Book of Abstracts

18th Conference on Physical Organic Chemistry

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Table of Contents

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Welcome address

Dear Colleagues and Friends,

On behalf of the Organising Committee we have great pleasure to welcome you to the 18th International Conference on Physical Organic Chemistry in Warsaw, Poland. It is delightful that so many leading researchers in the field of broadly understood physical organic chemistry are participating in the Conference, thus making ICPOC–18 one of the main scientific events this year.

Physical organic chemistry is a branch of organic chemistry that was born in the thirties of the 20th century and at the beginning it was mainly concerned with mechanisms and kinetics of organic reactions – and their dependence on structural and medium effects. The famous monograph by Louis P. Hammett entitled "Physical Organic Chemistry" was published in 1940 and may be considered as a landmark in the development of this field of research. Typically the research in physical organic chemistry was associated with an inclination to build up some empirical models which in a quantitative form allowed the investigator to interpret a vast amount of numerical data on kinetics, equilibria, and later, also other physicochemical, biochemical, medical, pharmaceutical and technological properties of organic systems. The early empirical equations and approaches should be mentioned here, such as:

The Hammett equation (1940) and its numerous modifications, the Taft and Charton works on separation of particular mechanisms acting in substituent effects; numerical estimation of the exaltation of substituent effect by use of the Yukawa – Tsuno equation.

The Grunwald – Winstein approach (1948) describing solvent effects, then extended by Kosower, Dimroth and Reichardt, multiparameter relations by Palm and Koppel later modified by Kamlet, Taft and their coworkers.

The relationships dealing with the correlation of reagent changes as the Broensted catalysis equation (1924), the Swain – Scott and the Edwards equations, dealing with the nucleophilic and electrophilic reagents and their efectivness in chemical reactions, recently developed by the reasearch group of Herbert Mayr.

Rapid development of spectroscopic techniques has extended the application of empirical approaches such as those mentioned above onto the data from UV/Vis, IR, Raman as well as NMR spectroscopies and other physical and physicochemical methods of investigation of organic systems. For many years structural chemistry with its diffraction techniques has been an important field of research supporting better understanding of the relations between structure and reactivity, or to put it more broadly physicochemical and biochemical properties. Many works in QSAR and related methods are also strongly related to the ideas originating from physical organic chemistry. The role of intermolecular interactions, including H-bonding, is also subject of interest for many physical organic chemists, similarly as problems of stability of chemical species including definition of aromatic stability and many other properties associated with aromatic character.

For decades now many significant works have been accomplished by applying of quantum chemical modelling. They are showing how old ideas may be now reinterpreted and refined by purely computational means. But the most spectacular progress within last years is achieved in biological applications of physical organic chemistry.

As a result of the development and expansion the field of research in physical organic chemistry, one of the leading journals in this branch, Journal of Physical Organic Chemistry focuses attention on the following fields: organic chemistry, bio-organic chemistry, organometallic chemistry, theoretical chemistry, catalytic chemistry, photochemistry, supramolecular chemistry, reaction mechanisms, reactive intermediates, novel structures, reactivity relationships, solvent, substituents, isotope and solid state effects, long-lived charges, sextet or open-shell species, magnetic, non-linear optical and conducting molecules, molecular recognition, weak interactions, molecular machines.

Undoubtedly, rapid development in research in the above mentioned branches of chemistry is associated with an important contribution of physical organic chemistry to the development of technologies leading to the general improvement of everyday life. It is one of the primary aims of the International Union of Pure and Applied Chemistry to support this kind of activity all over the world. Our Conference is one of many fields of IUPAC activities and we feel happy that we can contribute to this - as the organizers as well as participants of the ICPOC-18 Conference.

The most recent results of many of the above mentioned branches of physical organic chemistry will be presented at our conference. We are sure that this meeting of so many distinguished scientists will be fruitful not only as concerns scientific development but also will create new friendships and new cooperations.

We would like to highly acknowledge all institutions and companies which have supported us financially, especially the Polish Ministry of Science and Higher Education, Warsaw University and the Department of Chemistry of our University, Pharmaceutical Research Institute.

Finally, we would like to thank to our closest coworkers Dr Michał Cyrański, Dr Beata Stępień and Mrs Joanna Zachara–Horeglad, who have taken care of all details during organisation of this Conference. Without their extremely hard work, their dedication and devotion this Conference could not be organized. We also wish to acknowledge help of other coworkers: Professors Jan Jaworski, Aleksander Koll and Andrzej Kutner as well as Mrs Paulina Rogowska and Mr Michał Dobrowolski. We wish to convey them all our sincere thanks for their great contribution to the organisation of the Conference.

We hope that all of you will enjoy the Conference and time spent in the capital city of Poland. We wish you very fruitful participation in the Conference.

Tadeusz Marek Krygowski and Krzysztof Woźniak

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Practical Informations

Conference Reception

The Conference Reception is located near the Crystal Lecture Hall in the Gromada Hotel. The Registration desk will be open at the following hours:

Sunday, August 20: 12.00-19.30

Monday, August 21: 8.30-18.00

Tuesday, August 22: 8.30-16.30

Wednesday, August 23: 8.30-16.30

Thursday, August 24: 8.30-14.00

Friday, August 25: 8.30-13.00

Lunches are included in the registration fee and will be served in the Bakata Restaurant at the Hotel Gromada.

Warsaw

The beginnings of settlement in the Valley of Warsaw are dated to the tenth century. At the end of the thirteenth century, in the area where the Royal Castle stands, a new princely town was founded, that is, today's Warsaw. The earliest note about Warsaw appears in written records from 1313. After Mazovian Princes had died heirless, Mazovia was incorporated into the Polish Crown. Since 1569, it had been a place where sessions of the Sejm (Parliament) of Rzeczpospolita (the Joint Polish-Lithuanian Commonwealth) were held. After the fire of the Wawel Castle, King Sigismunt Waza III transferred permanent royal residence, courts and the Crown's offices from Cracow to the extended Warsaw's Royal Castle. In the seventeenth century, wars, disturbances and plagues brought on a slump in the economic growth of the town. In years 1655 – 1658 was Warsaw besieged, conquered and occupied three times by the Swedes. In the Sas dynasty reign, after the political situation had settled down, Warsaw regained its status of an important cultural centre. The next golden age of the capital city spins the years of the reign of the last King of Poland, that is, Stanisław August Poniatowski. At the end of the 18th century **Polish Constitution of May 3, 1791 was established in Warsaw**. Preceding the French September Constitution by several months, it was the Europe's first modern codified national constitution, and the world's second after the United States Constitution. The Constitution established three independent branches of government - executive, legislative and judiciary and introduced political equality between townspeople and nobility, while the peasants were placed under the protection of the government. Throughout the Constitution run the philosophy of humanitarianism and tolerance, such as perfect and entire liberty to all people, rule by majority, secret ballot at all elections, religious freedom and liberty. The Constitution influenced later democratic movements in the world. Soon after, in 1795, the third partition of Poland took place and the country disappeared from the map of Europe for 123 years. Through this period Warsaw was downgraded to the rank of the Russian province. Despite a disadvantageous political atmosphere, the town and its industry kept developing. In 1918, Warsaw became the capital city of reborn Poland. The process of tidying it up became especially intense during the presidency of Stefan Starzyński. It was however brutally interrupted by the outbreak of World War II and the German occupation. Warsaw was defended till 28 September

1939. Again, the city became the main centre of Resistance and conspiracy. The April of 1943 witnessed the outbreak of an uprising in the walled off Jewish Ghetto. After it had come to an end, the Jewish quarters with half a million people ceased to exist. On 1 August 1944, the Warsaw uprising organised by the Home Army broke out. The Honorary Capitulation Act was signed on the 2 October. After the uprising had been quashed, Warsaw was condemned to annihilation. Its citizens were exiled and transported to nazi concentration camps. The Germans started to destroy the city through systematic bombardments and approximately 85 per cent of buildings were destroyed. The process of rebuilding Warsaw started immediately in 1945. Today the capital city of Poland, which was to be erased from the map of Europe, is reborn and throbbing with life.

Scientific Programme

The scientific programme of the Conference comprises 8 plenary lectures, 19 invited lectures, 57 oral communications and 100 poster presentations, which cover the following topics:

Symposium 1: Structure vs. Chemical Properties and Biochemical Functions

The symposium covers the analysis of relation between structure and chemical properties and biochemical function, including those related to enzyme-catalyzed reactions, self-replicating systems and self-assembly of nanoobjects, genetic selection, chemical modulation of cell-surface architecture, mechanism of protein unfolding, thermodynamics and kinetics of chemical reactions important for biological reasons.

Symposium 2: New Machines and Materials, New Processes and Interactions

The symposium covers from one side the topics related to nanotechnology, including lectures on molecular-level devices, different new supramolecular objects, catenanes and rotaxanes, dendrymers, synthesis and operation of molecular motors and switches, millimeter-scale selfassembly and potential applications, new magnetic materials, new optoelectronic materials, and from the other side the topics related to chemical reactivity, new approaches to intermolecular recognition and interactions, solution reactivity and structure, catalysis of electron-transfer processes, organometallic reactive intermediates, different catalytic processes, surface processes, activation of molecules, femtochemistry and similar topics.

Two lecture halls will be used throughout the conference

1. Crystal Lecture Hall
2. Garnet Lecture Hall

Both lecture halls are located on the Reception floor of the Gromada Hotel. The total time assigned to each oral presentation is indicated in the programme. **Since the timetable is tight speakers and chairmen persons are urged to adhere strictly to the schedule.**

Poster presentations will be displayed in the **Coral Hall** in close proximity of both lecture halls. Two sessions are scheduled and the authors must present their posters as follows:

Poster Session I – Tuesday, August 22nd, 19.30-21.00 (posters I-1 to I-50)

Poster Session II – Wednesday, August 23rd, 19.30-21.00 (posters II-1 to II-50)

Posters should be mounted on Monday morning and removed on Thursday. Please check the number of your board in the Book of Abstracts. **All active participants are welcomed to take part in a secret ballot to award the best poster. Special voting cards will be given with the conference materials.**

Publication of the Scientific Contributions

A selection of papers based upon the scientific proceedings will be published in a forthcoming issue of the official IUPAC Journal 'Pure and Applied Chemistry'.

Social Programme:

The scientific program of the ICPOC-18 conference will be complemented by a range of social events, including Welcome Reception, Chopin Recital, the Conference Excursion and the Conference Dinner:

Sunday, August 20th

A welcome reception will be arranged in the Bakata Restaurant at Gromada Hotel. All participants and accompanying persons are cordially invited.

Time: 19.30-21.30

Monday, August 21st

The Chopin Recital by Mr Bartłomiej Kominek will be arranged in the Crystal Lecture Hall at Gromada Hotel. The concert is organized in cooperation with Towarzystwo im. Fryderyka Chopina (The Frederick Chopin Society). All participants and accompanying persons are cordially invited.

Time: 20.30-21.30

Thursday, August 24th

Conference Excursion. Includes: **Warsaw Old Town** and the **Royal Palace**, visit to the **Restaurant "U Dekerta" or “Trou Madame”** and the **Łazienki Palace**. The Old Town is by far the most attractive area of Warsaw. After the II World War it was beautifully rebuilt and entered in the World List of Cultural and National Heritage of UNESCO. The Warsaw Old town impresses tourists with its quaint, cobbled streets and unique old architecture. The heart of the area is the Old Town Market Square with its unique traditional Polish restaurants, cafes and shops. When the weather is warm the square becomes filled with cafe tables, various traders and street artists. Surrounding streets feature old architecture such as City Walls, The Barbican and St. John's Cathedral. The pride and joy of Warsaw's Old Town is the Royal Castle and its surrounding square, "Plac Zamkowy" in the local tongue. As all of its fellow Old Town (re)constructions, the Castle stands as a testament to the city's phoenix-like resilience. Originally a medieval residence of the Mazovian Princes, the Royal Castle in Warsaw had a number of occupants across the ages: the Polish kings from 1526 to 1795, the Sejm (Parliament) until 1569, again the monarchs and the Sejm at the time of the Dukedom of Warsaw and the Congress Kingdom, followed by the management of the National Holdings of Art from 1922 and the President of the Polish Republic from 1926. Restored and furnished with repossessed furniture and works of art, it was partly opened to visitors in 1922-39. Destroyed by the Nazi in 1944, it was rebuilt in 1971-84. The Łazienki Palace, the private residence of the last king of Poland, stands on an island situated in the park centre. The royal park is one of the most magnificent palace-park complexes in Europe.

Time: 13.30-19.30

Price: 50 Euro. The price includes: the coach, English speaking tour-guide, entrance card to the Royal Castle and Łazienki Palace, tour-guide to the Royal Castle and Łazienki Palace and entertainment in the restaurant "U Dekerta" or “Trou Madame”, where snacks will be served for visitors.

The conference dinner followed by a concert of Polish folk music and dance, performed by Promni Ensemble, to be held in the Emerald Hall at Gromada Hotel. Ticket costs 70 Euro and may be purchased at the Registration Desk till Tuesday noon. Participants who have already purchased their tickets will receive them together with the Conference Materials.

Time: 20.30-22.00

Accompanying Persons’ Programme:

Accompanying persons are invited to participate in the conference social program given above. In addition special programme for accompanying persons will be organised:

Monday, August 21st. Wilanów Palace, 3 hour tour. The tour will take you to the interiors of the Wilanów Palace, the Baroque residence of King John III Sobieski, the famous conqueror of the Turks at the battle of Vienna in 1683. He was the most colourful personage of 17th century Poland, a great army leader and accomplished diplomat. The palace, surrounding park and other premises have survived bad fortunes of wars and foreign occupation of Poland. They remained intact and retained their genuine historical and artistic merits to become one of the most cherished parts of the Polish cultural heritage. Price: 20 Euro.

Tuesday, August 22nd. In the footsteps of Frederick Chopin, half-day tour. The morning tour features the most important sights in Warsaw and surroundings, related to Chopin and his music and departure to Żelazowa Wola – Frederick Chopin’s Birthplace. Visit to Chopin’s family manor house, surrounded by beautiful park. This will be an excellent opportunity to listen to a regular summer Chopin’s music concerts in Żelazowa Wola. Transfer back to Warsaw. Upon arrival lunch at a local restaurant. Then visit to the Holly Cross Church, where the heart of Chopin is placed. The tour will end in the Ostrogski Palace housing Chopin Museum and Frederick Chopin Society. Price: 60 Euro.

Wednesday, August 23rd. The Warsaw Rising Museum and Ghetto Heroes Memorial, 3hour tour . The unprecedented brutality of the Second World War may have long been consigned to the history books in many countries. Poland lost seventeen percent of its population during the war, a staggering 6 million inhabitants. **The Warsaw Rising Museum** is devoted to one of the biggest struggles of the war, made by the Polish Home Army. The Uprise started on August 1st 1944, and sought to liberate Warsaw from German occupation and break the omnipresent Nazi terror and cruelty. The Museum uses the modern audiovisual techniques to recover the atmosphere of Warsaw under German Occupation (1939-1945) in all aspects of life, and to recreate the climate of great optimism, enthusiasm and heroism of people during the Warsaw Rise. From the other side it also documents many tragic events which happened those days. During 63 days of the Uprising over 250,000 civilians were killed, mostly in mass executions conducted by advancing German troops. The remaining citizens were expelled and transported to Nazi concentration camps. After the Uprising had been quashed, Warsaw was condemned to annihilation. Hitler ordered the city to be wiped off the face of the earth, and special units were brought in to systematically detonate any building of the remotest importance to Polish culture. The city was burned systematically, block after block, and approximately 85 per cent of buildings were utterly destroyed.

More than a year before, from April 19th to May 16th 1943, Warsaw was the scene of another struggle: the Warsaw Ghetto Uprising, one of first uprisings against Nazi occupation in Europe. The Warsaw Ghetto was the largest of the Jewish ghettos, established by the German Nazis in order to contain and starve Polish Jews before transporting them to extermination camps. In the three years of its existence (established in 1940) starvation, disease and deportations to extermination camps saw the Ghetto population fall from 450,000 to 37,000. The Uprising represented the last defiant attempt of those Jews who remained to fight against their total annihilation. The **Ghetto Heroes Memorial** was founded in memory and honor of the Jewish Uprisers.

This excursion is free of charge for all accompanying persons. Active participants may also join the excursion, provided that places are available. The number of participants for the excursion is limited, so acompanying persons are kindly asked to get the tickets from the Reception Desk on Sunday (August 20th) or latest on Monday (August 21st). The remaining tickets will be available for all other participants at the Reception Desk on Tuesday (August 22nd). Please be sure to retain these tickets, as you will need to show them in order to access the excursion.

