the acceptor groups.



$$\lg k_2\ (20\ °\text{C}) = s_N\,(N + E) \qquad (1)$$

The ring-opening reactions were monitored by UV-Vis spectroscopy at 20 °C in acetonitrile or DMSO. In general, the attack of the nucleophiles at the electrophilic cyclopropanes followed second-order kinetics. The corresponding second-order rate constants k_2 were then applied in Eq (1) along with the known nucleophilicity parameters N and s_N of the employed nucleophiles to determine the electrophilicity parameters E of the cyclopropanes.[3,4]

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AMBIPHILIC REACTIVITY OF DIMETHYL DIAZOMALONATE

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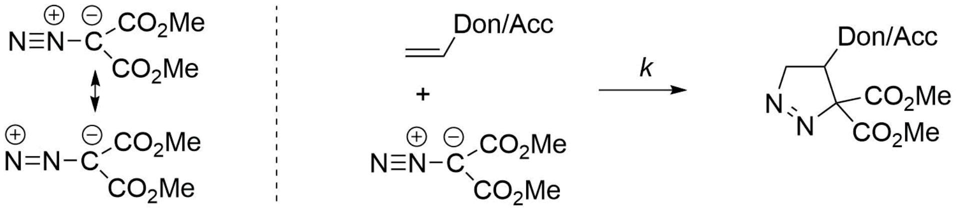
Countless formations of new C–C or C–X bonds proceed through combinations of nucleophiles with electrophiles. Kinetic investigations of reactions between electrophiles and nucleophiles in various solvents have shown that such reactions, in which only one new bond is formed in the rate-determining step, generally follow Equation (1).[1]

$$\lg k(20\ °\mathrm{C}) = s_\mathrm{N}(N + E) \qquad (1)$$

Equation (1), in which E is an electrophilicity, N is a solvent-dependent nucleophilicity, and s_N is a nucleophile-dependent sensitivity parameter, turned out to be reliable tool for predicting rate constants and differentiating reaction mechanisms of electrophile-nucleophile combinations.

Interestingly, dimethyl diazomalonate (DDM) is ambiphilic (Scheme) and acts as a carbon-centered nucleophile as well as a nitrogen-centered electrophile. Furthermore, DDM undergoes 1,3-dipolar cycloadditions with a wide range of dipolarophiles.[2]



Scheme Resonance structures of DDM and its reaction with dipolarophiles, electrophiles or nucleophiles.

The nucleophilicity (N, s_N) of dialkyl diazomalonates have already been determined.[3] We now set out to characterize the electrophilic reactivity of DDM by following the kinetics of its reactions with enamines by NMR techniques. The now available set of E, N (and s_N) parameters for DDM will be used to analyze the mechanism of further reactions, which lie in the range between the extremes of the unambiguous electrophilic or nucleophilic behavior of DDM.

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P-35

GEM-DIFLUORINATION OF TERMINAL ALKYNES USING ELECTRO-GENERATED ACID

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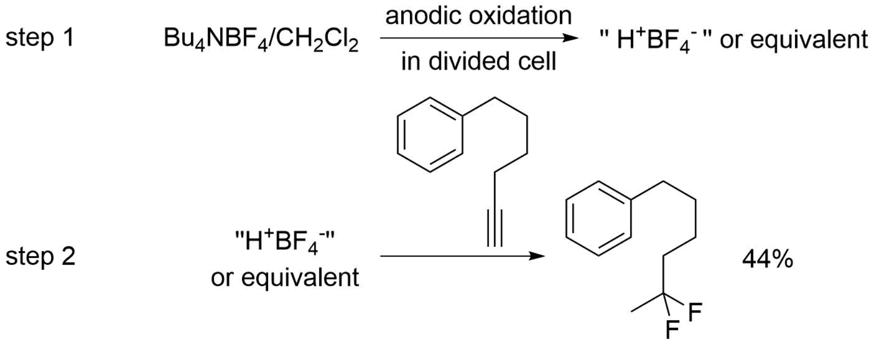
The synthesis of the organo-fluorine compounds is one of the important and challenging research topics. Among them, the introduction of two fluorine atoms toward carbon-carbon triple bond at *gem*-position is attractive for the preparation of the difluorinated molecules. So far, there have been some reports for the synthesis of *gem*-difluorinated compounds from carbon-carbon triple bonds, in which the chemical reagents such as $(HF)_n$/pyridine and HF/DMPU complex with Au catalyst have been employed.[1] However, these methods require dangerous reagents or expensive catalyst. In order to overcome these problems, we have focused on the use of the electro-generated acid (EGA), which can be prepared by the oxidation of Bu_4NBF_4/CH_2Cl_2. Herein, we wish to the report the electrochemical-generated acid promoted the *gem*-difluorination of the terminal alkynes.

The electrochemical oxidation of Bu_4NBF_4/CH_2Cl_2 in the divided cell was carried out to generate and accumulate the EGA, in which $H^+BF_4^-$ or its equivalent was assumed (step 1). In the step 2, thus accumulated EGA was allowed to react with the terminal alkyne bearing the aromatic ring shown in Scheme to give the corresponding *gem*-difluorinated compound in 44% yield (*ex-cell* method). The procedure of the direct electrochemical oxidation of the solution of Bu_4NBF_4/CH_2Cl_2 containing the substrate was also effective to drive reactions (*in-cell* method). In the presentation, the scope and limitations of alkynes and reaction mechanism will be discussed.



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P-36

REACTION ROUTE FOR ALLYLIC ARYLATION IN WATER CATALYZED BY METAL NANOPARTICLES

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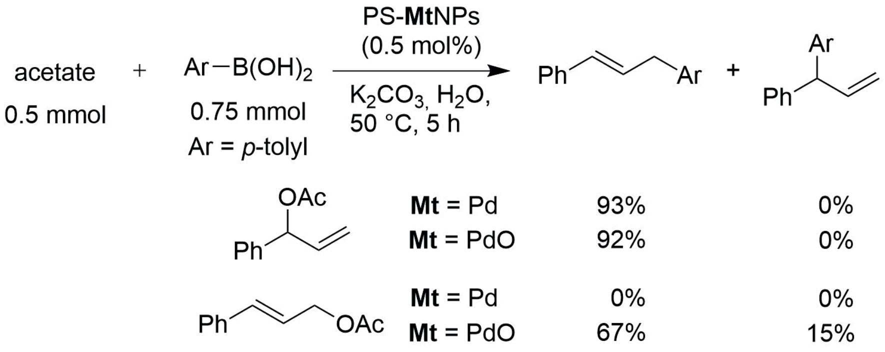
Allylic arylation of allyl substrates with boron reagents is one of the powerful tool for C-C bond formation. In general, even either linear-type substrate (e.g. cinnamyl acetate) or branch-type substrate (e.g. α-vinylbenzyl acetate) is reacted with arylboronic acids in the presence of $Pd^{(0)}$ catalyst, the same linear-type product is obtained because the reaction proceeds through the π-allyl palladium intermediate.

On the other hand, the reaction of α-vinylbenzyl acetate with 4-methylphenylboronic acid using PS-PdNPs ($Pd^{(0)}$ species) as a catalyst gave linear-type product in 93% yield although no coupling product was obtained from the reaction using cinnamyl acetate. In contrast, the reaction of cinnamyl acetate with 4-methylphenylboronic acid using PS-PdONPs ($Pd^{(II)}$ species) as a catalyst took place smoothly to afford both linear- and branch-type products in 67% and 15%, respectively. Recently we found the reaction route or the reactivity of metal NPs would be different from that in the case of a metal complex catalyst.[1] Our continuing interest in the reaction route of the catalytic reaction with metal NPs and the reactivity of metal NPs led us to examine the allylic arylation in water using PS-PdNPs and PS-PdONPs as the catalyst.