Conference Timetable

Sunday, August 20

12.00-19.30	Registration
19.30-21.30	Welcome reception

Monday, August 21

Plenary Session I	**Crystal Lecture Hall**
8.40-9.00	Opening Ceremony
9.00-10.00	**PL** R. Huber
10.00-10.30	**IL** H. H. Limbach
10.30-11.00	**IL** J. Tortajada
11.00-11.30	Coffee Break

Oral Session I	**Crystal Lecture Hall**
11.30-11.50	**OC** G. M. Blackburn
11.50-12.10	**OC** S. A. Glover
12.10-12.30	**OC** A. Santaballa
12.30-12.50	**OC** L. F. Szabó
12.50-13.10	**OC** P. R. Seidl
	Garnet Lecture Hall
11.30-11.50	**OC** M. Canle
11.50-12.10	**OC** S. Braverman
12.10-12.30	**OC** M. L. S. Cristiano
12.30-12.50	**OC** H. W. Lee
12.50-13.10	**OC** D. N. Kevill
13.10-14.30	Lunch

Plenary Session II	**Crystal Lecture Hall**
14.30-15.30	**PL** A. E. Yonath
15.30-16.00	**IL** W. Priebe
16.00-16.30	**IL** A. Pross
16.30-17.00	Coffee Break

Oral Session II	**Crystal Lecture Hall**
17.00-17.20	**OC** S. Kobayashi
17.20-17.40	**OC** H. Maskill
17.40-18.00	**OC** F. Terrier
	Garnet Lecture Hall
17.00-17.20	**OC** C. Bernasconi
17.20-17.40	**OC** M. Sigalov
17.40-18.00	**OC** R. A. More O'Ferrall
20.30-21.30	Chopin Recital

Tuesday, August 22

Plenary Session III	**Crystal Lecture Hall**
9.00-10.00	**PL** P. Coppens
10.00-10.30	**IL** F. Fillaux
10.30-11.00	**IL** S. J. Grabowski
11.00-11.30	Coffee break

Oral Session III	**Crystal Lecture Hall**
11.30-11.50	**OC** J. Błażejowski
11.50-12.10	**OC** M. Charton
12.10-12.30	**OC** J. R. B. Gomes
12.30-12.50	**OC** L. Sobczyk
12.50-13.10	**OC** A. Baidak
	Garnet Lecture Hall
11.30-11.50	**OC** M. Fujita
11.50-12.10	**OC** H. Yamataka
12.10-12.30	**OC** J. Spanget-Larsen
12.30-12.50	**OC** P. Rempala
12.50-13.10	**OC** Z. Dega-Szafran
13.10-14.30	Lunch

Plenary Session IV	**Crystal Lecture Hall**
14.30-15.30	**PL** K. S. Kim
15.30-16.00	**IL** P. W. Fowler
16.00-16-30	**IL** Z. Maksić
16.30-17.00	Coffee Break

Oral Session IV	**Crystal Lecture Hall**
17.00-17.20	**OC** P. Bultinck
17.20-17.40	**OC** E. D. Raczyńska
17.40-18.00	**OC** H. Fallah-Bagher-Shaidaei
18.00-18.20	**OC** S. E. Galembeck
	Garnet Lecture Hall
17.00-17.20	**OC** J. M. White
17.20-17.40	**OC** M. Eckert-Maksić
17.40-18.00	**OC** M. V. Diudea
18.00-18.20	**OC** K. S. Rangappa

Poster Session	**Coral Hall**
19.30-21.00	Poster Session I
21.00-22.00	Meeting of Subcommittee of Structural and Mechanistic Organic Chemistry (IUPAC)

Wednesday, August 23

Plenary Session V	**Crystal Lecture Hall**
9.00-10.00	**PL** I. P. Beletskaya
10.00-10.30	**IL** J. Jurczak
10.30-11.00	**IL** R. Moss
11.00-11.30	Coffee Break

Oral Session V	**Crystal Lecture Hall**
11.30-11.50	**OC** H. Mayr
11.50-12.10	**OC** Z. Rappoport
12.10-12.30	**OC** P. Guthrie
12.30-12.50	**OC** P. K. Sazonow
12.50-13.10	**OC** M. J. Mphahlele
	Garnet Lecture Hall
11.30-11.50	**OC** E. Humeres
11.50-12.10	**OC** H. F. Bettinger
12.10-12.30	**OC** A. Sporzyński
12.30-12.50	**OC** G. Kaupp
12.50-13.10	**OC** W. Grochala
13.10-14.30	Lunch

Plenary Session VI	**Crystal Lecture Hall**
14.30-15.30	**PL** S. Fukuzumi
15.30-16.00	**IL** A. Proń
16.00-16.30	**IL** D. Kost
16.30-17.00	Coffee Break

Oral Session VI	**Crystal Lecture Hall**
17.00-17.20	**OC** U. M. Domańska-Żelazna
17.20-17.40	**OC** P. Kaszyński
17.40.18.00	**OC** P. Naumov
18.00-18.20	**OC** G-Z. Ji
	Garnet Lecture Hall
17.00-17.20	**OC** G. A. DiLabio
17.20-17.40	**OC** J. Christoffers
17.40-18.00	**OC** H. Detert

Poster Session	**Coral Hall**
19.30-21.00	Poster Session II

Thuersday, August 24

Plenary Session VII	**Crystal Lecture Hall**
9.00-10.00	**PL** D. Braga
10.00-10.30	**IL** W. Jones
10.30-11.00	**IL** A. Hirsch
11.00-11.30	Coffee Break

Plenary Session VIII	**Crystal Lecture Hall**
11.30-12.00	**IL** J. Klinowski
12.00-12.30	**IL** W. Szelejewski
12.30-13.30	Lunch
13.30-19.30	Conference Excursion
20.30-22.00	Conference Dinner

Friday, August 25

Plenary Session IX	**Crystal Lecture Hall**
9.00-10.00	**PL** L. Latos-Grażyński
10.00-10.30	**IL** R. Bilewicz
10.30-11.00	**IL** O. A. El Seoud

11.00-11.30	Coffee Break

Oral Session VII	**Crystal Lecture Hall**
11.30-11.50	**OC** M. Stępień
11.50-12.10	**OC** T. B. Phan
12.10-13.30	**OC** M. Szafran
	Garnet Lecture Hall
11.30-11.50	**OC** D. D. Sung
11.50-12.10	**OC** P. Pięta
12.10-12.30	**OC** T. Drewnowski

12.30-12.35	Short Break

Plenary Session X	**Crystal Lecture Hall**
12.35-13.05	**IL** J. R. Leis
13.05-13.15	Closing Ceremony

13.15-14.30	Lunch

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The Warsaw Rising Museum

Warsaw Tourist Office

Warsaw University

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Symposia

Plenary session

Programme

Monday, 21 August

Plenary Session I

Monday morning, 21 August, 9:00
Chair: George M. Blackburn

9:00	plenary lecture

Molecular Machines in Biology

Robert Huber

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Within cells or subcellular compartments misfolded and/or short-lived regulatory proteins are degraded by protease machines, cage-forming multi-subunit assemblages. Their proteolytic active sites are sequestered within the particles and located on the inner walls. Access of protein substrates is regulated by protein subcomplexes or protein domains which may assist in substrate unfolding dependent of ATP. Five protease machines will be described displaying different subunit structures, oligomeric states, enzymatic mechanisms, and regulatory properties.

Proteasome

[1] M. Groll, L. Ditzel, J. Löwe, D. Stock, M. Bochtler, H. D. Bartunik, R. Huber, Nature 1997, 386, 463-471: Structure of 20S proteasome from yeast at 2.4 Å resolution.

[2] M. Groll, W. Heinemeyer, S. Jäger, T. Ullrich, M. Bochtler, D. H. Wolf, R. Huber, Proc. Natl. Acad. Sci. USA 1999, 96, 10976-10983: The catalytic sites of 20S proteasomes and their role in subunit maturation: A mutational and crystallographic study.

[3] M. Groll, M. Bajorek, A. Köhler, L. Moroder, D. M. Rubin, R. Huber, M. H. Glickman, D. Finley, Nature Struct. Biol. 2000, 7, 1062-1067: A gated channel into the proteasome core particle.

HslV/HslU

[1] M. Bochtler, C. Hartmann, H. K. Song, G. Bourenkov, H. Bartunik, R. Huber, Nature 2000, 403, 800-805: The structure of HslU and the ATP-dependent protease HslU-HslV.

[2] H. K. Song, C. Hartmann, R. Ramachandran, M. Bochtler, R. Behrendt, L. Moroder, R. Huber, Proc. Natl. Acad. Sci. USA 2000, 97, 14103-14108: Mutational studies on HslU and its docking mode with HslV.

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Tricorn

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10:00	invited lecture

NMR Studies of Hydrogen Bond Structure and Dynamics: from Crystals, Liquids, Mesoporous Media to Enzymes

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Recent applications of low-temperature liquid and solid state NMR spectroscopy in the study of H-transfer and H-bonding are described. "H-transfer NMR" focuses on the kinetics of H and D transfers in weak hydrogen bonds [1], "H-bond NMR" on strong hydrogen bonds [2]. Using low-temperature NMR methods acid-base interactions in polar solvents can be studied. Dipolar solid state NMR of selected systems provides a link between crystallography and the world of NMR parameters. Applications to mesoporous silica host-guest systems [3], transition metal complexes and nanoparticles [4, 5], poly-L-lysine, as well as enzyme models and enzymes are presented.

I thank for their contribution to this work: G. Buntkowsky, Jena, G. S. Denisov, N. S. Golubev, St. Petersburg, I. Shenderovich, P. Tolstoy, Berlin, B. Chaudret, Toulouse, J. Elguero, R. Claramunt, Madrid, D. Silverman, Gainesville, M. Toney, Davis.

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10:30 invited lecture

Reactions Involving Metal Dications and Biological Models in The Gas Phase

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Whilst the reactivity of multiply-charged ions is quite well understood in the context of aqueous media and solid phases, relatively little is known of their chemical behaviour in the gas phase. It is only since the 1980's, due mostly to advances in experimental technology, that their role in the chemistry and more recently in biological processes has been revealed. Among such species, metal ion complexes are of great importance in biological function and gas-phase organometallic ion chemistry has witnessed a great development from both the theoretical and the experimental points of view. In gas-phase, the cationization of neutral molecules by metal dications is often accompanied by bond activation effects, which can lead to specific fragmentations. Then, depending on a specific dication attachment site, the establishment of diagnostic ion fragmentations, observed in mass spectrometry experiments, is of potential interest for the structural characterization. In this context, the development of electrospray ionization techniques has indeed opened up the possibility of producing clusters involving metal dications in the gas phase, and the interest in dication-molecule reactivity grew significantly. Studies of reactions involving metal dications and organic bases reveal a clear distinction between alkaline-earth metal and transition metal dications. In the first case, $[\text{base-M}]^{2+}$ complexes could be isolated in the gas phase and their unimolecular reactivity be investigated. For transition metals, it appears that dications are instable and lead to monocations species after the loss of a proton from $[\text{base-M}]^{2+}$. These features will be illustrated in this presentation, through theoretical (DFT calculations) and experimental approaches (mass spectrometry), for complexes involving prototypical biological molecules (urea, amino acids, natural and modified nucleic basis) and Ca^{2+}, Mg^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+} and Co^{2+} dications.

Plenary Session II

Monday afternoon, 21 August, 14:30

Chair: Michael Schmittel

14:30 plenary lecture

The Spectacular Ribosomal Architecture: Nascent Proteins Voyage Towards Folding via Antibiotics Binding-pockets

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Ribosomes position their substrate at stereochemistry suitable for peptide bond formation and for substrate-mediated chemical catalysis. Their active site is located within a universal internal symmetrical region, which connects all ribosomal features involved in its functions, hence can transfer intra-ribosomal signals between them. The symmetry relates RNA backbone and nucleotides orientation but shows no sequence homology, thus demonstrating the superiority of the functional requirements over sequence conservation, and suggesting that ribosomes evolved by gene-fusion.

The linkage between substrate positioning and the symmetrical region indicates a guided rotatory motion of the aminoacylated-tRNAs along a path created by the ribosome, which enables ribosomal polymerase action, and advances the nascent chain into the exit tunnel at an extended conformation. This tunnel was shown to possess significant dynamics that facilitate its interactive participation in gating, elongation arrest, discrimination and cellular signaling. Likewise, initial steps in chaperon-aided folding are associated with the mobility of the first chaperone to encounter the emerging polypeptides, named trigger factor in eubacteria. Adjacent to the tunnel is a crevice to which a hydrophobic compound that could mimic a secondary structure element binds selectively, thus indicating a possible co-translational chaperoning role of the ribosome.

Structures of over a dozen antibiotics complexes, obtained at clinically relevant concentrations with ribosomes of eubacteria suitable to serve as pathogen models, illuminated the fundamental principles of antibiotics inhibitory action, provided the structural basis for antibiotics selectivity, and revealed the molecular mechanisms of antibiotics resistance. Comparison to antibiotics complexed with ribosomes from an archaeon that shares properties with eukaryotes, and its mutant, allowing antibiotics binding, illuminated structural elements required for therapeutical effectiveness and indicated that optimal antibiotics binding may require drug's conformational rearrangements. It also showed that whereas the identity of a single nucleotide determines drug's binding, the proximal nucleotides govern the binding-modes and, consequently, the clinical effectiveness.

15:30 invited lecture

Targeting DNA: A Modular Approach Using Structure-Based Design and Combinatorial Libraries

Waldemar Priebe

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The ongoing explosion of genomic information is creating an astounding increase in the number of biological targets for new drug discovery. Massive efforts by university research centers and the pharmaceutical industry to identify gene targets are driving the development of drugs that can control the expression of specific genes. Current techniques involving antisense approaches or proteins have inherent problems such as the large mass, rapid metabolism, and reduced cellular uptake of these compounds. These drawbacks can be overcome by the use of small-molecule DNA-binding agents displaying high DNA affinity and sequence specificity that can also penetrate cell membranes.

To exploit this concept, we developed a modular design approach that combines intercalation and groove binding modes into molecules with the requisite binding site size to impart meaningful sequence selectivity. Such an approach, which can be visualized as playing molecular "Lego" with DNA, allows libraries of compounds to be built using rational structure-based and combinatorial design. We used an anthracycline-antibiotic scaffold to develop our modular approach, which has provided the key intercalating and minor groove-binding modules that can be exploited for their known sequence-binding preferences and their proven clinical worth.

Our new strategy has succeeded in creating four related but distinct classes of novel DNA-targeting agents that might have significant medical application. These four classes include (1) 6-bp-long DNA-binding agents with bisintercalating and groove-binding properties and picomolar DNA binding affinity that can act as small-molecule modulators of gene expression, (2) WP900, the first molecule that binds selectively to Z-DNA, (3) medium-affinity DNA-binding anticancer agents that have distinct advantages over existing chemotherapeutic drugs, and (4) base-specific highly cytotoxic DNA-crosslinking agents. Our lead drug (WP744) is in clinical studies for brain tumors, and our second drug candidate (WP760), which targets selectively malignant melanoma, is in preclinical evaluation.

16:00	invited lecture

On the Chemical Nature of Purpose (Teleonomy)

Addy Pross

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Chemistry enables us to understand the properties of chemical systems based on their chemical structure. For example, we understand why water is soft, why ice is hard, and why metals are shiny and conduct electricity. However this kind of understanding is lacking for the basic properties of living systems. For example, one of living systems' most striking characteristics is their purposeful (teleonomic) character, but a *chemical* understanding of that character and, in particular, how it might have emerged, remains missing. In this talk we will explore the chemical nature of purpose within a general framework that attempts to further clarify the physico-chemical relationship between animate and inanimate systems. One key element of the analysis is our proposal that all living systems constitute a **kinetic state of matter** as opposed to the traditional thermodynamic states that dominate the inanimate world. Thus we will argue that a traditional physical organic approach, based on the well-established concepts of kinetic and thermodynamic selection, can help explain the emergence of biological systems with their striking properties - such as purpose - in relatively simple chemical terms.

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Tuesday, 22 August

Plenary Session III

Tuesday morning, 22 August, 9:00
Chair: Zvi Rappoport

9:00	plenary lecture

Time-Resolved Diffraction Studies of Molecular Excited States and Beyond

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As Chemistry is the Science of Molecular Change, experimental and theoretical studies of short-lived species are central to Chemistry. Time-resolved (TR) crystallography can reveal the geometry of excited states, and in studies still to be realized, the mechanism of light-induced chemical reactions. Since photoinduced biological processes are typically triggered by chemical reactions such as cis-trans isomerization, chemical and biological time-resolved diffraction are intrinsically related.

In a first series of studies we have used a stroboscopic time-resolved diffraction technique [1] to determine the geometry of the microsecond-lifetime excited states of a series of binuclear Pt, Rh and Cu metalloorganic complexes, in which large metal-metal-distance shortening occurs on excitation. The rapidly reversible bond-shortening is intermolecular in a trinuclear Cu(I) pyrazolate complex [2]. The results agree qualitatively with theory, but are not always quantitatively reproduced by calculations on the isolated molecules.

In a second phase of the work TR diffraction has been applied to species incorporated as guests in extended organic frameworks, synthesized by using the methods of crystal engineering. The corresponding solid-state dilution has several advantages and allows assessment of the effect of the matrix on ground- and excited state molecular properties. Eight different phases incorporating the Cu(I) bis(2,9-dimethyl-1,10-phenanthroline) ion have been prepared. They show different states of aggregation of the cations and exhibit large variations in luminescence lifetimes [3]. The ultimate goal of the work is to study the mechanism of photo-induced chemical reactions in fully-ordered three-dimensional frameworks on timescales of picoseconds and less. Specific reactions and technical developments in progress will be discussed [4].

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10:00	invited lecture

Proton Transfer Across Hydrogen Bonds: From Reaction Path to Schrödinger's Cat

Francois J. Fillaux[1], Alain Cousson[2], Matthias J. Gutmann[3]

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Macroscopic quantum entanglement at the scale and temperature of our everyday world enlightens the foundations of quantum mechanics and reveals unforeseen mechanisms for proton transfer across hydrogen bonds in the solid state. We utilize neutron scattering techniques to study dynamical correlation of protons in potassiumhydrogencarbonate ($KHCO_3$) and benzoic acid (C_6H_5COOH) crystals, both composed of planar centrosymmetric dimer entities linked by moderately strong hydrogen bonds.

All protons are indistinguishable, they behave as fermions, and they are degenerate. We define pseudoprotons to account for proton dynamics. As a consequence of the symmetrization postulate of quantum mechanics, the sublattice of protons is a superposition of macroscopic single-particle states such that each pseudoproton occupies simultaneously all sites. The sublattice has no internal dynamics and decoherence is forbidden. Coherent elastic neutron scattering gives rise to quantum interferences, in addition to Bragg's peaks.

Between 15 and 300 K, protons are progressively transferred, to secondary sites at ~ 0.6 Å from the main position, *via* tunneling along hydrogen bonds. The macroscopic quantum entanglement, still observed at 300 K, reveals that proton transfer is a coherent process throughout the crystal arising from a superposition of macroscopic tunneling states.

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10:30	invited lecture

Hydrogen Bonds - the Case of π and σ-Electrons as Proton Acceptors

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Different types of interactions are analyzed for which the classical Pauling definition of hydrogen bonding [1] is hardly accepted. These are X-H...π (especially C-H...π) [2] and X-H...σ interactions [3, 4]. It is often stated that such interactions are rather weak if compared with typical hydrogen bonds, there are only few, mostly theoretical exceptions. However the new type of interactions was investigated recently using ab initio calculations. These are $\pi...H^+...\pi$ bonded complexes where the proton is strongly connected with one of π-electron systems which may be treated as the proton donating species and where the second π-electron system performs the role of acceptor. Such systems are characterized by meaningful binding energies (for some of cases over 20 kcal/mol) and the covalent character of both $H^+...\pi$ contacts [5]. There are the other unique interactions, $\pi...H^+...\sigma$ and $\sigma...H^+...\sigma$ where also the $H^+...\sigma$ interactions are rather strong. The mentioned above interactions often fulfill the criteria and definition rules of hydrogen bonding and may be classified as the latter type of interaction. Additionally, it seems they are important interactions in crystal engineering and numerous physical and biochemical processes.

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Plenary Session IV

Tuesday afternoon, 22 August, 14:30
Chair: Eduardo Humeres

14:30	plenary lecture

De Novo Design Approach Based on Nanorecognition: Functional Molecules/Materials and Nanosensors/Nanodevices

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Design of functional molecules and nanodevices has been a fascinating issue in these days. To develop innovative nanomaterial systems, it is necessary to create a new paradigm for the design approach because the systems involved in quantum phenomena are hardly comprehensible by intuition and simple experiences. For practical utility, functional materials need to be self-assembled, and nanodevices would be self-engineered. To this end, the nanorecognition should play an important role. The nanorecognition is governed mainly by interaction forces such as hydrogen bonding, ionic interaction, π-H/π-π interactions, and metallic interactions as well as the capture / transport/ release of electrons /photons/ protons. The manifestation of these interaction forces has led us to the design and realization of diverse ionophores/receptors, organic nanotubes, nanowires, molecular mechanical devices, molecular switches, enzyme mimetics, protein folding/unfolding, etc. In this talk, we focus on the following topics. (i) We discuss ionophores/receptors with chemo-sensing capability for biologically important cations (ammonium cations and acetylcholine by utilizing cation-π interactions, directional hydrogen bonding, charge-charge/charge-dipole interactions) and anions (F^-, Cl^-, Br^-, I^-, phosphate, pyrophospate, ATP, GTP, etc., by utilizing the CH^+-X^- ionic hydrogen bonds,based on tweezer structures to accommodate a nearly free excess electron in a large empty space as a surface bound form). (ii) We discuss how the understanding of hydrogen bonding and pi-interactions has led to the design of nanotubes from calix[4]hydroquinone (CHQ). The CHQ tubes are self-assembled to form long tubular structures in the presence of water with the formation of one dimensional short H-bonds relay. The bundles are formed with the intertubular π-π stacking interactions. The binding situations of neutral and cationic transition metals with the redox system of hydroquinone and quinone predicts what kind of nanostructures (nanoclusters, nanowires, and nanofilns) would form. (iii) We observed that the conformational change between stacked and edge-to-face conformers in p-benzoquinone-benzene complexes is controlled by electrochemical potential. This flapping motion illustrates a promising pathway toward the design of mobile nanomechanical devices.

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15:30 invited lecture

π-Electron Delocalisation and Ring Currents

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Theory and application of the CTOCD (Continuous Transformation of Origin of Current Density) method to the computation, visualisation and interpretation of ring-current aromaticity and antiaromaticity will be discussed. In this Ansatz (due to Keith and Bader), calculation of induced current density at any point in space takes that point as origin. It will be shown here that this 'ipsocentric' choice brings with it, in addition to computational economy, an important conceptual advantage: unique decomposition of properties into occupied-orbital contributions, free from unphysical mixing, and subject to selection rules based on orbital symmetry, energy and nodal characteristics. This leads to rationalisations of where the currents in aromatic systems come from, why they have the sense that they do, and how they are affected by changes in geometry, substitution and charge. Results for a range of π and σ systems will be presented and new applications to 'homo-aromatic' systems will be described.

16:00 invited lecture

Design of Neutral Organic Superacids and Superbases Ex Machina

Zvonimir Maksić

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Recent advances in studying Brønsted (organic) superbases and superacids, attained by the modern computational chemistry methods, will be presented. It will appear that, by following a simple strategy developed by us [1], one can tailor a dense ladder of neutral organic superbases up to the proton affinity (*PA*) of 300 kcal/mol [2-4]. Since the *PA* of the archetypal DMAN (1,8-*bis*-dimethylaminonaphthalene) superbase in the gas phase (GP) is 245.7 kcal/mol, it follows that the most powerful designed superbases are stronger by 40 orders of magnitude than the reference compound. Their pK_a in acetonitrile is about 50 units implying that they retain superbasic properties in solutions too. Analogously, it is possible to construct a dense scale of organic superacids with ΔH_{acid} as low as 245 kcal/mol in the GP by using a concept of the anionic resonance in deprotonated polycyano substituted hydrocarbons [4-8]. Taking into account that pK_a of sulphuric acid (H_2SO_4) in DMSO is 1.99, it turns out that the designed superacids are stronger by some 40 orders of magnitude than this molecule taken as a standard of superacidity. Some aspects of syntheses of organic superbases and superacids and possible applications will be discussed.

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Wednesday, 23 August

Plenary Session V

Wednesday morning, 23 August, 9:00
Chair: Guo-Zhen Ji

9:00 plenary lecture

Mechanistic Aspects and Synthetic Application of Carbon-Carbon and Carbon Heteroatom Bonds Formation in Substitution and Addition Reactions Catalyzed by Transition Metal Complexes

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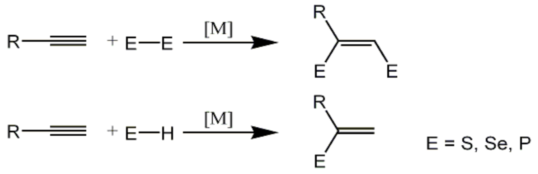
1. Pd-catalyzed reaction of carbon-carbon (cross-coupling reactions, Heck reaction, carbonylative cross coupling) and carbon-heteroatom (C-S, C-Se, C-P, C-N) bonds formation will be shortly considered from the viewpoint of generality and differences in their mechanisms.

$$\mathrm{ArX + Pd(0)} \longrightarrow \mathrm{ArPdX} \xrightarrow{\mathrm{Nu^-}} \mathrm{ArPdNu} \longrightarrow \mathrm{ArNu + Pd(0)}$$

$\mathrm{X = Hal, OTf}$ $\mathrm{Nu = PR_2, P(O)(OR)_2, SR, SeR, NR_1R_2}$

2. The addition of element-element and element-hydrogen bonds to triple bond of alkynes (terminal and internal) will be illustrated by the examples of S-S, Se-Se, P-P and S-H, Se-H, P-H bonds addition and considered from the viewpoints of their mechanism, regio- and stereoselectivity.



The influence of the nature of transition metal (Pd, Pt, Ni) on the product formation, the effect of using heterogeneous *viz* homogeneous catalysts will be considered from the viewpoints of intermediates formed and the size of nanoparticles involved.

3. Several examples of Pd- and Ni-catalyzed addition reactions of E-H bonds to the double bond of nonactivated alkenes will be also discussed.

10:00 invited lecture

Synthesis, Structure and Complexing Properties of Receptors for Anions

Tomasz Zieliński[1], Michał J. Chmielewski[1], Janusz Jurczak[1,2]

1. *Polish Academy of Sciences. Institute of Organic Chemistry, Kasprzaka 44/52, Warszawa 01-224, Poland* **2.** *Uniwersytet Warszawski, Wydział Chemii, Warszawa, Poland*

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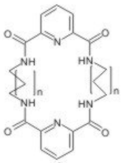
The development of neutral receptors for recognition of anions has attracted much attention in supramolecular chemistry during recent years. Although there are many remarkable achievements in this area, the design of the efficient and selective receptors is still a challenging task. Our group has been focused on the relationship between the structure and binding properties of anion receptors, and in this communication we would like to present results of these studies.



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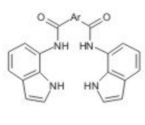

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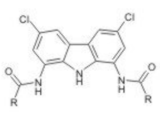

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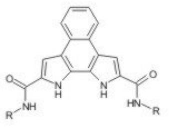

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We investigated properties of macrocyclic tetraamides type **1** derived from dipicolinic or isophthalic acid. Using these models, we found the correlation between the ring size and anion affinity, and showed undoubtedly the macrocyclic effect. Furthermore, we revealed that the weaker binding of the isophthalic-based receptors is due to the poor preorganisation of the ligands, and we showed how this obstacle can be overcome.

The other field of our interest is the application of benzopyrrole subunits as building blocks for anion receptors. In the course of these studies we examined the derivatives of indol-7-amine (**2**), diaminocarbazole (**3**) and dipyrrolonaphtalene (**4**). We found that replacement of aniline with indolamine can lead to over five times higher anion affinity. Bisamides of diaminocarbazole turned out to bind anions very efficiently, whereas, derivatives of dipyrrolonaphtalene could act as fluorescent sensors.

10:30 invited lecture

New Mechanisms Centered on Reactive Intermediates

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Methylchlorocarbene. Solution electronic spectroscopy of alkyl- and alkylhalocarbenes is sparse because these species generally have weak absorptions and undergo rapid rearrangements. Nevertheless, we describe the sigma-p absorption of MeCCl at 545 nm obtained by laser flash photolysis (LFP) of methylchlorodiazirine in pentane at ambient temperature. Evidence is presented for complexation of MeCCl in anisole, which affects both its UV spectrum and the rate of its reaction with alkenes.

Dichlorocarbene. A new synthesis of dichlorodiazirine is described. LFP studies in solution at ambient temperature afford evidence for the reactions of dichlorocarbene with oxygen and pyridine. The sigma-p absorption of CCl_2 has thus far proven too weak to observe in solution.

Diazirinone. Diazirinone, the diaza analogue of cyclopropenone, is generated by ipso attack of fluoride ion on *p*-nitrophenoxychlorodiazirine. Diazirinone has a lifetime of about 5 minutes near ambient temperature, and its exothermic decomposition to N_2 and CO can be followed by IR spectroscopy.

Carbanions from carbenes. Reactions of phenylhalocarbenes (PhCX) with halide ions produce phenyldihalomethide carbanions ($PhCXY^-$) which add to electron deficient alkenes. Cyclization of the adduct anions with expulsion of halide ion then generates cyclopropanes. The kinetics of these processes are readily visualized by LFP. Examples are provided for the formation and reactions of $PhCBr_2^-$ and $PhCFBr^-$.

Plenary Session VI

Wednesday afternoon, 23 August, 14:30
Chair: Lucjan Sobczyk

14:30 plenary lecture

New Development of Electron-Transfer Catalytic Systems

Shunichi Fukuzumi

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The importance and the complexity of biological electron-transfer catalytic systems such as photosynthesis and respiration have prompted the development of electron-transfer catalytic systems, which can mimic functions of redox enzymes [1]. We have developed simple donor-acceptor dyads to attain a long-lived and high energy charge-separated state without significant loss of excitation energy, by fine control of the redox potentials and of the geometry of donor-acceptor dyads that have small reorganization energies of electron transfer. Such simple molecular dyads, capable of fast charge separation but extremely slow charge recombination, have significant advantages with regard to synthetic feasibility, providing a variety of applications, which are presented herein [1].

A simple molecular electron donor-acceptor dyad, 9-mesityl-10-methylacridinium ion (Acr^+-Mes), capable of fast charge separation but extremely slow charge recombination [2], allows us to develop efficient photocatalytic oxygenation of anthracenes with oxygen [3]. Formation of 1,2-dioxetane of tetraphenylethylene (TPE) also occurs via formation of the electron-transfer state of Acr^+-Mes under visible light irradiation, followed by electron transfer from TEP to the $Mes^{•+}$ moiety together with electron transfer from the $Acr^•$ moiety to O_2, and the subsequent radical coupling between $TEP^{•+}$ and $O_2^{•-}$ to yield the corresponding 1,2-dioxetane [4]. The dioxetane thus formed was isolated using column chromatography for the first time.

The electron-transfer state of Acr^+-Mes is also capable of oxidizing DNA bases and the transient absorption spectra of four nucleotide radical cations have been successfully detected in the electron-transfer oxidation of the corresponding DNA bases with the $Mes^{•+}$ moiety of $Acr^•$-$Mes^{•+}$, which is produced upon photoexcitation of Acr^+-Mes [5]. DNA is also efficiently oxidized by the $Mes^{•+}$ moiety of $Acr^•$-$Mes^{•+}$, leading to efficient DNA cleavage in the absence of O_2, as compared with acridinium ions without a donor moiety [5].

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[3] H. Kotani, K. Ohkubo, S. Fukuzumi, J. Am. Chem. Soc. 2004, 126, 15999.

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15:30 invited lecture

Molecular Hybrids of Conducting Oligomers and Polymers with Semiconductor Nanocrystals of A(II)B(VI) Family - Synthesis, Electronic and Electrochemical Properties

Adam Pron[1], Claudia Querner[1], Julia De Girolamo[1], Peter Reiss[1], Malgorzata Zagorska[2]

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We have developed a new class of solution processible organic-inorganic hybrids based on monodispersed semiconductor nanocrystals and conjugated oligomers (polymers). These new nanomaterials can act as active components in organic and molecular electronics. The organic-inorganic nanohybrids can be obtained in a three step procedure involving nanocrystals synthesis (CdSe, ZnSe etc), exchange of the initial surface ligands by bi-functional ones, and finally attaching the conjugated oligomers (polymers) on the functionalized nanocrystal surface either by grafting or by molecular recognition procedures. Two families of the polyconjugated molecules have been investigated: oligo- and polyanilines and oligo- and polythiophenes. As the obtained nanohybrids can be considered as an association of two electrochemically active systems of different nature, we have studied their voltammetric and spectroelectrochemical (UV-visible-NIR, Raman, EPR) behaviour. In several cases, the resulting properties have shown synergic rather than additive nature, proving that the obtained nanohybrids are not simple adducts but constitute a new class of organic-inorganic nanomaterials in which both components strongly interact. The conjugated surface ligands in the prepared nanohybrids can be reversibly switched between their semi-conducting and their conducting states, either electrochemically, by imposing an appropriate potential, or chemically, by selecting an appropriate doping reaction. Thus, the obtained systems can be considered as semiconductor-semiconductor or semiconductor-conductor molecular junctions of a new type.

16:00 invited lecture

Silicon Hybridization Energy Probed by Changes in Ligand Donor Strength and Molecular Rearrangements in Hexacoordinate Silicon Dichelates

Daniel Kost[1], Boris Gostevskii[1], Inna Kalikhman[1], Mark Botoshansky[2], Menahem Kaftory[2]

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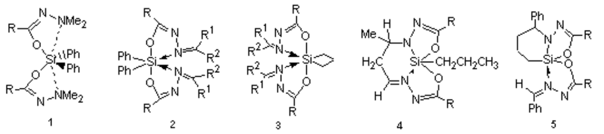
Neutral hydrazide-based hexacoordinate silicon bis-chelates with no halogen ligands, but with two monodentate alkyl (aryl) or hydrido ligands, are described.



Dimethylamino complexes (**1**) form weakly coordinated "bicapped tetrahedral" geometries in the solid state (Figure 1), while imino-coordinated complexes (**2**) are more strongly bound and form distorted octahedral structures (Figure 2). The difference in donor strengths of these two nitrogen-donor types determines whether the dative bonds (in **2** and **1**, respectively) provide sufficient energy to promote silicon from tetrahedral to octahedral configuration.

Hexacoordinate silacyclobutane complexes (**3**) have been prepared. Upon mild heating or photolyzing they undergo a skeletal rearrangement involving cleavage of the four-membered heterocycle (**4**). In the absence of imino α-protons (**3**, R^1 = Ph, R^2 = H) addition of the four-membered ring residue to the imino double bond takes place, forming a new chelate ring (**5**).

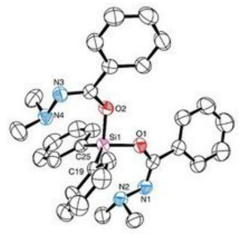
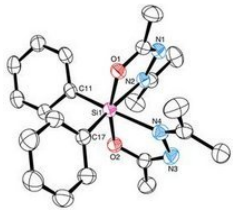
	

Figure 1: Crystal structure of **1**	Figure 2: Crystal structure of **2**

Thursday, 24 August

Plenary Session VII

Thursday morning, 24 August, 9:00
Chair: Arturo Santaballa

9:00 plenary lecture

Making Crystals from Crystals: a Green Route to Crystal Engineering and Polymorphism

Dario Braga

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Supramolecular reactions between crystalline materials or reactions between a crystalline material and a vapour can be used to generate new crystalline substances as well as crystal polymorphs, solvates, salts and co-crystals. These solvent-free processes can be exploited to prepare both hydrogen bonded co-crystals and coordination networks by non-solution solvent-free methods. Solid-vapour reactions do not differ from solid-gas uptake/release processes, and can also be used to prepare polymorphs and solvates. It is argued that solvent-less reactions involving molecular crystals represent a green route to supramolecular solid state chemistry and a viable alternative to solution methods for a thorough mapping of the "crystal space" (crystal reactivity, stability, vapour uptake/release, behaviour under mechanical stress, etc.). Examples will be provided in a broad range from organic molecular crystals, to coordination networks and salts.

10:00 invited lecture

Synthesis and Properties of Inorganic-Organic Hybrids Using Layered Hydroxides

William Jones

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Clays and other layered ion-exchangers find a range of applications. Some uses, for example as re-enforcers in clay-polymer composites, depend heavily on the physical nature (integrity) of the sheets whereas others, for example intragallery catalysis, depend much more on the nature of the charge-balancing ions.

Layered double hydroxides (so-called anionic clays) are currently of considerable interest for the considerable potential they have for providing tuned functionality. Their original applications as anion exchangers and in base catalysis have now been extended to slow release vehicles for drugs and pesticides, flame retardants, scavengers in polymers, nanocomposites, as well as environmental used in toxic waster management and SOx emission control.

A further group of anion exchangers is also seen as offering advantages – this group is the layered basic hydroxides (or layered basic salts). These currently have received less attention but offer some advantages. Certainly they present interesting physical and chemical properties worthy of study. This lecture will highlight the similarities and differences amongst these different layered materials.