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P-37

THE ENHANCEMENT OF THE ANTITUMOR EFFECT OF TEMOZOLOMIDE ON GLIOBLASTOMA CELLS BY NOVEL DEHYDROABIETYLAMINE DERIVATIVES

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Alexandra Zakharenko,[c] Alena Kononova,[a] Nadezhda Dyrkheeva,[c] Sergey Cheresiz,[a]
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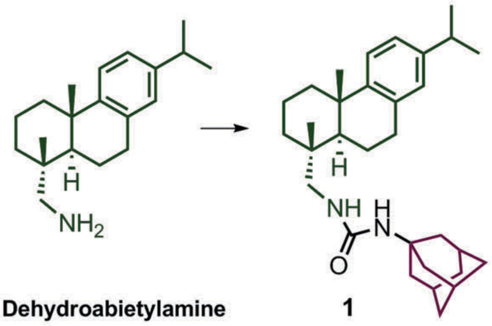
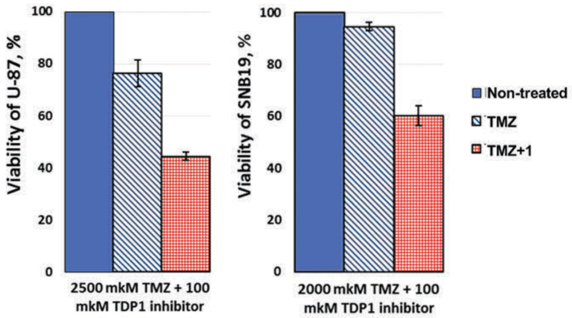
The search for the inhibitors of key DNA repair enzymes is a promising field of medicinal chemistry. The tyrosyl-DNA-phosphodiesterase 1 (TDP1) enzyme is an attractive target in antitumor therapies. TDP1 inhibition may enhance the sensitivity of tumor cells to the drugs used in the standard therapies of malignant tumors.[1] A new class of tyrosyl-DNA phosphodiesterase 1 inhibitors was found among resin acid derivatives. Several novel ureas and thioureas were prepared by interaction of dehydroabietylamine with the appropriate isocyanate or isothiocyanate and tested for TDP1 inhibition.



Dehydroabietylamine **1**



The synthesized compounds showed IC_{50} values in the range of 0.09 to 3.7 µM and demonstrated low cytotoxicity against human tumor cell lines (U-937, U-87MG, MDA-MB, A-549, WI-38, and SK-Mel8). Several compounds show the enhancement of cytotoxic activity of the alkylating agent, temozolomide, used as a first line therapy against glioblastoma (GBM), in two GBM cell lines U-87MG and SNB19.

Acknowledgement. This work was supported by Foundation by the Russian Foundation Research (N 18-33-00297).

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SYNTHESIS OF (+)-CAMPHOR-10-SULFONIC ACID AND (+)-CAMPHORIC ACID DERIVATIVES AS POTENTIAL ANTIVIRAL AGENTS

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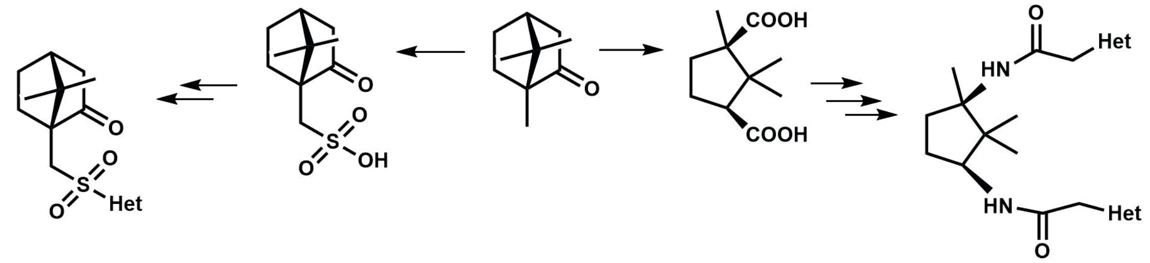
According to previously works,[1,2] it can be assumed that compounds containing a natural skeleton such as 1,7,7-trimethylbicycloheptane and a heterocyclic fragment show a good inhibitory activity against various viral infections. Therefore, in this work, (+)-camphor-10-sulfonic acid and (+)-camphoric acid were used as starting materials for the synthesis of potential antiviral agents. A modification of the starting compounds is shown in scheme 1.



Scheme 1.

Thus, a series of derivatives of (+) - camphor-10-sulfonic acid and (+) - camphoric acid was obtained. The synthesis of (+) - camphor-10-sulfonic acid derivatives was carried out through the formation of (+)-camphor-10-sulfonyl chloride, which further interacts with various nucleophiles. As a result of biological studies found that these compounds are active in the inhibition of viral infections. In the preparation of heterocyclic derivatives of (+) - camphoric acid, the first stage was the formation of the diamine, which was later used for introducing a heterocyclic fragment. Previously, these compounds have not been described. The structure of the compounds obtained was established on the basis of the ^{1}H and ^{13}C NMR spectra and high-resolution mass spectra.