10:30 invited lecture

Functional Carbon-Rich Architectures: Synthesis and Supramolecular Organization

Andreas Hirsch

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The core surface of C_{60} provides an ideal platform for the attachment of functional addends in a globular arrangement. The defined addition of a selected combination of functional groups at specific sites of the fullerene framework allows for the synthesis of new molecular architectures with unprecedented properties. For this purpose the complete control over the regioselectivity of subsequent additions to the [6,6]-bonds of the C_{60} framework is an important requirement. We achieved this goal by the introduction of new functionalization concepts. One strategy takes advantage of the even distribution of strain within flexible macrocyclic malonate addends. Based on these synthetic methods the tailor design of a large variety of functional fullerene derivatives with properties such as photoinduced charge separation, liposome formation and biological activity was possible. Typical examples are the π-stacked dyads and the first globular amphiphiles. In water these amphphilesforms pH-switchable and functionalizable liposomes (buckysomes) which represent a new type of drug delivery vehicles. Related calixarene based architectures allowed for the first self-assembly of completely uniform and stable micelles. This C_2-symmetric supramolecular architecture has a diameter of 7 nm and consists of exactly seven amphiphilic molecules. It is the first micelle which is structurally characterized. Finally, methods for the chemical functionalization of SWNTs will be presented.

Plenary Session VIII

Thursday morning, 24 August, 11:30

Chair: Krzysztof Woźniak

11:30 invited lecture

Designing Novel Organic-Inorganic Frameworks

Filipe A. Almeida Paz, Jacek Klinowski

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Ever since the publication of the pioneering 1990 paper by Hoskins & Robson [1], “crystal engineering of coordination frameworks” has attracted growing interest, and there are now 2882 published papers on the subject. We have synthesized large crystals of novel and potentially useful organic-inorganic compounds by hydrothermal synthesis at high temperatures (>100°C) and high autogeneous pressures (>1 atm), and slowly cooling the reaction mixture. Their structures were determined by X-ray crystallography and NMR, and their properties were examined. Until recently this synthetic approach was relatively unexplored.

A number of compounds with interesting topologies will be discussed. For example, a mixture containing 2,6-naphtalenedicarboxylic acid (H_2NDC) and a Cd^{2+} salt gives a 3D structure with diamondoid topology containing zig-zag metallic chains. A ternary reactive mixture composed of triethylamine (TEA), Cd^{2+} and H_2NDC leads, depending on experimental conditions, to a range of products. Thus large single crystals of $[Cd_2(NDC)(OH)_2]$ are formed when the molar fraction of $Cd^{2+} > 0.6$. When $Cd^{2+} < 0.6$, large crystals result when the molar fraction of $H_2NDC > 0.25$. When the molar fraction of TEA > 0.7, a new layered structure is formed. A mixture containing a metal, biphenyl-4,4‘-dicarboxylic acid (H_2BPhDC) and 1,2-bis(4-pyridyl)ethane (BPE) leads to a 3D framework assembled by a centrosymmetric dimeric secondary building unit (SBU). 3D repetition of the SBU leads to a highly porous framework with large cavities filled by the interpenetration of two identical frameworks. Trimesic acid (H_3BTC) and BPE also lead to a porous 3D structure of unusal topology and containing triple metallic layers interconnected by disordered BPE ligands. Because of their interesting electronic and optical properties (photoluminescence), we are now particularly interested in metal-organic frameworks containing lanthanide metals.

[1] Hoskins & Robson, J. Am. Chem. Soc. 1990, 112, 1546.

12:00 invited lecture

Polimorphism of Active Pharmaceutical Ingredients

Wiesław Szelejewski, Andrzej Kutner

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Polymorphism of active pharmaceutical ingredients is becoming an increasingly important issue in the contemporary drug development. Polymorphic form of an active pharmaceutical ingredient (API) might influence it’s kinetics of solubilization and thus affect the release of API from the finished dose of a drug. This is especially in a case for solid dosages like tablets. The release process of API from dosage form is crucial for drug bioavailability and therapeutic function. Due to the higher activity of new generation of API’s and lower doses of API in drugs (from former 200 – 600 mg down to sometimes submilligram level) the studies of polymorphic forms of API’s in finished doses have become recently a tough task. Therefore, there is a need for analytical methods to determine the polymorphic form of API not only in a plain crystalline substance but also in its finished dose. The later is to make sure that selected polymorphic form of API is preserved in a number of mechanical and thermal processes like wet granulation, fluid bed drying, grinding, mixing, sieving and tableting, in the manufacturing of a finished dose of a drug. When single crystal diffractogram for API can not be obtained a combination of several other method is to be used, as there is still no single method replacement for this analysis. In order to define a polymorphic form of API in such a quite common case standards of all existing polymorphs are to be prepared and methods developed for defining of their identity and content in mixtures of polymorphs.

In this presentation a number of examples will be discussed of determination of polymorphic forms of API’s in crystalline substances and in finished doses, carried out at Pharmaceutical Research Institute in Warsaw over the last several years. To define the polymorph of API a set of diffractometric, spectroscopic and thermal methods are used at this laboratory. First and second order spectra in FT-IR spectroscopy were used to develop a method for identification and quantitative determination of contaminating polymorph II in an API that should be present in a tablet exclusively as a polymorph I. Due to the overlapping of signals originated from API with that from excipients (placebo), selection of diagnostic regions in XRPD profiles is usually very much limited and it was successful in a very few cases that will be shown. In our examination of differences between polymorphs and pseudopolimorphs (solvates) of API the most supportive results were obtained by thermal analyses. For a number of solvates studied the additional endothermic peak in differential scaning calorimetry (DSC) is usually recorded at lower temperatures, as compared with the non-solvated substance. Combination of DSC and termogravimetric (TG) techniques allows to discriminate between a signal originated from a solvent and a signal originated from a phase transition in a DSC thermograms.

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[2] J. Piechaczek, J. Serafin, W. Maruszak, R. Balicki, W. Szelejewski, M. Cybulski, G. Maciejewski, M. Wysoczyńska, M. Glice, K. Korczak: Method of preparation of crystalline form I of clopidogrel, PCT/PL2003/00130.

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Friday, 25 August

Plenary Session IX

Friday morning, 25 August, 9:00
Chair: William Jones

9:00 plenary lecture

Carbaporphyrinoids: Exploring Metal Ion - Arene Interaction in a Macrocyclic Environment

Lechosław Latos-Grażyński

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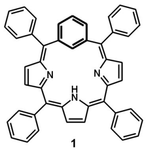
The interactions between arene (heteroarene) rings and metal ions, observed in solution and in the solid state, provide examples of particular geometrical flexibility. A CH moiety of the arene may participate in π-bonding but can also form a σ-bond or an agostic bond with the metal. On the other end of the scale lies the van der Waals interaction, wherein no sharing of electron density occurs between the metal and arene. Unusual cases of metal-arene bonding are encountered in various areas of inorganic chemistry. The strength of the interaction can be varied by appropriate modifications of the coordinating environment of the metal. The weaker interactions are often insufficient to stabilize the M-arene complex, which is held together by additional intramolecular restraints, such as those imposed by a pincer ligand or a cage structure. Such restraints can be readily introduced by incorporating the arene (heteroarene) moiety into a porphyrin-like macrocycle. Thus the macrocyclic brace binds the metal ion and holds it close to the arene moiety.



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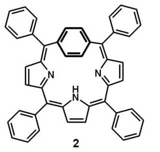

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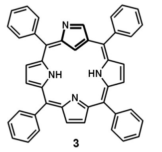

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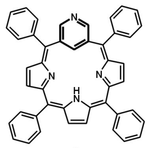

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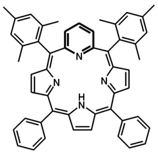

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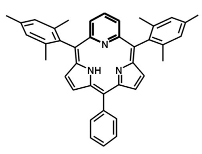

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Carbaporphyrinoids, a recently developed class of macrocycles realize the above concept of ligand construction by fusing the structural motifs of porphyrin and arene (heteroarene). These new molecules belong to the family of carbaporphyrins, porphyrin analogues with a C-H bond in the coordination core. The goal of the present studies is to investigate metal-arene interactions in diamagnetic and paramagnetic complexes of carbaporphyrinoids including of *meta*-benziporphyrins **1**, *para*-benziporphyrin **2**, 2-aza-21-carbaporphyrin **3** and 3-azabenziporphyrin **4** to show how the bonding affects NMR spectroscopic parameters. In the course of this work the simplest homologues of porphyrin - pyriporphyrin **5** and subporphyrin - subpyriporphyrin **6** with a supplementary CH unit "incorporated" in a pyrrolic β-β bond were synthesized [1]. Subpyriporphyrin **6**, the novel type of the contracted porphyrin, provided an environment for the shortest ever N-H···N hydrogen bond with the N···N distances equal 2.370 Å.

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10:00 invited lecture

Molecular Motions in New Catenanes

Renata Bilewicz[1], Agnieszka Więckowska[1], Bohdan Korybut-Daszkiewicz[2]

1. *Warsaw University, Faculty of Chemistry, Pasteura 1, Warszawa 02-093, Poland* **2.** *Polish Academy of Sciences. Institute of Organic Chemistry, Kasprzaka 44/52, Warszawa 01-224, Poland*

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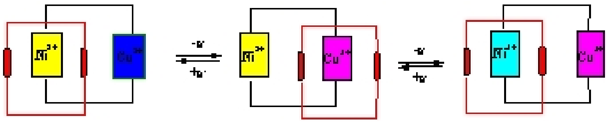
Construction of molecules exhibiting controlled directional motions at the molecular level is, at present, a great scientific challenge. Such motions can be realised in several model molecules, for example, bistable catenanes and rotaxane. In order to control molecular devices one has to understand factors influencing the motions and the nature of interactions defining the mechanical bonds in model systems.

We have recently proposed a new type of catenanes consisting of bismacrocyclic transition metal complexes linked by aliphatic chains and interlocked with substituted crown ether. Under an external stimuli - electrochemical pulses - they exhibit controlled intramolecular relocation of the crown ether between two positions. This relocation is possible due to π...π interactions between the aromatic fragments of the crown ether and the metal centres (Ni, Cu) embedded in the macrocyclic rings [1-4].

By changing properties of components of mechanically bonded molecules, one can modify the properties of resulting complex structures. Such a tuning of properties can be achieved by severe measures as, for example, replacement of the metal ions, elongation of the aliphatic linkers or change of macrocycles. More subtle changes of properties can be introduced by proper chemical modifications of particular positions of the parent systems.

The development of appropriate physical methods useful for monitoring the dynamics of supramolecular systems is currently of utmost importance. We demonstrate using voltammetry that interlocking of the dibenzocrown ether with the homodinuclear bismacrocyclic transition metal complexes leads to increased stability of the mixed-valence states, which was reflected in higher values of comproportionation constants We present a heterodinuclear bismacrocyclic transition metal complex exhibiting potential-driven intramolecular motion of the interlocked crown ether unit. We would like to point out here the unique ability of the Osteryoungs square wave and reverse pulse techniques to detect potential triggered intramolecular motion. By applying appropriate potentials either copper or nickel (or both) are reversibly oxidized to the higher (+3) oxidation state. This favours interaction with the π-electron-rich aromatic system of the crown unit which relocates the crown towards the oxidized metal center.



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10:30 invited lecture

Solvation in Pure and Mixed Solvents: An Overview

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Understanding solvation is a prerequisite to delineate the effects of solvents and their mixtures on reaction rates and equilibria. These effects cannot be satisfactorily described in terms of a single solvent property. For pure liquids, use of multiple-parameter equations has proved to be a more successful approach. The parameters employed include solvent acidity, basicity and dipolarity/polarizability. The success of these correlations has lead to a wide interest in studying the phenomena of solvatochromism and thermosolvatochromism (effects of temperature on solvatochromism). Solvation is a function of the properties of both probe and solvent, in particular, their pKa and hydrophobic/hydrophilic character. Increasing temperature leads to desolvation; the corresponding energy is ca. 1-2 kcal/mol, i.e., is not negligible compared to the enthalpy of activation of typical organic reactions. Solvation in binary solvent mixtures is more complex than in pure solvents because of “preferential solvation” of the probe by one component of the mixture. That is, the composition of the probe solvation micro-sphere does not match that of bulk solvent. This composition is given by the so-called solvent “fractionation factors”, j, whose value, relative to unity, indicates the solvent that is preferentially solvating the probe. Recently, a general model has been introduced to calculate j in which the formation of the hydrogen-bonded species (e.g., ROH--OH$_2$) both in bulk solvent and in the probe solvation microsphere was explicitly considered. Application of this model to solvation in binary mixtures has shown that the probes are preferentially solvated by the hydrogen-bonded species. Solvation of a single probe in a series of aqueous alcohols depends on the pKa and hydrophobicity of the alcohol. Additionally, temperature increase affects the structure of alcohol more than that of water.

Conclusions and perspectives

The study of solvatochromism and thermo-solvatochromism has shown the complexity and interplay of the factors involved. This subject is generating increased interest because of the intense research on “green” solvents. The main conclusion of these studies is that the composition of the solvation microsphere of the species of interest (reagents and/or activated complexes) differs from that of bulk binary mixture. An example of application is the judicious choice of the organic component of the mixture (protic or aprotic solvent) in reactions where desolvation is important, e.g., S$_N$2, acyl transfers, etc.

I would like to thank FAPESP and CNPq for financial support and a research productivity fellowship and my research co-workers for doing the work reported.

Plenary Session X

Friday afternoon, 25 August, 12:35

Chair: Tadeusz M. Krygowski

12:35 invited lecture

Chemical Reactivity in Colloidal Microheterogeneous Media

José R. Leis[1], Luis Garcia-Rio[1], Juan C. Mejuto[2]

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Colloids form homogeneous solutions although at microscopic level they are highly structurated microheterogeneous media with domains of very different properties. Good examples are micellar solutions, microemulsions, liposomes and vesicles. The driving force of this particular behaviour is hidrophobicity regulated by the particular properties of surfactants.

Along the last decades models to explain chemical reactivity in those media has been developed. All of them are based on the distribution of reagents among the different parts of the microheterogeneous structure and in general they are based on the pseudophase approach, which assumes equilibrium distribution of reagents among pseudophases (i.e. micellar, aqueous and interphase). This approach is generally valid for chemical reactions slower than rate of exchange of material (monomers and reagents) among pseudophases. This model alow us to obtain information about rate constants and distribution constants and concentrations of each reagent and intermediate in each pesudophase.

Dramatic changes in reaction rates have been reported for very different chemical reactions. We will discuss some of these results focussing in mechanistic changes induced by these systems. Particular properties of each pseudophase dielectric constant and water content are finally responsible for dramatic changes in nucleophilic-electrophilic power of different reagents.

A different approach that will also be discussed is the use of well known chemical reactions as probes to get valuable information about the structure and properties of the pseudophases, in particular about the key structure the interphase.

Symposium 1

Programme

Monday, 21 August

Oral Session I
Monday morning, 21 August, 11:30
Chair: Sławomir J. Grabowski

11:30 oral

Enzyme Catalysed Phosphoryl Transfer Reactions: Magnesium and Other Metal Fluorides as Substrate and Transition-State Analogs

George M. Blackburn

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Magnesium trifluoride, MgF_3^-, has been assigned [1, 2] and under-assigned [3] as the molecular species seen in x-ray structures of trigonal-bipyramidal species (tbp) of enzymes catalysing phosphoryl transfer. A structure of ß-phosphoglucomutase (ßPGM) complexed with G6P has been presented as a pentacovalent tbp phosphorus intermediate [3]. Our alternative attribution of MgF_3^- as the tbp species [4] has been strongly rejected [5].

Kinetic, spectroscopic, and structural data confirms MgF_3^- as a TSA for ßPGM. F^- is a strong inhibitor for ßPGM and 19F NMR analysis shows three F^- ions are recruited into the active site of the enzyme in the presence of G6P. NOE analysis using 15N,2H-labelled ßPGM shows 4 amino acids in close contact with two F^-; the third F^- is co-ordinated to a catalytic Mg_2^+ ion. This accurately locates the binding site for MgF_3^- which is further co-ordinated to G6P C1-OH group and to Asp8. In examples of metal fluoride complexes of phosphoryl transfer enzymes identified by x-ray analysis, the presence of F^- (rather than OH^-) must be inferential at the resolutions achieved. Our results constitute the first direct observation of a metal fluoride complex as a TSA for a phosphoryl transfer enzyme. The bonding in the tbp accurately portrays the transition state for phosphoryl transfer in ßPGM and reveals the details of protein catalysis.

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11:50 oral

Mutagenicity of N-Acyloxy-N-alkoxyamides as Probes for Drug-DNA Interactions

Luke E. Andrews[1], Antonio M. Bonin[2], Samuel F. Clay[1], Linda E. Fransson[1], Ashley-Mae E. Gillson[1], Stephen A. Glover[1], Jonas S. Nordström, Rhiannon R. Schumacher

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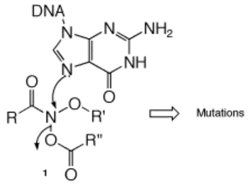
Electrophilic *N*-acyloxy-*N*-alkoxyamides (1), a class of synthetic mutagens [1], exhibit remarkably well behaved mutagenicity in Salmonella TA100. As a consequence, they can be used to quantify the role played by various organic groups in promoting or interfering with the way a drug can associate with DNA.

The versatile synthetic protocol for these permits incorporation of a wide range of different substituents on any of the three side chains, R, R' and R'' and almost all of the seventy compounds we have tested to date are directly mutagenic in the Ames test.



Hydrophobicity (log P), electronic effects (pK_a of R''CO_2H), steric effects (Taft E_s) have enabled establishment of an extensive QSAR [2], which predicts activities of mutagens in this class that are "well-behaved", i.e. that do not impede binding or reaction with DNA (two different processes) or have intercalating groups or substituents tailored to the groove characteristics. Deviation from this QSAR, in either a positive or a negative sense, highlights special structural features and the manner in which they impact upon DNA association. So far we have been able to detect steric inhibition of DNA binding and reactivity [3] and, importantly, activity enhancement through non-specific incorporation of planar polycyclic aromatics. Naphthalenes and pyrenes on any side chain lift activity in line with the equivalent of 3 LogP units worth of hydrophobic binding. Side chains bearing biphenyl, fluorene and anthraquinone that are purported to intercalate have no effect.