Acknowledgement. This work was supported by the Russian Science Foundation (N 17-73-10153)

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P-39

COMPARATIVE STUDY OF SI-DOPED GRAPHENE AND FULLERENE IN OXYGEN REDUCTION REACTION (ORR). A QUANTUM CHEMICAL INSIGHT

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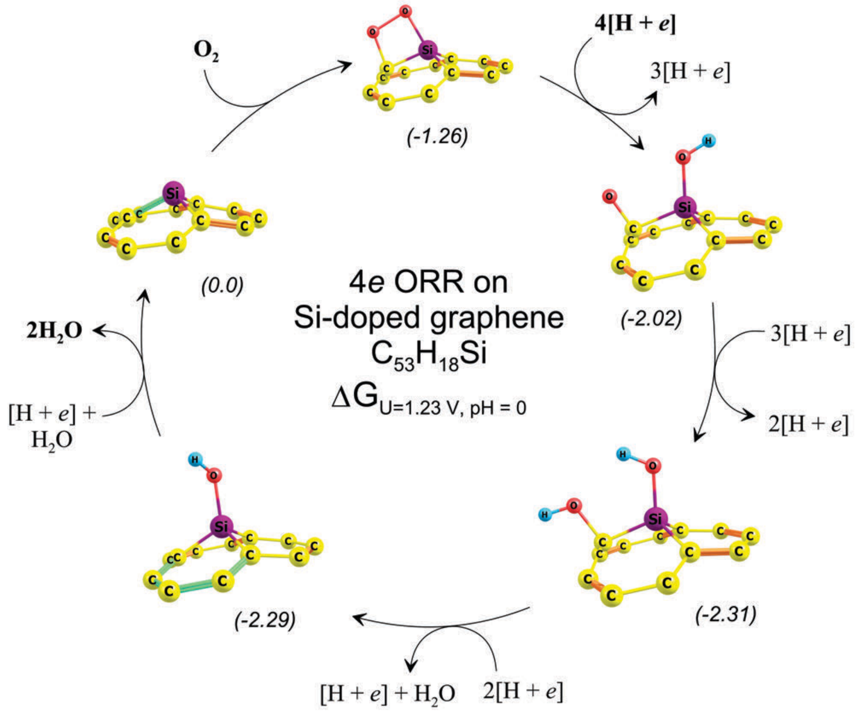
The comparative ability of the Si-doped graphene $C_{53}H_{18}Si$ and fullerene $C_{59}Si$ to catalyze the oxygen reduction reaction (ORR) in acidic and alkaline media have been studied by DFT calculations. The active sites for oxygen adsorption were determined from the distribution of the charge density difference (CDD) analysis. For the Si-doped graphene $C_{53}H_{18}Si$ the barrierless formation of the intermediate HO*–$C_{53}H_{18}Si$ was found corresponding to the transfer of three hydrogens [$H^+ + e^-$] at all overpotentials. For the Si-doped fullerene $C_{59}Si$, the global minimum has the structure HO*O*–$C_{59}Si$ generated by only one hydrogen transfer [$H^+ + e^-$] under the equilibrium potential, but shifts to the structure HO*–$C_{59}Si$ at overpotentials below 0.8 V or 0 V in acidic or alkaline media, respectively. A comparison of the 2*e* and 4*e* pathways of ORR showed a low probability of the former due to the formation of intermediates suffering the O–O bond breaking (HO*O*). According to free energy plots, the Si-doped graphene $C_{53}H_{18}Si$ has a higher catalytic activity in 4*e* ORR as compared to the Si-doped fullerene $C_{59}Si$, due to its lower adsorbance activity toward molecular oxygen and oxygen-related species.



CONFORMATIONAL SPIN SWITCHING AND SPIN-SELECTIVE HYDROGENATION OF A MAGNETICALLY BISTABLE CARBENE

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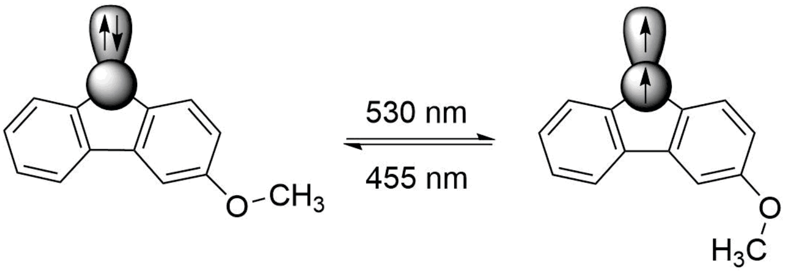
The control of the spin states of molecules opens the path to tuning selectivity in chemical reactions and to developing switchable magnetic materials. 3-Methoxy-9-fluorenylidene is a carbene that is trapped in cryogenic matrices both in its singlet and triplet states.[1] The spin states are nearly degenerate in energy, and no thermal intersystem crossing is observed. However, the ratio of these states can be shifted by selective irradiation into absorption bands of the singlet (green light) or the triplet state (blue light). The spin interconversion is induced by a conformational change of the methoxy group: switching the methoxy group into the "up" position (*u*) results in the singlet state and switching into the "down" position (*d*) in the triplet state.

Spin control makes this carbene unique for the study of spin-selective reactions such as hydrogenation.[2] In solid H_2, both the singlet and triplet state of the carbene rapidly react to give the H_2-insertion product as a mixture of the *u*/*d* conformers. In solid D_2, the singlet carbene (*u*) is stable, whereas the triplet (*d*) reacts affording the product in its *d*-conformation. Hence, the methoxy group acts as a conformational label and the reacting spin state can be traced in the products. Conformational spin switching is a novel phenomenon that can be used to study the spin dependence of reactions and has potential applications in information recording.



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P-41

PHOTOCHEMISTRY OF 2-IODOTHIAZOLE IN INERT GAS MATRICES

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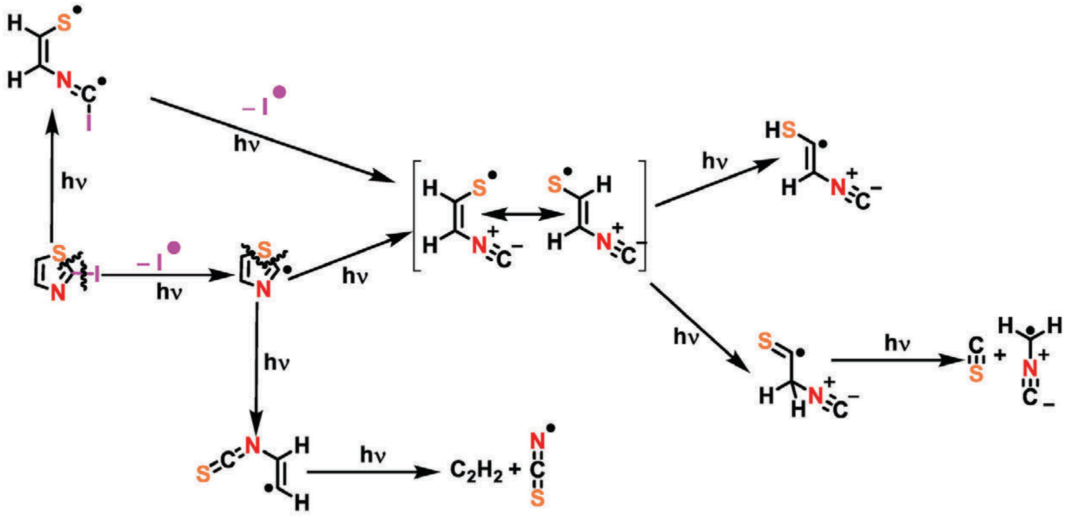
Thiazole is a biologically and pharmaceutically important heterocyclic moiety. The generation and catalysis of bio-inspired *N*-heterocyclic carbene based on thiamine molecule is well known in the literature.[1] However, the formation and reactivity aspects of simpler dehydro-radical derivatives of the thiazole have not been experimentally explored yet. Based on our groups earlier computational investigations on various thiazole radicals, the electronic structure, stability and unimolecular decomposition channels, several insights and properties of them have been investigated.[2] In particular, the kinetic stability of these radicals were found to be low. Apparently, matrix isolation and photofragmentation studies on thiazole by Miyazaki J. et al. revealed that C-S in thiazole can be cleaved easily that can lead to multiple photoproducts.[3]

In this current work, we have targeted 2-dehydrothiazole radical using its iodo precursor. Interestingly, the competition between the cleavage of C-I and the two C-S bonds under photochemical conditions will decide the photoproducts, and also their selectivity (Scheme 1). The photochemistry of 2-iodothiazole, and characterization of various photoproducts have been carried out using matrix isolation infrared spectroscopy in combination with computations. The preliminary results of this investigation will be presented through this contribution.