DNA damage studies provide direct evidence for the primary event in their mutagenicity, namely electrophilic attack on Guanine-N7 and damage profiles are in line with the variations in mutagenicity

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12:10 oral

How do Biocides Derived from Sym-Triazines Start Their Fate?

Isabel Fernández[1], Josep M. Oliva[2], Moisés Canle L[1], Arturo Santaballa[1]

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Governments and environmental agencies agree that fresh water is a scarcer resource. On the other hand, the world-wide implementation of intensive agriculture has led to an exponential increase in the variety and quantities of agrochemicals in natural waters, most of which are somehow resistant to degradation. Consequently, it has been claimed the need of ecoefficient water treatment methods to achieve a sustainable society.

Many different techniques have been attempted with questionable success to promote the degradation of these persistent organic pollutants. One of the most efficient alternatives to natural degradation of pollutants involves the use of UV/Vis radiation.

In this context, we present a study of the first stages of the photodegradation of *sym*-triazine-based herbicides. Geometries of neutral species are known, but this is not the case for the radical charged species that are short-lived intermediates in oxidative or reductive processes of these compounds. Laser flash photolysis and pulse radiolysis studies evidenced the participation of short-lived radical cations and anions in the mechanism.

Spectroscopic features of the radical cation and radical anion derived from *sym*-triazines are given. Red-ox potentials and pKa values of these short-lived species have been measured. Rate constants for reaction of *sym*-triazines with several radicals were used to establish linear free energy correlations.

The complementary computational study was done by using DFT at the B3LYP/6-31++G** computing level. The optimised structures of the radical cation and radical anion derived from sym-triazine undergo respectively an in-plane and out-of-plane Jahn-Teller distortion due to the presence of doubly degenerate HOMOs and LUMOs. Red-ox potentials and pKa values have been also calculated.

Acknowledgements. This work was funded by the *Xunta de Galicia* (Spain), project code: PGIDIT05TAM10301PR. We are indebted to the *Centro de Supercomputación de Galicia(CESGA)* for computer capabilities.

12:30 oral

Reaction Mechanism and Chemotaxonomy in the Formation of Type II and Type III Indole Alkaloids Derived from Secologanin

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It is well known that the special group of indole alkaloids derived from strictosidine is produced mainly by three tightly related plant families (Rubiaceae, Loganiaceae and Apocynaceae) from secologanin and tryptamine. The high number of alkaloids (more than 2500 isolated compounds) of common origin supposed a high degree of common chemical background, and suggested the possibility to detect at least the key steps of their formations by considering their structures, chemotaxonomic properties and the usual organic reactionmechnisms. This coherence could be demonstrated in the first part of our work (1) in alkaloids having the secologanin substructure in unrearranged form (type-I alkaloids). In the present work, the type II and type III alkaloids were investigated with the same method and according to the same aspects. The rearrangement of the type-I skeleton was interpreted by dissociation of bond C-15-C-16 (2) followed by association of C-17 to C-14 (in type II) or to C-20 (in type III) alkaloids in frame of an intramolecular Diels-Alder reaction. The position of the double bonds before and after the rearrangement and derivatives of secodine-type intermediates in plant species supported this mechanism. Further transformations involving cyclizations, fragmentations, rearrangements and functional group transformations afforded more than 500 ibogan (mainly type II), plumeran and eburnan (mainly type-III) alkaloids in great structural variety. Nearly all of them could be derived in the interplay of organic reactionmechanisms and chemotaxonomic properties (3) in a special stereochemical framework.

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12:50 oral

Locating and Evaluating Steric Effects by NMR

Peter R. Seidl[1], Julliane D. Yoneda[2], Kátia Z. Leal[2]

1. *Universidade Federal do Rio de Janeiro (UFRJ), Centro de Tecnologia, bloco E, Ilha do Fundão, Rio de Janeiro 21949-900, Brazil* **2.** *Universidade Federal Fluminense (UFF), Outeiro de São João Batista s/n, Rio de Janeiro 24020-150, Brazil*

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The rapid advance of supramolecular chemistry has led to a better understanding of the forces and interactions that are responsible for many different phenomena. Among these, steric effects play an important role in determining the constraints to association between the species involved. Although the role of steric effects has been recognized for a long time, quantitative information has been mainly related to the magnitude of these effects rather than the properties of the group of atoms that is responsible for them. This situation has been changing with the increase in the power of modeling tools and the accumulation of data on models that can be used for the purpose of comparison. The results of our studies on substituted model compounds such as adamantanes, norbornanes, norcamphors and camphors, show how NMR can be used to locate the segment of a molecule that is subjected to steric effects and evaluate the degree to which these effects will distort its geometry.

Oral Session II

Monday afternoon, 21 August, 17:00
Chair: Mirjana Eckert-Maksić

17:00 oral

Time-Resolved IR Detection of the Ylide Structure by Intramolecular Cyclization of Photoreaction of 2-Azaaromatic Substituted Diazomethyl Ketones

Shinjiro Kobayashi[1], Thomas T. Tidwell[2], Annette Allen[2], Nanyan Fu[2]

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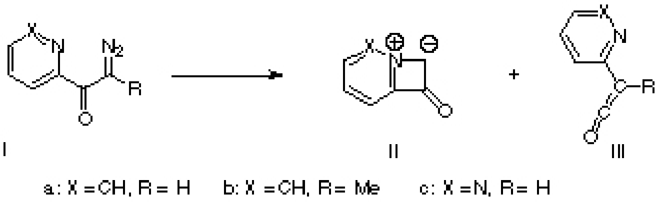
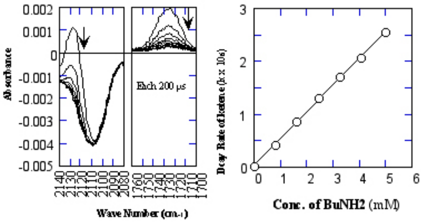
We have been studying ketene formation by laser flash photolysis of aromatic α-diazoalkyl ketones. Among them 2-azaaryl sustituted compounds give species which have longer wave length absorption than do the corresponding ketenes. This absorption does not decay upon addition of amine nucleophiles. Wentrup found the ylide structure (IIa) coming from photolysis of 2-pyridyl diazomethyl ketone (Ia) by matrix isolation method [1]. We will report here the detection of the ylides by time-resolved IR technique.



The solution of Ia in MeCN (0.02 mM) was irradiated with 266 nm laser light (2 mJ) and the change at different wave numbers was recorded. The results are shown in the left figure. The large depletion at 2107 cm^{-1} comes from the decrease of Ia by laser irradiation. The absorption at 2127 cm^{-1} shows the formation of ketene IIIa and the one at 1725 cm^{-1} derives from IIa. Similarly, Ic shows the depletion of Ic at 2112 cm^{-1}, the formation of ketene IIIc at 2132 cm^{-1}, and the ylide IIc at 1758 cm^{-1}. For Ib depletion of Ib and the ketene IIIb were observed at 2076 and 2104 cm^{-1}, respectively, but no ylide absorption is detected. In the presence of butylamine the ylide IIa and IIc had longer life times, while the decay rates of ketenes III were accelerated linearly with the concentration of the amine and gave second order rate constants of 2.15 x 10^8 $M^{-1}s^{-1}$ for IIIa, 1.92 x 10^6 $M^{-1}s^{-1}$ for IIIb, and 5.10 x 10^8 $M^{-1}s^{-1}$ for IIIc. (see right Figure).



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17:20 oral

New Chemistry of N-Nitroso-N,O-dialkylhydroxylamines and Related Compounds

Howard Maskill, Juan Crugeiras, Ana Rios, William McFarlane, Miguel A. Rios

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A. The kinetics of nitrosation of dialkylhydroxylamines (RNHOR') have been investigated in aqueous acidic solution and shown to be compatible with a mechanism involving two channels. One involves direct reaction of the free hydroxylamine with nitrous acid, and the other involves reaction of the hydroxylamine with protonated nitrous acid.

$$\mathrm{R\overset{+}{N}H_2OR'} + \mathrm{H_2O} \rightleftharpoons \mathrm{RNHOR'} + \mathrm{H_3O^+}\ ;\quad K_{a1}$$

$$\mathrm{H_2\overset{+}{O}NO} + \mathrm{H_2O} \rightleftharpoons \mathrm{HONO} + \mathrm{H_3O^+}\ ;\quad K_{a2}$$

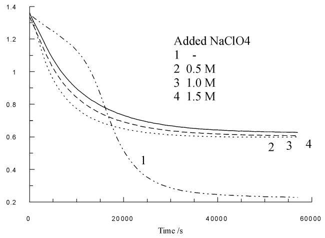
$$\mathrm{RNHOR'} + \mathrm{HONO} \xrightarrow{k_1} \mathrm{RN(NO)OR'} + \mathrm{H_2O}$$

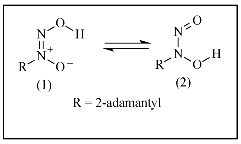
$$\mathrm{RNHOR'} + \mathrm{H_2\overset{+}{O}NO} \xrightarrow{k_2} \mathrm{RN(NO)OR'} + \mathrm{H_3O^+}$$

$$\text{Overall Rate} = k_1\,[\mathrm{RNHOR'}][\mathrm{HNO_2}] + k_2\,[\mathrm{RNHOR'}][\mathrm{H_2\overset{+}{O}NO}]$$

B. The interconversion of rotational isomers of N-nitrosodimethylhydroxylamine, MeN(NO)OMe, has been investigated by temperature-dependent NMR spectroscopy, and the enthalpy and entropy of activation have been determined. Comparison of the experimental results and values computed using high level MO theory indicates differing states of solvation of stable *cis* and *trans* isomers and the transition structure for their interconversion.

C. UV-Absorbance *versus* time data for the acid-catalysed decomposition of N-(2-adamantyl)hydroxydiazenium oxide indicate an unprecedented electrolyte-dependent autocatalytic mechanism *via* the less stable N-nitroso,N-adamantylhydroxylamine tautomer. The products of the reaction are 2-adamantanol and nitrous oxide (N_2O).





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17:40 oral

Connecting the Superelectrophilic and Diels-Alder Reactivities of Nitrobenzofuroxans

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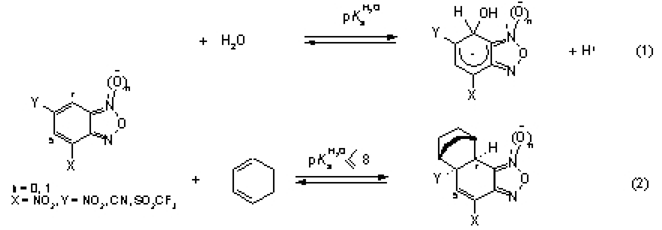
Nitrosubstituted 2,1,3-benzoxadiazoles and related 1-oxides, commonly referred to as nitrobenzofurazans and nitrobenzofuroxans, respectively, represent a class of neutral heteroaromatic structures which exhibit an extremely high electrophilic character in nucleophilic addition and substitution processes [1]. As an illustration of this behaviour, the assessment of both carbon and nitrogen nucleophilicities of 2-aminothiazoles through coupling of these ambident derivatives with 4,6-dinitrobenzofuroxane (DNBF) will be discussed [2].

Recently, it has been shown that the carbocyclic ring of a number of nitrobenzofuroxans and related heterocycles, e.g. nitrotetrazolopyridines, can also be involved in a variety of Diels-Alder reactions, contributing both to normal and inverse processes which often proceed with high stereoselectivity [3]. In this regard, we will highlight our finding that there is a close relationship between superlectrophilicity and pericyclic reactivity of our substrates [4]. Compounds which are the most prone to undergo s-complexation, as measured by the pK_a values for water addition (eq. 1), are also those which exhibit the greatest pericyclic reactivity. For reactions involving such common dienes as 2,3-dimethylbutadiene, cyclopentadiene or cyclohexadiene (eq. 2), a value of 8-8.5 defines the frontier demarcating those electrophiles which can exhibit dual pericyclic and electrophilic behaviour from those which do not [4]. Importantly, this frontier can also be defined with reference to the ranking of nitrobenzofuroxans on the comprehensive electrophilicity scale of Mayr et al (Acc. Chem. Res. 2003, 36, 66) as well as the theoretical electrophilicity scale of Parr (J. Am. Chem. Soc. 1999, 121, 1922).

Last, the dual electrophilic and pericyclic reactivity of 4-nitrobenzodifuroxan and the demonstration that this compound behaves as a superelectrophilic nitroolefin will be presented.



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Tuesday, 22 August

Oral Session III

Tuesday morning, 22 August, 11:30

Chair: Dennis N. Kevill

11:30 oral

Tautomerism of Acridin-9-amines

Jerzy Błażejowski[1], Youssif Ebead[1], Karol Krzymiński[1], Artur Sikorski[1], Agnieszka Wróblewska[1], Alexander D. Roshal[2], Andrey O. Doroshenko[2]

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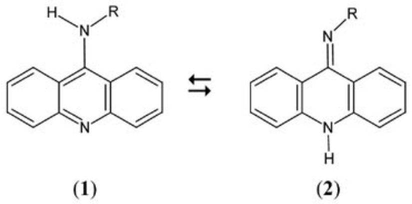

(1) (2)

Acridin-9-amines and their derivatives substituted at the exocyclic nitrogen atom can co-exist in amino (**1**) and imino (**2**) tautomeric forms. Electron-donating substituents (R) cause the amino form to be more stable, but electron-attracting ones cause the imino tautomer to prevail. Crystals of acridin-9-amines substituted with -t-Bu or -CH_2CH_2Cl at the exocyclic nitrogen atom consist of molecules of the amino tautomer, but those with -OCH_3 or -$COCl_3$ - contain molecules of the imino form. NMR investigations have shown that if R is -OCH_3 or -NH_2, the respective acridin-9-amines occur in the imino tautomeric form in various media. When R is -CH_2CH_2Cl or 5-methylpyridin-2-yl, the preference for a particular tautomeric form depends on the properties of the medium. The results of stationary absorption and fluorescence, time-resolved fluorescence investigations and computational studies have demonstrated that if -CH_2CH_2Cl is a substituent, it is mainly the imino form that absorbs radiation, whereas the amino form fluoresces. When the substituent is 5-methylpyridin-2-yl, the absorbing form is mainly the amino tautomer, and the emitting form is the imino one. As tautomeric forms of the latter two compounds that absorb radiation do not emit it, is probable that H-atom transfer takes place in the excited state. The spectral properties of these acridin-9-amines, both NMR and UV-Vis, thus depend markedly on the properties of the solvent, which makes them potent indicators of the properties of liquid phases. On the other hand, the tautomerism of acridin-9-amines is an interesting subject for investigating the fundamental behavior of chemical systems.

(Study supported by state funds for scientific research under DS/ 8000-4-0026-6)

11:50 oral

The Mode of Transmission of Electrical Effects: Evidence from NMR Spectra

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We have studied the transmission of electrical effects [1-4] as a function of substituent chemical shifts, scs, in ^1H, ^{13}C, and ^{19}F NMR spectra of XGY in which X is the substituent, Y is the atom responsible for the chemical shift and G is the skeletal group to which X and Y are bonded. The C atom of G which is bonded to X is sp^2 hybridized. We have shown that L values obtained from correlation with the LDR equation are a measure of the magnitude of electrical effect transmission. Preliminary results for correlation of -L values of XG-19F scs with the equation

$\log(-L) = a_1 \log n + a^0$ (1)

gives the regression equation (2) on exclusion of the value for G of 6,2-naphthalene.

$\log(-L) = -3.20\ (\pm 0.580) \log n + 2.99\ (\pm 0.401)$ (2)

r^2, 83.59; F, 30.56; S_{est}. 0.206; S^0, 0.468; N_{dp}, 8 .

This corresponds to a modified field effect with a dependence on 1/r3.

We have also examined the composition of the group electronegativity parameters often used in the description of ^{19}F scs. They are a function of electrical effect and polarizability parameters [5]. The regression equation is:

$\sigma_\chi = 0.424(\pm 0.107)\ \sigma_e - 0.329\ (\pm 0.0929)\sigma_d - 1.10(\pm 0.468)$ (3)

R^2, 84.23; A100R^2, 81.36; F, 17.80; S_{est}, 0.0897; S^0, 0.470; N_{dp}, 14.

It seems likely that there is at least one additional variable as yet undiscovered.

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12:10 oral

Computational Study on the Thermochemistry of β-Diketones and Their Radicals: O-H vs C-H Homolytic Bond Cleavage

José R B Gomes, Manuel Anibal V. Ribeiro da Silva

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The strengths of bonds between transition metals or metallic ions and ligands are of deep interest due to their involvement in important chemical and biological processes and have been widely studied in the past years [1]. Among the large number of ligands appears the family of β-diketones, which in general are bidentate ligands, and that are known to form complexes with almost all metal atoms in the periodic table of elements [2]. The metal complex formation can be described by the following reaction in solution:

Mn+ + n HL → MLn + n H+ **[1]**

The thermochemistry of the ligands (HL) and of the metal complexes (ML), both in the condensed and gas-phases, was investigated experimentally in the past [3]. However, the determination of metal-ligand enthalpies for the dissociation of the complex in the gas-phase and described by reaction **[2]**:

ML → M + L **[2]**

requires the gas-phase enthalpies of formation for the three species included in reaction **[2]** and, unfortunately, it was not possible to obtain any result for the L radicals, except that for acetylacetone reported very recently [4].

In this communication, a computational study on the thermodynamic properties of thirteen β-diketones, with general formula $R_1C(-OH)C(-R_3)C(=O)R_2)$, will be presented. The semi-empirical B3LYP method was employed to compute the O-H and C-H bond dissociation enthalpies, enthalpy of tautomerization and to estimate standard gas-phase enthalpies of formation for the radicals and for the parent molecules. The gas-phase enthalpies of formation for the neutral molecules are in excellent agreement with available experimental values, supporting the estimates made for the radicals. The latter are very important for the clarification of the thermochemistry of many β-diketonato metal complexes previously reported in the literature. Importantly, when substituents R= -CHR' are attached to the β-diketone's carcass, C-H homolytic bond cleavage is always favored with respect to O-H bond scission [5].