Scheme 1. Generation and photochemistry of 2-dehydrothiazole radical

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P-42

MAKING CARBON–PHOSPHORUS BONDS WITH VISIBLE LIGHT: CHALLENGES AND OPPORTUNITIES

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Reactions involving phosphorus centered radicals play a pivotal role in the construction of organophosphorus ligands, biologically active and π–conjugated molecules. Common synthetic approaches for the generation of such radicals imply the use of harsh reaction conditions.

In this presentation, we show that access to a large variety of organophosphorus compounds can be achieved under mild reaction conditions through: *i*) visible light photoredox catalysis or *ii*) visible light irradiation of Electron–Donor-Acceptor complexes (EDA). The scope and limitations of these methods will be discussed with a special focus on their mechanistic aspects.

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P-43

ELECTRON TRANSFER REACTIONS AT CRYOGENIC TEMPERATURE

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According to the IUPAC Gold Book, solvated electrons are free electrons, which are not bound to any particular nucleus. Discovered and reported by radiation chemists, the solvated electrons provide a great potential for interpreting reaction mechanisms in chemistry. In 1884, Weyl[1] reported solvated electrons for the first time formed by dissolving sodium in liquid ammonia, which resulted in a blue colored solution. Since, plenty of research has been carried out in this field and showed that the generation of solvated electrons can be achieved by several methods such as irradiation of solvents, deposition of alkali metals on organic glasses of polar solvents and pulse radiolysis of alkali halides.[2–4] Our approach is aimed at trapping free electrons by solvating sodium in reactive matrices in the presence of electron scavengers (CH_2Cl_2, C_6H_5Cl) and to perform electron transfer reactions at cryogenic temperature using the matrix isolation technique.

$$\mathrm{Na} \xrightarrow{\text{Solvation}} \mathrm{Na}^{\oplus} + \mathrm{e}^{\ominus}$$

$$\mathrm{CH_2Cl_2} + \mathrm{e}^{\ominus} \longrightarrow \dot{\mathrm{C}}\mathrm{H_2Cl} + \mathrm{Cl}^{\ominus}$$

In the present work, we successfully deposited sodium in argon as well as in low-density amorphous (LDA) water, methanol and ethanol ices. In case of argon, isolated sodium atoms are observed, whereas in case of polar solvent matrices solvated electrons with an intense blue color are observed and characterized using electron spin resonance (ESR) spectroscopy. Köppe et al. observed spontaneous transfer of electron from sodium to molecules during collision in space or in a fluid surface layer of the matrix during deposition, if the electron affinity of the acceptor molecule is sufficiently high.[5] This phenomenon was also observed in our case when sodium is co-deposited with argon doped with dichloromethane (DCM). We also observed transfer of electrons in argon without solvation of sodium by water by photolysis with visible light. As a follow up, transfer of electrons to electron-deficient organic molecules like cations or radicals is currently under investigation.