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12:30 oral

Studies of the Methyl Groups Dynamics in Molecular Complexes

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In the present contribution a review of selected applications of spectroscopic methods, including the inelastic neutron scattering techniques, in studies of hydrogen bonded (HB) and charge transfer (CT) molecular complexes. Of particular interest is the CT interaction effect on the dynamics of methyl groups represented by the low frequency torsional modes and tunnel splittings. Our studies are focused on complexes of hexamethylbenzene (HMB) with tetracyanoquinodimethane (TCNQ), tetracyanoethylene (TCNE) and tetracyanobenzene (TCNB) as well as of tetramethylbenzene (durene) with TCNB and of tetramethylpyrazine (TMP) with chloranilic acid (CLA) squaric acid (H2SQ) and TCNB and finally of three isomeric dimethylpyrazines with CLA. Some of these complexes were obtained for the first time so that the standard information on the structure, phase transitions and infrared and Raman spectra was collected.

In the case of the TMP.CLA complex a remarkable drop of the barrier to internal CH_3 group rotation was found that enabled to perform detailed studies of the tunnel splitting and influence on the rotation of various parameters such like temperature, pressure and isotopic substitution. The results collected so far seem to indicate unequivocally on the substantial contribution of the charge transfer degree to the shaping of the rotational potential.

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[6] A. Pawlukojć, W. Sawka-Dobrowolska, G. Bator, L. Sobczyk, E. Grech, J. Nowicka-Scheibe, Chem. Phys. submitted.

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12:50 oral

Ionization of Various Monofunctional Derivatives of Naphtalene by Bimolecular Free Electron Transfer

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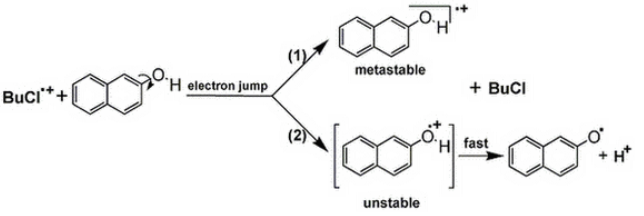
Radiolysis of non-polar media leads to the formation of radical cations. Parent radical cations derived from non-polar solvents such as n-alkanes, cycloalkenes and alkyl chlorides are extremely efficient electron acceptors. Easily they ionize practically all solutes with a diffusion-controlled reaction which is called as free electron transfer (FET) [1]. This reaction type is well studied by pulse radiolysis. FET exhibits some peculiarities which are determined by the properties of non-polar system. In the case of FET the ions are weakly solvated and possess the high excess energy of the reaction, and, accordingly, only limited stabilization of the products is possible. It must be stressed that the electron jump takes place in the first encounter of the reactants in extremely short time (≤10^{-15} s), without the formation of encounter complex.

For pulse radiolytically initiated electron transfer from α- and β-naphtols as well as naphtylamines and thionaphtols, two reaction pathways have been observed, resulting in simultaneous formation of **(1)** metastable radical cations of solutes with lifetimes in μs time range, and **(2)** unstable radical cations, which deprotonate immediatly after formation, producing heteroatom-centred radicals ($-O^{\cdot}$, $-NH^{\cdot}$, $-S^{\cdot}$).

These experimental facts can be explained if one takes into account that electron transfer takes place in a singe rapid step which is faster than molecule deformation motions.



So the distribution of rotation-conditioned conformers of the solute is reflected by the geometry of the radical cations produced. In this manner product radical cations of different stability are produced, which are distinguishable by their properties.

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Oral Session IV

Tuesday afternoon, 22 August, 17:00

Chair: Andreas Hirsch

17:00 oral

Measuring Electron Delocalization in Aromatic Molecules

Patrick Bultinck[1], Robert Ponec[2], Ramon Carbó-Dorca[1,3]

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Aromaticity, although introduced long time ago, remains a challenging chemical concept. The basic reason is that there is no clear definition based on quantum chemical description, yet it persists as a very powerful idea, allowing the interpretation of many chemical phenomena. As a consequence there exist many indices aimed at quantifying molecular aromaticity. An especially intriguing finding is that some of these measures are mutually orthogonal or divergent, an unacceptable situation in front of the necessary aromaticity index uniqueness. Moreover, there exist many ambiguities about how to exactly compute many of these measures.

The present paper introduces two novel approaches, solving many of the problems related to other ways to assess aromaticity. The first method is based on powers of the density matrix and proper projection operators, allowing to quantify aromaticity as a *6-center chemical interaction (SCI)* [1-3]. The second method is based on Molecular Quantum Similarity [4] measures, which permit to compare quantitatively the first order density matrices of molecular fragments to a reference system, thereby obtaining a new aromaticity index.

Both new indices are found to correlate very well. Lack of correlation with some other indices is discussed and shown to be due to shortcomings of or debatable arbitrary choices in many other techniques. The SCI model is critically examined for clamped benzenes and distorted benzenes. The grounds for the lack of correlation with NICS aromaticity indices are examined and the effects on the multidimensional character of aromaticity reported.

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17:20 oral

On Geometry-based HOMED (a Measure of Hyperconjugation, n-π, and π-π Conjugation) and HOMA Index (a Measure of Aromaticity)

Ewa D. Raczyńska[1], Tadeusz M. Krygowski[2], Kinga Duczmal[1], Małgorzata Hallmann[1]

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The geometry-based HOMA (Harmonic Oscillator Model of Aromaticity) index, has been defined more than thirty years ago [1] and reformulated in 1993 [2] to describe quantitatively π-electron delocalization in strongly conjugated aromatic systems [3]. This reformulated index applied recently [4] to simple acyclic systems has led to some expected results: the HOMA values are close to zero or even negative showing that π-electrons are considerably less delocalized in these acyclic molecules than in reference systems applied for HOMA.

In majority of simple acyclic compounds, weakly delocalized by hyperconjugation (e.g., aldehydes, ketones, imines), or n-π conjugation (e.g., amides, amidines, guanidines), one part of atoms occurs in sp^3 state of hybridization and the other one in sp^2 state of hybridization. This dramatically differs from situation in majority of aromatic compounds, where solely sp^2 atoms form pi-electron system and mainly π-π conjugation takes place (e.g., benzene, naphthalene, antracene, pyridine, pyrimidine). The n-π conjugation is only possible for five-membered systems (e.g., pyrrole, furan, thiophene).

Taking these hybridization state and resonance conjugation differences into account, the reference CX single and double bond lengths were defined for the geometry-based HOMED (Harmonic Oscillator Model of Electron Delocalization) index in order to describe properly π-electron delocalization in acyclic systems containing C, N, O and/or S atoms. We propose to use the HOMED abbreviation for the modified index, based on the old HOMA idea, to distinguish it from the HOMA index defined for strongly delocalized aromatic systems. The HOMED index applied to keto-enol, imine-enamine, amide-iminol, thione-thiol, thioamide-thioiminol systems describes better the π-electron delocalization for individual tautomers than the HOMA index.

Acknowledgments. Ab initio calculations were carried out at the Interdisciplinary Center for Molecular Modeling (ICM, Warsaw).

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17:40 oral

Evaluations of NICS Aromaticity Indexes for Planar π Rings

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1. *Islamic Azad University-Rasht Branch, Department of Chemistry, Pole-taleshan-Lakan street, Rasht 41335-3516, Iran* **2.** *University of Georgia, Department of Chemistry, Center for Computational Chemistry, 1004 Cedar Street, Athens, GA 30602-2556, United States*

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Aromaticity is of fundamental importance to chemistry. Even after two centuries, the concept that electron delocalization in closed circuits endows molecules with special properties continues to increase in its scope of applicability and in its importance. Since aromaticity is not a directly measurable quantity, its magnitude is now generally evaluated in terms of structural, energetic, and magnetic criteria. However, magnetic properties are the most closely related to aromaticity, as they depend directly on the induced ring currents associated with cyclic electron delocalization.

Since its introduction in 1996 [1], NICS (nucleus-independent chemical shift) continues to gain popularity as an easily computed, generally applicable criterion to characterize aromaticity and antiaromaticity of rings, clusters, transition states, and transition-metal complexes. NICS is based on the magnetic shielding (with the sign reversed) computed at chosen points in the vicinity of molecules. Significantly negative (shielded) NICS values inside rings or cages are due to induced diatropic ring currents and denote aromaticity, whereas positive (deshielded) values denote paratropic ring currents and anti-aromatic behavior.

Five increasingly sophisticated aromaticity indexes, based on nucleus-independent chemical shifts (NICS), were evaluated against a uniform set of aromatic stabilization energies (ASE) for 75 mono- and polyheterocyclic five-membered rings. While acceptable statistical correlations were given by all of the NICS methods, the most fundamentally grounded index, $\mathrm{NICS}(0)\pi_{zz}$ (based on the π contribution to the out-of-plane zz tensor component), performed best statistically (cc = 0.980) and in practice. The easily computable $\mathrm{NICS}(1)_{zz}$ index is a useful alternative (cc = 0.968) [2].

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18:00 oral

Effect of Substituents and Protonation on the Electronic Structure of [2.2]Paracyclophane

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The [2.2]cyclophanes are the simplest [2n]cyclophanes that present two benzene rings connected by two ethanediyl linkages. The [2.2]paracyclophane, (1), is considered the most tensioned [2.2]cyclophane, which has face-to-face benzene rings connected by alkane bridges. The structural characteristics of these compounds make possible to investigate the presence of the transannular interactions, which are classified as through-space interactions (π-π interaction between the aromatic rings) or through-bond interactions (σ-π interaction between the benzene rings and the methylene bridges), and how these interactions affect the chemical properties. In this sense, the aim of this work is to investigate the effects of different substituents, as -F, -CN, -C=O, $-NH_2$ and $-H^+$ on the electronic structure and on the chemical properties of 1. All calculations were made by B3PW91/6-31+G(d,p). The geometries indicate that the dihedral angles of the bridges are the most affected by the substituents, independent of their nature (electron-withdraw or electron-donor). The aromaticity was evaluated by using NICS and HOMA criteria. The presence of C=O and the protonation reduce drastically the aromaticity by breaking off the electron delocalization. The NBO, NRT, and NSA analyses showed that the substitution induces the presence the transannular interactions. In addition, the AIM analysis pointed out through-space interactions only in two compounds. In general, it can be concluded that some substituents induces the presence of a large number of through-space interactions with small second-order stabilization energy and the protonation causes a small number of through-space interactions but with large second-order stabilization energy.

Wednesday, 23 August

Oral Session V

Wednesday morning, 23 August, 11:30
Chair: Patrick W. Fowler

11:30 oral

Quantifying Electrophilicity and Nucleophilicity

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Reactions of donor stabilized carbocations with electron-rich π-systems and reactions of acceptor substituted carbanions with electron-poor π-systems are often treated as representatives of different classes of reactions - carbocation chemistry on one side, and carbanion chemistry on the other side.

$$\log k\,(20\ ^\circ\mathrm{C}) = s(N + E) \qquad (1)$$

We now demonstrate that the nucleophilicity parameters N and s, as defined by eq. 1 and previously derived from reactions of carbanions with benzhydrylium ions and quinone methides [1], can also be employed for describing the reactions of carbanions with various other types of Michael acceptors (Figure). In this way, carbocations and electron-deficient ethylenes can be located on a common electrophilicity scale while carbanions and electron-rich ethylenes can be located on a common nucleophilicity scale.

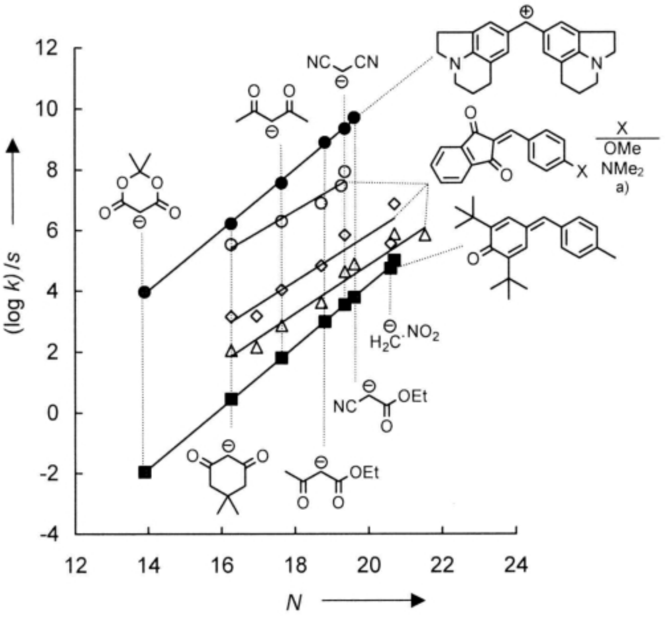

Figure. Plot of (log *k*)/*s* for the reactions of carbanions with electrophiles in DMSO at 20 °C versus the nucleophilicity parameters *N* of the carbanions. a) C_6H_4X = julolidyl

Figure shows that the slopes of (log *k*)/*s* plots versus the nucleophilicity parameters *N* of carbanions deviate from the slope of 1, indicating that eq. 1 does not properly describe these reactions, as previously reported for S_N2 type reactions [2].

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11:50 oral

Cyclization of Active Methylene Compounds with ω-Chloroalkyl Isocyanates and Isothiocyanates and Related Species

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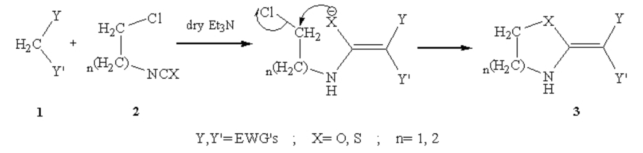
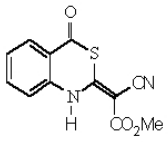
Enols and thioenols Y'YC=C(XH)NHR (X=O,S) were previously obtained by condensing CH_2YY' with isocyanates or isothiocyanates. These dipolar polyfunctional (NHR, OH, electrophilic C=C) species are potential synthons. In the present work we prepared >25 heterocyclic compounds by reaction of active methylene compounds **1** with organic isocyanates or isothiocyanates carrying a terminal nucleofuge, such as Cl. Compounds **1** gave with 2-chloroethyl isocyanate (or isothiocyanate) **2** (n= 1, X=O, S) the 1,3-oxazolidines and 1,3-thiazolidines **3** (n=1, X=O, S), respectively.



Reaction of **1** with **2** (n= 2, X= O) gave the 1,3-oxazines **3** (n=2, X=O). The analogous asymmetric 1,3-thiazolidine **3** (n= 1, X= S) showed E and Z isomers, the one displaying the lower field NH group being in excess. Replacing the Cl by a CO_2Et, e.g. in ethyl 2-isothiocyanatobenzoate **4a** and reacting with $CH_2(CN)CO_2Me$ gave E/Z methyl cyano (1,4-dihydro-2-oxo-1H-3,1-benzothiazin-2-ylidene) acetate **5**, while the ethyl 2-isocyanatobenzoate analogue **4b** gave with **1** the non-cyclized enols 2-$(EtO_2C)C_6H_4NHC(OH)=CYY'$ **6**. Ethoxycarbonyl isothiocyanate **7** and $CH_2(CN)CO_2Me$ gave the non-cyclized thioenol $EtO_2CNHC(SH)=C(CN)CO_2Me$ **8**. Finally, while **3** was formed from NaCH(CN)CONHMe with **2** (n=1, X=O) in dry THF, reaction of $CH_2(CN)CONHMe$ with **2** (n=1, X=O) in the presence of dry Et_3N/ dry DMF gave the bicyclic aminopyrimidinedione **9**. Possible mechanisms for formation of the products will be discussed.



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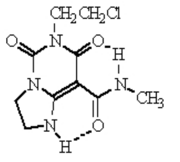

9

12:10 oral

Predicting the Rates of Organic Reactions in Solution: Addition of Thiols and Sulfite to Carbonyl Compounds

Peter Guthrie

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"No Barrier Theory" asserts that when only one thing happens in a chemical reaction there is no kinetic barrier, but only a quadratic potential function, and that the kinetic barriers associated with almost all chemical reactions result form the need for more than one simple thing to happen simultaneously for the reaction to occur. This theory permits calculation of the free energies of activation for chemical reactions given only the equilibrium constants in solution and the distortion energies corresponding to the hypothetical "one thing at a time" transformations. The calculations are much less demanding than direct calculation of the structure and energy of the solvated transition state and generally come within 2 kcal of the observed value.

This approach has now been applied to the addition of thiols and sulfite to carbonyl compounds. As has been shown for the addition of water to carbonyl compounds, the No Barrier Theory approach allows calculation of the rate constants corresponding to a mechanism of reaction.

12:30 oral

An Expanded Nucleophilicity Range of Metal Carbonyl Anions in Vinylic Substitution Reactions

Petr K. Sazonov, Galina A. Artamkina, Irina P. Beletskaya

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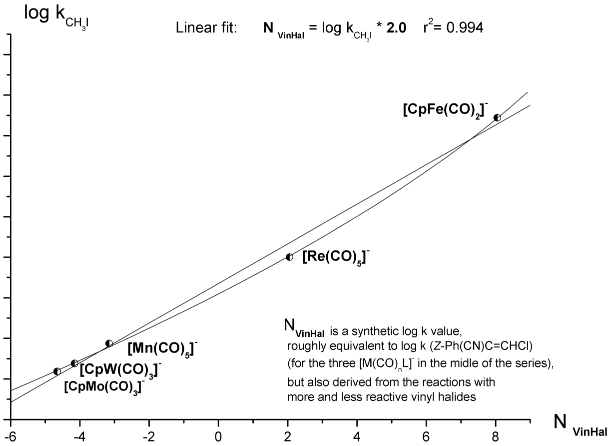
Metal carbonyl anions ($[M(CO)_nL]^-$) are characterized by a very broad nucleophilicity span, which in aliphatic S_N2 reactions increases by eight orders of magnitude from $[Co(CO)_4]^-$ to super-nucleophilic $[CpFe(CO)_2]^-$. Studying the nucleophilic vinylic substitution (SNV) reactions with $[M(CO)_nL]^-$ anions [1] allowed us to compile a nucleophilicity scale of these anions in vinylic substitution (**Ad_NE** mechanism). The scale was obtained by combining the kinetic data from several overlapping series of $[M(CO)_nL]^-$ anions reacting with vinyl halides of different activity (PhCF=CFHal, Ph(CN)C=CHHal, Ph(Cl)C=(CN)$_2$, ets.). The nucleophilicity span of $[M(CO)_nL]^-$ anions found in SNV reactions is **twice** as large as in aliphatic S_N2 reactions, though good correlation exists between the N_{VinHal} and log(k $_{CH3I}$) parameters (see the Figure). The problem of interpreting the nucleophilicity data in terms of reaction mechanism, and the question whether it is indicative of latent single electron transfer (SET) step are to be discussed in the presentation.