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P-44

CATALYSIS BY PURE GRAPHENE - FROM SUPPORTING ACTOR TO PROTAGONIST THROUGH π-π INTERACTIONS

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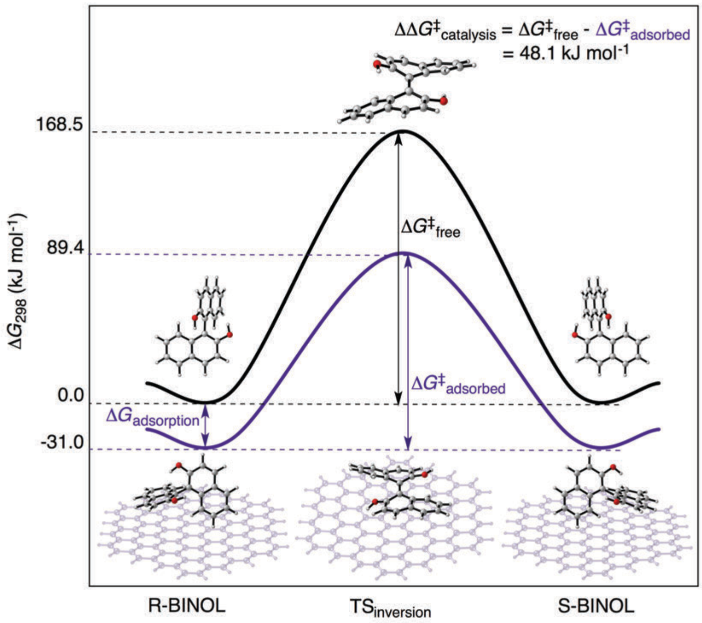
Graphene, a honeycomb lattice consisting purely of carbon, has been extensively studied for its numerous exceptional properties.[1] While its ability to non-covalently bind ground state molecules has been well studied and led to applications in sensors and extraction devices,[2] this principle remains surprisingly unexplored for transition structures. Given the current interest in metal-free catalysis,[3] expanding the application of this concept to transition structures has the potential to open up opportunities for applications of graphene as a catalyst. Herein, we explore the possibility to lower the activation energy of a chemical process purely through stabilizing π-π interactions between transition structure and graphene on the simple example of binaphthyl racemizations. We demonstrate a significant collective catalytic potential of multiple π-π interactions and show up transition structure shape complementarity with a carbon nanomaterial as a potential alternative strategy towards reducing reaction energy barriers.



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P-45

ACTIVATION OF AMMONIA BY TRIPLET ARYLCARBENES

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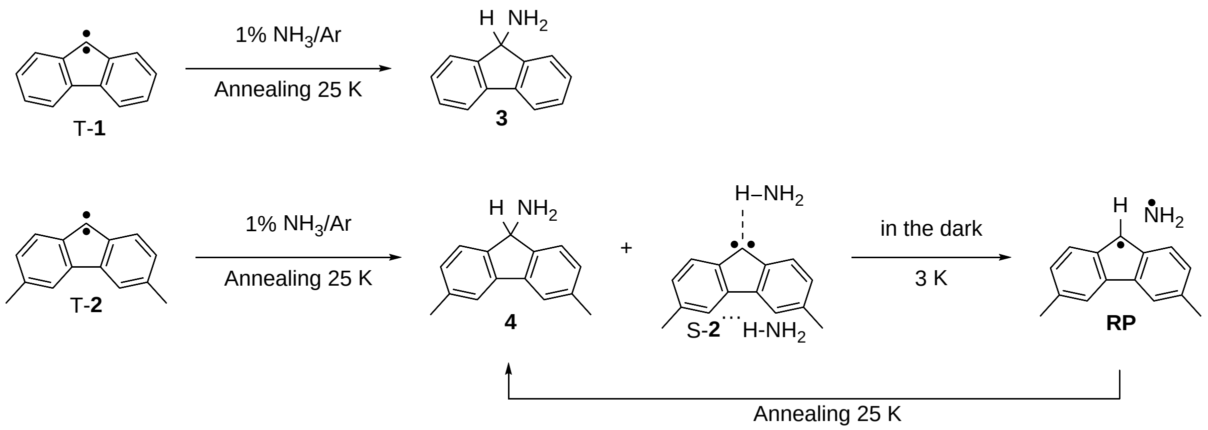
While activation of hydrogen has become one of the fundamental processes in chemistry, activation of ammonia remains particularly difficult due to its affinity to form stable Lewis acid-base complexes with transition metals, also referred to as "Werner-type" complexes.[1,2] Up to date, there are only few systems known to be able to activate ammonia, among them carbenes.[1] However, only reactions of singlet ground state carbenes with ammonia are reported so far. In this study, the reaction of two triplet ground state carbenes, namely fluorenylidene **1** and 3,6-dimethylfluorenylidene **2**, with ammonia is studied using the matrix isolation technique. While Carbene **1** directly forms the insertion product **3** in 1% NH_3-doped argon matrix upon annealing, carbene **2** forms not only the insertion product **4** but also the singlet hydrogen-bonded ammonia complex S-**2**···H-NH_2. It is metastable and rearranges to 3,6-dimethylfluorenyl radical **RP** in the dark at 3 K. Annealing of the matrix containing **RP** results in the formation of the corresponding amine **4** via radical recombination. The difference in reactivity is rationalized by the larger singlet-triplet gap of **1**; ammonia does not stabilize the singlet state of **1** below its triplet state by hydrogen bonding.