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12:50 oral

Regio- versus Non-Regioselectivity of Haloenolcyclization of 2-Allylcyclo-1,3-hexanediones Using Iodine in Methanol and Pyridinium tribromide in Dichloromethane

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We have previously employed iodine in refluxing methanol and pyridnium tribromide (PTB) in acetic acid to convert the 3-(phosphonoalkyl)cyclohexenones to a series of benzylphosphonic esters substituted in the aromatic ring with methoxy or hydroxyl group, respectively [1]. In a recent communication [2], we have demonstrated that iodocyclization of α-allylcyclohexane-1,3-diones using iodine-methanol mixture, leads exclusively to *exo*-cyclized 2-iodomethyltetrahydrobenzofuran-4-ones (minor) and 2-iodomethyl-4-methoxydihydrobenzofuran derivatives (major) according to Baldwin's rules [3]. On the other hand, bromoenolcyclization using PTB in dichloromethane was found to afford both the 2-bromomethyltetrahydrobenzofuran-4-ones (major) and 3-bromomethyltetrahydrobenzopyran-5-ones (minor) through exo-cyclization and endocyclization, respectively [2]. These observed results demonstrate the combined electrophilic and oxidative potentials of I_2-MeoH and PTB. Experimental evidence in the form of isolated intermediates will also be presented to support the proposed mechanisms.

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We are grateful to the National Research Foundation (NRF) and the University of South Africa (UNISA) for financial assistance.

Oral Session VI

Wednesday afternoon, 23 August, 17:00

Chair: Herbert Mayr

17:00 oral

Thermodynamic Phase Behavior of Ionic Liquids

Urszula M. Domańska-Żelazna

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The solid-liquid and liquid-liquid phase equilibria of ionic liquids (ILs) basing on alkyl-(2-hydroxyethyl)-dimethyl-ammoniumcation $[C_n]$ and different anions $[Br^-$, or $N(CN)_2^-$, or PF_6^-, or BF_4^-, or $N(CF_3SO_2)_2^-]$ [1] and 1-alkoxymethyl-3-methyl-imidazolium, ($[C_nH_{2n+1}OCH_2mim]$) or 1,3-dialkoxymethyl-imidazolium ($[(C_nH_{2n+1}OCH_2)_2im]$) cations with different anions $\{BF_4^-$, $N(CF_3SO_2)_2^-\}$ [2] have been measured. The determination of the IL - solvent interaction of these salts and alkyl-methyl-imidazolium cations with $\{[CH_3SO_4^-]$, or $[OcSO_4^-]$, or $[MDEGSO_4^-]$, or $[TOS^-]\}$ anions via the solubility measurements, or excess molar volumes or activity coefficients at infinite dilution measurements have been performed. The influence of high pressure up to 600MPa on IL's SLE has been also investigated. These salts mainly exhibit simple eutectic systems with immiscibility in the liquid phase with upper critical solution temperatures (UCST).

The SLE and LLE curves were correlated by means of the different G^{Ex} models utilizing parameters derived from the SLE or LLE. The root-mean-square deviations of the solubility temperatures for all calculated data depend on the particular system and the equation used. The (liquid + liquid) phase equilibria was predicted for many systems with COSMO-RS model.

Due to the fascinating physico-chemical properties of these ionic liquids, they seem to be significant in development of new technologies.

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17:20 oral

New Persistent Heteroaromatic Radicals as Building Blocks for Paramagnetic Liquid Crystals

Jozef Zienkiewicz, Anna Fryszkowska, Katarzyna Zienkiewicz, Piotr Kaszynski

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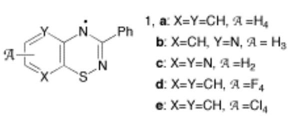
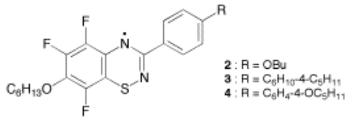
In pursuit of paramagnetic liquid crystals for the study of molecular magnetism in organized media, we focused on the -N-S- fragment as the spin source. The thioaminyl fragment was incorporated into aromatic hydrocarbons leading to de novo designed π-delocalized heteroaromatic radicals that satisfy electronic and geometrical requirements for this new class of materials [1, 2]. In this context, we have recently investigated a series of thiadiazinyl radicals **1** [3]. We studied the efficiency of radical generation and their stability as a function of the adjacent ring structure. The high stability of the halogenated radicals **1d** and **1e** permitted their isolation and complete structural, spectroscopic, and electrochemical characterization. Experimental data was rationalized with the results of DFT calculations. The particularly promising parent radical **1d** was further substituted with groups that promote liquid crystallinity to give radicals **2**-**4**. Out of the three radicals, only 4 was successfully generated, and showed liquid crystalline properties.





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17:40 oral

Direct Observation of the Photoinduced Phase Transition of the Stable Organic Radical TTTA by Powder Photodiffraction

Pance Naumov[1,2], Jonathan P. Hill[2,3], Kenji Sakurai[3]

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We report on the first direct observation of photoinduced domain formation by photocarrier doping of the stable organic radical TTTA (1,3,5-trithia-2,4,6-triazapentalenyl), which exhibits unusually large thermal hysteresis width of 75 K of the paramagnetic-to-diamagnetic phase transition around room temperature. For that purpose, a new setup for powder photodiffraction was developed, composed of a second harmonic pump (532 nm) of Nd:YAG laser coupled with powder diffractometer using synchrotron radiation as probe at the beamline BL15XU at the 8 GeV third generation synchrotron SPring-8 in Hyogo (Japan). Lowering of the lattice symmetry by thermally induced and photoinduced formation of structural domains of two different phases was observed. Both phases can be decayed by thermal treatment. The results show, for the first time, that the photoinduced and the thermally induced phases in this open-shell spin-Peierls system are structurally different, in accordance with the different proposed mechanisms for their creation.

18:00 oral

Deaggregation Behaviors of Organic Compounds

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The aggregates of electrically neutral organic molecules are formed solely by hydrophobic lipophilic interaction (HLI) in water or aquiorgano mixtures. And we have found that the coaggregating tendencies of cholesterol esters and triglycerides might be one of the culprits of the arteriosclerosis. Therefore to find an organic molecules which can prevent or cure the arteriosclerosis would be very interesting and important. These molecules are called deaggregators (deAgr). We visualize that an effective deAgr might break up or reduce the size of aggregates.

We have searched and synthesized a variety compounds and quantitatively measured their deaggregating abilities, *e.g.n*-alkyl-glucopyranosides, *n*-alkyl-maltosides, phospholipids, saponins, dipeptides, phenols and phenol gemini compounds. The relationship between structure and the deaggregating ability is discussed. The results are consistent with the proposed hypothesis.

In this work the deaggregating abilities of the phenol and geminis compounds as shown were evaluated by following methodologies; (1) **Fluorescence measurements.** (2) **Coaggregation experiment**. (3) **Aggregation number measurement.** (4) **Study on the restraint of cell conglutination**

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Friday, 25 August

Oral Session VII

Friday morning, 25 August, 11:30
Chair: Irina P. Beletskaya

11:30 oral

22-Hydroxybenziporphyrin: Switching of Antiaromaticity by Phenol-Keto Tautomerization

Marcin Stępień, Lechosław Latos-Grażyński, Ludmiła Szterenberg

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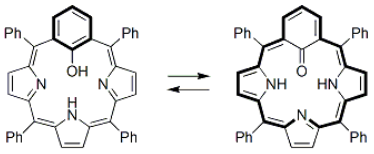
Benziporphyrins constitute a class of porphyrin analogs in which one of the pyrrole rings is replaced with a benzene ring [1]. The aromaticity of these molecules depends on their topology [2, 3], tautomerism [4, 5], and coordination chemistry [5]. Here we will describe 22-hydroxybenziporphyrin 1, which has been shown to exist as an equilibrium mixture of the 6-π electron phenolic tautomer 1 and the 20-π electron keto form 2. Aromaticity and tautomerism of these two forms has been probed with proton NMR spectroscopy and DFT calculations.



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11:50 oral

Towards a General Scale of Nucleophilicity?

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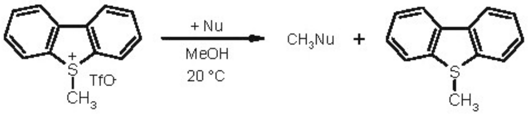
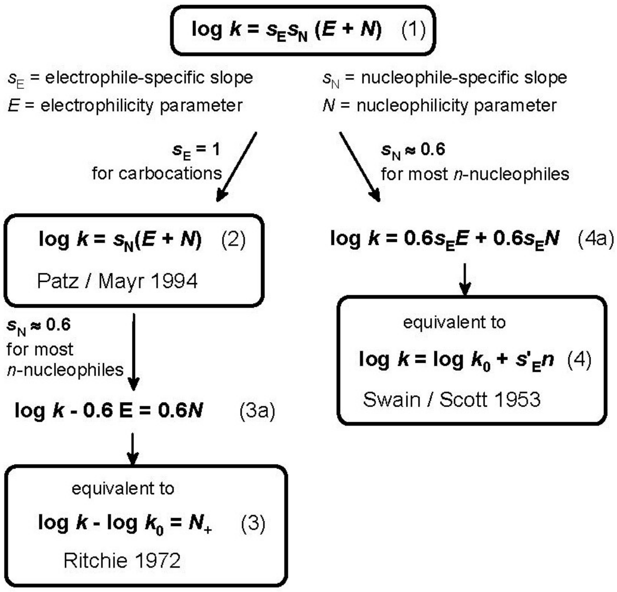
Benzhydrylium ions and structurally related quinone methides have been employed as reference electrophiles for establishing a comprehensive nucleophilicity scale comprising *π*-, *n*- and *σ*-nucleophiles [1].

Bunting [2] and Richard [3] have previously shown that, with few exceptions, Ritchie´s N_+ parameters (reactions with Ar_3C^+) are linearly correlated with Swain and Scott´s *n* parameters (reactions with CH_3X).

We have now found that the rates of the S_N2 reactions of a large variety of nucleophiles with the *S*-methyldibenzothiophenium ion correlate linearly with the *N* parameters derived from reactions with benzhydrylium ions.



We, therefore, propose a new correlation (equation 1) which describes reactions of nucleophiles with carbocations, Michael acceptors, and alkyl halides and includes previous nucleophilicity correlations as special cases [4].



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12:10 oral

Structural, Spectroscopic and ab initio Studies of N-methyl-pyridine-carboxylate Inner Salts and Their Complexes with Mineral Acids

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Pyridine carboxylic acids (picolinic, nicotinic and isonicotinic) on methylation are converted into inner salts (betaines, zwitterionic molecules): homarine (2-carboxy-1-methylpyridinium inner salt), trigonelline (3-carboxy-1-methylpyridinium inner salt) and 4-carboxy-1-methylpyridinium inner salt. The first two betaines, homarine and trigonelline have been isolated from various plants, seeds and animal tissues. All these betaines form 1:1 and 2:1 crystalline complexes with mineral acids. Most of the 2:1 complexes crystallize as monohydrate.

Crystal structures of the 3 inner salts and their 1:1 and 2:1 complexes with HCl were determined by X-ray diffraction and analysed by DFT calculations. FTIR spectra of the 2:1 complexes show a broad and intense absorption in the 1600-400 cm^{-1} region, similar to these in the spectra of acid salts of carboxylic acids. This type of absorption is typical for short hydrogen bonds (O···O distance ≤ 2.5 Å). In Raman spectra the broad absorption is absent in agreement with weak intensities of OH vibrations.

The experimental solid-state vibrational spectra of the investigated betaines and their 1:1 complexes with HCl have been assigned on the basis of the MP2/ccpVDZ calculated frequencies and intensities. Analysis of the effect of quaternization of pyridine carboxylic acids on the chemical shifts of the ring carbons and protons revealed correlations between the experimental carbon-13 and proton chemical shifts and the computed magnetic isotropic screening tensors.

The discussion will be focused on the effect of hydrogen bond and electrostatic (Coulombic) interactions between the oppositely charged groups on structure, stability and conformation of complexes investigated in the crystal and isolated molecules. The obtained results will be compared with data of acid salts of carboxylic acids.

Symposium 2

Programme

Monday, 21 August

Oral Session I

Monday morning, 21 August, 11:30
Chair: Dae Dong Sung

11:30 oral

Mechanisms of Direct and TiO_2-Photocatalysed UV-Photodegradation of Environmentally Relevant N-Phenyl Derivatives

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N-phenyl derivatives are relevant in different fields, and eventually dispersed in the environment. Thus, N-phenyl ureas, a group of herbicides believed to inhibit photosynthesis, are highly persistent, with half-life times of several months. N-phenyl carbamates are widely used insecticides (inhibiting acetylcholinesterase) and herbicides (inhibiting e^--transfer in thylakoids, uncoupling photo- and oxidative phosphorylations). An additional example may be N-Phenyl-Glycine, commonly used in the synthesis of textile dyes. The available mechanistic studies on the direct and photocatalysed photodegradation of these compounds are conflicting and scarce [1]. We decided to carry out comparative mechanistic studies on their direct and TiO_2-photocatalysed UV aqueous photodegradation [2].

We report on both the photophysics and photochemistry of different N-phenyl derivatives, including photoproducts, rate studies, quantum yields, ionization potentials, reduction potentials and pKa's of short-lived intermediates, etc. These data help us elucidate the mechanisms of the different processes under study, both for the direct and for the TiO_2-photocatalysed UV photodegradation.

Acknowledgement: the Xunta de Galicia (Spain) financed this research through project PGIDIT05TAM10301PR.

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11:50 oral

Noteworthy Reactivity of β-Halo-α,β-Unsaturated γ-Sultones*

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The literature on the chemistry of α,β-unsaturated γ-sultones in general, and of their β-halo derivatives in particular, is very sparse. Following our previous reports of convenient paths to such β-bromo and β-iodo compounds, [1, 2] we have now embarked on a systematic study of the chemistry of such systems. We hereby report some intriguing observations.

The treatment of 4-iodo-1-oxa-2-thiaspiro[4.5]dec-3-ene 2,2-dioxide (1a) with excess NaI in acetone (or DMSO) at RT for ~3 hrs lead to their quantitative conversion to the corresponding allenesulphonate salt. This halophilic E_2 elimination is not unexpected, and is noteworthy only for the mild conditions under which it occurs. A similar elimination occurs, albeit more slowly (2 days, acetone, 56 ^{0}C, or DMSO, RT with NaI or NaCN or thioacetate) in the case of 4-iodo-5-methyl-5*H*-1,2-oxathiole 2,2-dioxide (1b) whose γ-carbon is secondary, whereas in the case of 4-iodo-5-phenyl-5*H*-1,2-oxathiole 2,2-dioxide (1c) elimination is immediate at RT with either NaI or NaBr. Displacement of the β-halogen was achieved only when using the 'harder' nucleophile, azide ion. Thus sodium azide in DMSO (RT) converted both 1b and 4-bromo counterpart, 1d, to the 4-azido-5-methyl-5*H*-1,2-oxathiole 2,2-dioxide (1e). The fact that the bromo sultone 1d reacted about twice as fast as the iodo sultone 1b ($t_{1/2}$ 15 vs 29 min) indicates that the reaction proceeds via an addition-elimination mechanism in which the first step is rate determining. In the reaction of the compound 1a with azide ion in DMSO elimination to the corresponding allenesulphonate salt competed with the formation of the 4-azido-1-oxa-2-thiaspiro[4.5]dec-3-ene 2,2-dioxide and a mixture of products was isolated and separated. Our most surprising finding is that 1b in CD_3OD solution at RT, in the presence of various nucleophiles, undergoes neither elimination nor displacement reactions, but rapidly exchanges its α-hydrogen for deuterium. Thus exchange is complete with azide or triethylamine (<1 min), acetate (30 min), thioacetate (3 hrs), iodide (9 hrs). 1c similarly exchanged its α- but not its benzylic hydrogen. The possible mechanisms of this intriguing rapid exchange will be discussed.

* This work has been supported by a grant from the Israel Science Foundation (Grant No.919-05).

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12:10 oral

Reductive Cleavage of Heteroaromatic Naphthyl Ethers: Structural Effects on Reactivity

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Naphthols and naphthyl derivatives are widely used in organic synthesis, as starting materials, protecting groups or synthetic intermediates [1] and show important applications in pharmaceutical and biotechnological industries [2, 3]. Tetrazoles and benzisothiazoles have been the subject of extensive investigations due to their important practical applications, in key areas such as medicine and agriculture [4]. Tetrazolyl and benzisothiazolyl ethers have demonstrated important synthetic applications, for instance as intermediate compounds in the transformation of alcohols [5]. Heterogeneous catalytic transfer hydrogenolysis of benzyloxy- aryloxy- and allyloxy-tetrazoles and -benzisothiazoles has been used in the hydrogenolysis of phenols and allylic and benzylic alcohols, and presents a practical and selective synthetic alternative to other methods [6]. Hydrogenolysis of the C-OH bond is achieved after conversion of the hydroxyl group into an ether with the electron-withdrawing tetrazole or benzisothiazole. Continuing our ongoing research program on the reactivity of tetrazolyl and benzisothiazolyl derivatives, we have now investigated the efficiency of tetrazole and benzisothiazole as leaving groups for heterogeneous catalytic reduction of the p-extended 1- and 2-naphthols and 2-naphthylic methanols over Pd/C, using a hydrogen donor or molecular hydrogen. An interpretation of the reactivity will be provided, based on their structural and electronic features and on comparative adsorption abilities onto the catalyst surface.

Acknowledgements: The authors are grateful to Fundação para a Ciência e Tecnologia (FCT- POCTI/P/FCB/33580/00) and FEDER for financial support. . N.C.P.A. and L.M.T.F. are grateful to FCT for Grants SFRH/BPD/20587/2004 and SFRH/BD/17945/2004.