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P-46

NON-IDEALITY IN IONIC LIQUID MIXTURES AND THE POTENTIAL FOR RATIONAL CONTROL OF REACTION OUTCOME

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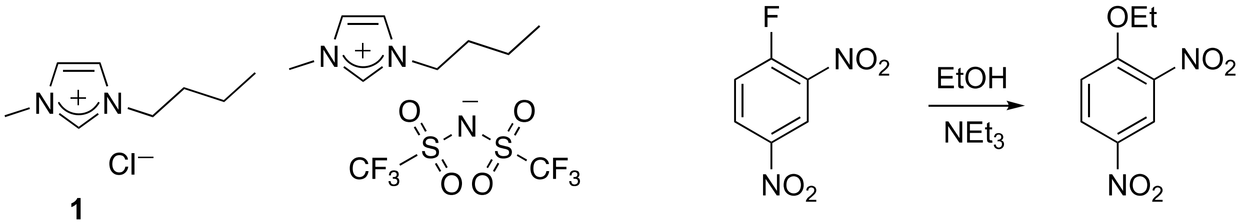
Significant data have been accumulated on the origins of solvent effects in ionic liquids. With these data available, such solvent effects can be reasonably predicted based on an understanding of the microscopic interactions in solution[1] and hence a particular ionic liquid chosen to give a desired reaction outcome.[2] All of the work so far has covered the solvent effects of ionic liquids containing only one type of cation and one type of anion. There is the potential to vastly expand the range of ionic liquids available through using combinations of multiple cations and multiple anions, however the effects of such mixtures on even physical properties are poorly understood.[3]

The work described will build on initial single point analyses[4] and focus on the effects of mixtures of the ionic liquids **1** and **2** on the ethanolysis of the activated benzene **3** (Scheme 1). This reaction is well-described in a range of individual ionic liquids[5] and serves as the ideal starting point to consider (non-)ideality of the effects of mixtures on reaction outcome, with the potential to vastly increase the effectiveness of ionic liquids.



1 **2** **3**

Scheme 1. Ethanolysis of the benzene **3** examined in mixtures of salts **1** and **2**.

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P-47

KINETIC ANALYSES TO DRIVE SOLVENT CHOICE – SELECTING AN IONIC LIQUID TO GET THE DESIRED SYNTHETIC OUTCOME

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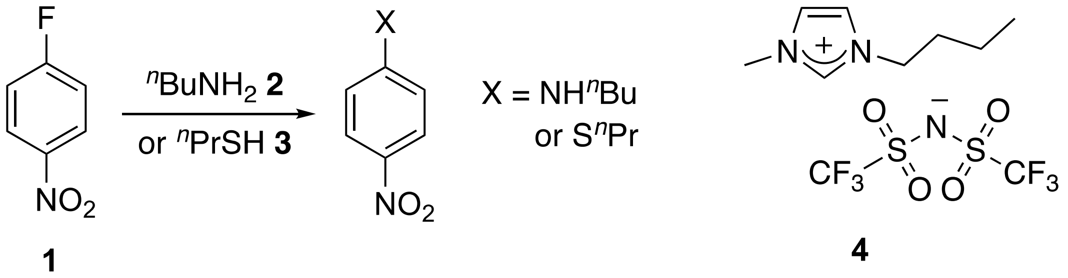
Whilst initially the solvent effects of ionic liquids seemed unusual relative to those effects in molecular solvents,[1] through considering the microscopic interactions in solution involving the ionic liquid components, these solvent effects can now be reasonably understood and predicted.[2] However, these effects are yet to be extensively exploited in a synthetic sense. Ideally, an understanding of how ionic liquids affect the rates of multiple different processes can be applied to choosing a solvent to favour one process over another.

Previous work has demonstrated ionic liquids having different effects on the rate constants of different reaction pathways,[3] however it is the understanding of the reaction of benzene **1** with each of the nucleophiles **2** and **3** in ionic liquids such as the salt **4** (Scheme 4) that provides significant opportunity for synthetic application.[4] The rate of reaction of the amine **2** is enhanced in low proportions of the ionic liquid **4** in the reaction mixture, whilst the thiol **3** rate constant is most increased at high proportions of the salt **4**. The work described will discuss rational selection of solvent, time and temperature to maximise this selectivity in a practical sense.



Scheme 1. Ethanolysis of the benzene **3** examined in mixtures of salts **1** and **2**.

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