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12:30 oral

Kinetics and Mechanism of the Anilinolysis of Aryl Phenyl Chlorothiophosphates in Acetonitrile

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The kinetics and mechanism of the aminolysis of aryl phenyl chlorothiophosphates with anilines are investigated in acetonitrile at 55.0° C . A variation of $\rho_Y(\delta\rho_Y)$ with the change of substituent on the nucleophile ($\delta\sigma_X$) leads to a negative cross-interaction constant, $\rho_{XY} = (\delta\rho_Y)/(\delta\sigma_X) = -0.2$ while a large negative value, $\rho_{XY} = -1.31$, was observed for the anilinolysis of aryl phenyl chlorophosphates. The primary kinetic isotope effects with deuterated aniline nucleophiles are observed ($k_H/k_D = 1.11$-1.34) in contrast to the inverse secondary kinetic isotope effects ($k_H/k_D = 0.61$-0.87) of the anilinolysis of aryl phenyl chlorophosphates. These results and theoretical calculations are consistent with a concerted process with front side attack of nucleophile while a concerted process with a late, product-like transition state in which both bond making and leaving group departure are extensive in the anilinolysis of aryl phenyl chlorophosphates.

12:50 oral

Rate and Product Studies with Methanesulfonic Anhydride Under Solvolytic Conditions and a Comparison with Methanesulfonyl Chloride Solvolysis

Dennis N. Kevill[1], Zoon Ha Ryu[2], Malcolm J. D Souza[3], Lamia Yaakoubd[3], Fumie Koyoshi[3]

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The specific rates of solvolysis of methanesulfonic anhydride have been measured conductometrically at -10 °C in 41 solvents. Use of the extended Grunwald-Winstein equation (with the N_T scale of solvent nucleophilicity and Y_{OTs} scale of solvent ionizing power) leads to an l value of 0.95 and an m value of 0.61 with a multiple correlation coefficient (R) of 0.973. Selectivity values in binary hydroxylic solvents favor alcohol attack in EtOH-H_2O (S value of 1.2 in 90% EtOH rising to 4.0 in 40% EtOH) and in MeOH-H_2O (S value of 3.7 in 90% MeOH rising to 6.0 in 50% MeOH). In 2,2,2-trifluoroethanol-H_2O, S values are much lower (at about 0.1). Entropy of activation values are appreciably negative (-12 to -34 cal mol^{-1} K^{-1}).

Literature values (I. S. Koo, K. Yang, S. K. An, S.-K. Lee, I. Lee, Bull. Korean Chem. Soc. 2000, 21, 1011) for the specific rates of solvolysis of methanesulfonyl chloride have been extended to fluoroalcohol-containing solvents and for 42 solvents at 45.0 °C values are obtained (using N_T and Y_{Cl} values) of 1.29 for l and of 0.55 for m ($R = 0.964$).

It is proposed that both substrates solvolyze by an S_N2 pathway.

Oral Session II

Monday afternoon, 21 August, 17:00

Chair: Daniel Kost

17:00 oral

Hydrolysis of α-Alkyl-α-(methylthio) Methylene Meldrum's Acides. A Kinetic and Computational Investigation of Steric Effects.

Claude Bernasconi[1], Shoshana D. Brown[1], Mahammad Ali[1], Zvi Rappoport[2], Hiroshi Yamataka[3], Hatim Salim[2]

1. *University of California, Department of Chemistry, California, Santa Cruz 95064, United States* **2.** *The Hebrew University of Jerusalem (HUJI), Givat Ram, Jerusalem 91904, Israel* **3.** *Rikkyo University, Nishi-Ikebukuro, Toshima-ku, Tokyo 171-8501, Japan*

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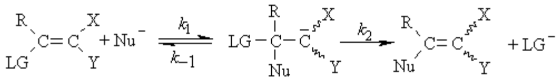
Steric effects are known to play an important role in S_NV reactions that follow the two-step mechanism (eq 1). However, most studies aimed at quantifying the steric effects have been hampered by the difficulty of distinguishing between steric and electronic effects on the rate of these reactions. The present investigation of the hydrolysis of **1** with R = H, Me, Et, *s*-Bu and *t*-Bu was designed to minimize this problem since the R groups can be expected to have very similar electronic effects but should lead to substantial variation in the steric crowding at the transition state of the k_1-step. Even though this expectation was met up to a point, our study indicates that the situation is more complex than anticipated because steric crowding in the *reactant* plays an important role as well and, for R = *t*-Bu, leads to a steric *acceleration* of the reaction. Furthermore, changing the size of the R-group leads to a change in rate limiting step under acidic conditions, i.e. for R = H conversion of the intermediate to products is rate limiting while for the other R groups nucleophilic attack is rate limiting.



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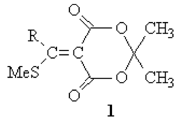

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17:20 oral

Do Enol Forms of Cyclic 1,3-diketons Really Exist in Solution?

Mark Sigalov, Lev Shapiro, Pnina Krief, Vladimir Khodorkovsky

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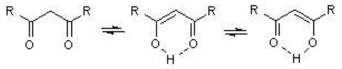
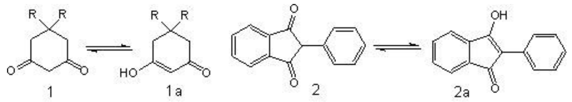
Keto-enol tautomerism is one of the fundamental concepts of organic chemistry and is a subject of detailed discussions in most of organic chemistry textbooks. The enol forms of simple ketones are thermodynamically less stable than the keto forms and only small amounts of the enols can usually be detected in solution. Enols can be stabilized when the steric hindrance in the keto form is larger and in cases when intramolecular hydrogen bonds can form. For instance, the content of the enol form in solution for open chain 1,3-diketones such as acetylacetone can reach 80-90%, which is explained by intramolecular hydrogen bonding:



The NMR spectra of enols of the symmetrically substituted diketones show symmetrical patterns, such that the chemical shifts of the carbonyl and enolic carbon atoms and those of the substituents R are identical. This is explained by rapid proton migration from one oxygen atom to the other so that only the average signals are measured by the NMR technique, known to be sensitive to dynamic phenomena.However, this approach meets considerable difficulties when applied to the cyclic 1,3-diketones, which cannot form intramolecular hydrogen bonds but their NMR spectra are still symmetrical. The results of our reinvestigation on keto-enol tautomerism of dimedone (**1**, R=Me) and phenindione (**2**), which show that the species assumed to be the enols are, in fact, anionic complexes, will be presented. These are both commercially available, and have been intensively studied in the past. The existence of the enol form of **2** has been postulated by A. Hantzsch as long as 94 years ago.



The spectroscopic (NMR, UV-VIS) behavior indicates that their free enol forms do not exist in solution. The behavior of both derivatives is better described by the two-stage equilibria. The anionic species formed at the first ionization stage strongly interact with the neutral species at the second complexation stage, shifting the equilibrium on the first stage to the right. Existence of the two-stage equilibria involving the anionic species accounts for the observed anomalies in the spectroscopic behavior of the cyclic 1,3-diketones and is well supported by the quantum mechanical calculations. Fast exchange between the anionic and enol form of 1 and the anionic and diketo form of 2 in the dimeric complexes gives rise to the observed symmetrical patterns in the NMR spectra.

17:40 oral

Thiazolidine Ring-Opening: Baldwin's Rules and Rate-determining Proton Transfer

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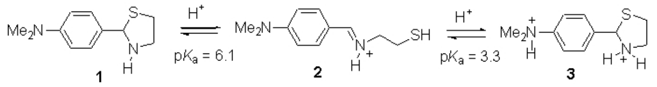
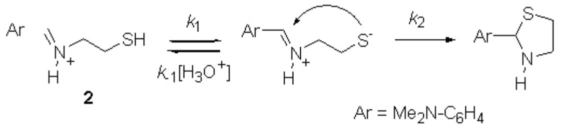
The 4-dimethylaminophenyl substituted thiazolidine 1 is subject to pH-dependent ring-opening and ring-closing equilibria yielding the resonance stabilised thiol iminium ion 2 and diprotonated thiazolidine 3 shown in Scheme 1.



Scheme 1

Rate constants for ring-opening or ring-closing can be measured spectrophotometrically using stopped flow or temperature jump fast reaction techniques taking advantage of the absorption of the iminium ion at λ_{max} = 400nm. In the ring-opening direction the reaction is acid-catalysed at low pH but becomes inversely dependent upon acid concentration above pH 1.5 and independent of acid concentration above pH 3.5.

The inverse acid dependence is consistent with a rapid deprotonation of the thiol group of the iminium ion 2 followed by rate-determining ring-closure, as shown in Scheme 2. The pH-independent reaction implies that at low acid concentrations the deprotonation step becomes rate-determining. This is a rare example of rate-determining proton transfer between electronegative atoms (S and H_2O) and is confirmed by pronounced catalysis by buffer acids in carboxylic, cacodylic, imidazole and lutidine buffers.



Scheme 2

Assignment of a rate constant k_{-1} = 3 x 10^{10} $M^{-1}s^{-1}$ for protonation of the thiolate anion by H_3O^+ implies a rate constant k_2 = 10^7 s^{-1} for closing of the thiazoldine ring. This is a large rate constant for a 5-endo trig transformation, which is formally disfavoured by Baldwin's rules. Interestingly, the rate constant is reduced by factors of up to 10^8-fold by replacing the *N*-H of the thiazoldine ring by *N*-butyl or *N*-phenyl groups. The interpretation of these results will be discussed.

Tuesday, 22 August

Oral Session III

Tuesday morning, 22 August, 11:30
Chair: Janusz Jurczak

11:30 oral

Stereoselective Addition of Singlet Oxygen to Naphthalenes and Transformation to Optically Active Peroxides

Morifumi Fujita

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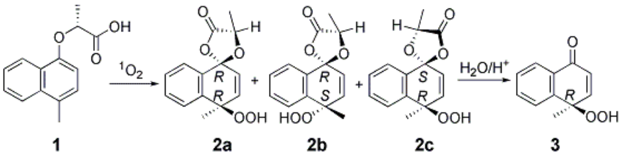
Reaction of singlet oxygen with the naphthalene **1** containing a carboxylic acid side chain gave a mixture of diastereomeric hydroperoxides **2a**-**c**. The stereoselectivity depends on the concentration of the substrate **1**; the fraction of **2a** increases with the increase of the concentration of **1**. The reaction in non-polar benzene or at lower temperature also gave more **2a**. We propose that the stereoselectivity is controlled by hydrogen-bonding association of the substrate **1** at the higher concentration of **1** and at the lower temperature. The association of the carboxylic acid side-chain may induce steric hindrance for addition of singlet oxygen to increase the stereoselectivity. Proton NMR chemical shift of **1** depends on the concentration of **1** and temperature, and this is consistent with the association of the carboxylic acid.

Elimination of chiral auxiliary of **2** was carried out under acidic conditions to give optically active hydroperoxide **3** (up to 94% enantiomeric excess). Stereoselective reaction of **2** with siloxyalkenes also gave perlactone and perhemiacetal as optically active form.



11:50 oral

The α-Effect in the Gas-Phase S_N2 Reactions at Saturated Carbon Centers

Yi Ren[1,2], Hiroshi Yamataka[1]

1. *Rikkyo University, Nishi-Ikebukuro, Toshima-ku, Tokyo 171-8501, Japan* **2.** *Sichuan University, ChengDu 610064, China*

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The existence and the nature of the α-effect in the S_N2 reactions have been examined computationally by using the high level G2(+) method. The reactions include: $Nu^- + RX \rightarrow RNu + X^-$ [R = Me, Et, and *i*-Pr; X = F and Cl; Nu^- = HO^-, CH_3O^-, HS^-, Cl^-, Br^-, NH_2O^-, HOO^-, FO^-, HSO^-, ClO^-, BrO^-, and HC(=O)OO-]. It was found that all α-nucleophiles examined exhibit downward deviations from the correlation line between the overall barriers and basicities for normal nucleophiles, indicating the existence of the α-effect in the gas phase. The transition states (TSs) for the α-nucleophiles are characterized by less advanced C-X bond cleavages than the normal nucleophiles, leading to smaller deformation energies and overall barriers. The size of the α-effect is related to the electron density on the α-atom, and increases when the position of α-atom is changed from left to right and from bottom to top in the periodic table. The reaction with CH_3F exhibits a larger α-effect than that with CH_3Cl, which can be explained by a later TS and a more positively charged methyl group at the TS for CH_3F, $[Nu{-}{-}{-}CH_3{-}{-}{-}F]^{\neq}$. Thus, a higher electron density on the α-atom and a more positive methyl moiety at the TS result in a larger size of the α-effect.

12:10 oral

Formation of the N-Iodopyridinium Cation in an Alkane Environment. Mid-Infrared Linear Dichroism Investigation of the Pyridine-Iodine System in Stretched Polyethylene.

Jens Spanget-Larsen

Dept. Life Sciences and Chemistry, Roskilde University (RUC), Universitetsvej 1, Roskilde DK-4000, Denmark

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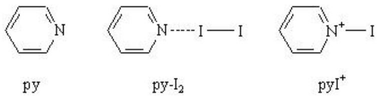
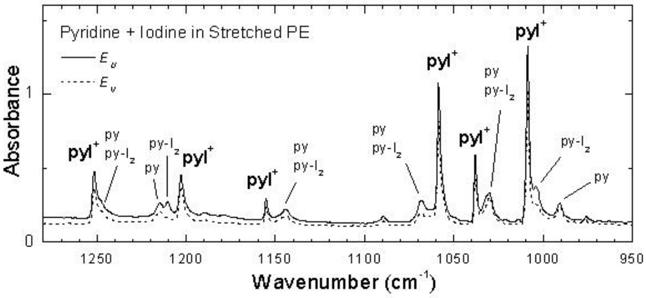


It is well known that pyridine (py) and iodine (I$_2$) form a 1:1 molecular complex, py-I$_2$. Within the framework of a student project at Roskilde University [1], we have recently investigated the formation and mid-infrared linear dichroism of the complex in a stretched polyethylene matrix. However, the observed spectra displayed not only the expected transitions due to py and py-I$_2$, but also a third, prominent series of sharp transitions, evidently due to at least one additional product. On the basis of a comparison with literature spectra, these transitions can be assigned to the N-iodo-pyridinium cation, pyI$^+$. This assignment is consistent with the observed polarization data.

Ionic side reactions such as py-I$_2$ → pyI$^+$ + I$^-$, *etc.*, are easily observed in binary pyridine-iodine mixtures and in polar solvents, but not so easily in non-polar media. We are thus surprised to see the apparent efficiency with which the pyI$^+$ cation is formed in a non-polar medium like polyethylene. With excess iodine, the peaks assigned to pyI$^+$ dominate the observed mid-infrared spectrum (see below). We suspect that a driving force for the ionic reaction is the formation of polyiodide anions in the channels of the polymer medium. Further investigation of the phenomenon is in progress.



[1] H. S. van Deurs, M. L. M. Espersen, R. Nissen, M. H. Rasmussen, C. J. S. Schönbeck, Student Project Report, Roskilde University, June 2006 (in Danish).

12:30 oral

Polyelectrolyte Helicenes as Potential Actuators - Molecular Dynamics Modeling

Pawel Rempala, Benjamin T. King

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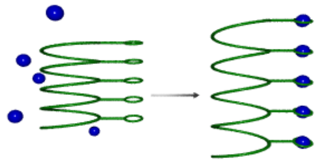
Several functionalized helical molecules were investigated using molecular dynamics methods as potential linear actuators. Basic or acidic functional groups were introduced on the periphery. Extension upon ionization of pendant groups as compared to neutral species is observed in most cases in aqueous solution simulations. The best results (largest extension) were obtained for molecules with amino or phosphate groups attached directly to the [6.3.1] helicene backbone, where the ionized forms after equilibration are longer than the neutral forms by factor ~1.8.



12:50 oral

The Complex of N-methylmorpholine Betaine with 3,4-dinitrophenol Studied by FTIR, UV, NMR Spectroscopies, X-ray Diffraction and DFT Calculations

Zofia Dega-Szafran, Andrzej Katrusiak, Mirosław Szafran

Adam Mickiewicz University, Faculty of Chemistry, Grunwaldzka 6, Poznań 60-780, Poland

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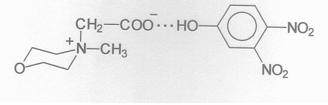
N-methylmorpholine betaine forms a crystalline 1:1 complex with 3,4-dinitrophenol. Its structure was solved by X-ray diffraction; the crystal is monoclinic in space group P2$_1$/c. The morpholinium ring has a chair conformation with the CH$_2$COO$^-$ substituent in the axial and the methyl group in the equatorial positions. The hydroxyl group of phenol and the carboxylate group of betaine are engaged in the O-H···O hydrogen bond of 2.471 Å.



The FTIR spectrum shows an intense broad absorption in the 1500-800 cm^{-1} region, characteristic for the short hydrogen bond.
The UV absorptions depend on the polarity of solvents used (DMSO, CH$_3$CN). Two bands at ca. 310 and 425 nm suggest an equilibrium between the molecular complex and the hydrogen-bonded ion-pair in solution.
The optimized geometry of the complex investigated by the B3LYP/6-31G(d,p) approach is in a good agreement with the crystal structure. Linear correlations have been found between the experimental ^{1}H and ^{13}C chemical shifts and the magnetic isotropic shielding tensors computed by the GIAO/B3LYP/6-31G(d,p) method, which confirm the correct assignments of the proton and carbon chemical sfifts.

Oral Session IV

Tuesday afternoon, 22 August, 17:00
Chair: Robert A. Moss

17:00 oral

Applications of the Structure Correlation Principle to Pericyclic and Pseudopericyclic Fragmentation Reactions, Including the Retro Diels Alder and Retro Chelotropic Reactions

Jonathan M. White[1], Yit Wooi Goh[1], David Birney[2]

1. *The Univeristy of Melbourne (UNIMELB), Grattan Street, Melbourne 3052, Australia* **2.** *Texas Tech University, Lubbock TX79409-1, United States*

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Structural changes which occur during a chemical reaction can manifest in the ground state structure as deviations of bond distances and angles from 'normal values' along the reaction coordinate [1]. We have applied this principle to pericyclic fragmentations including the retro Diels Alder and retro Cheletropic reactions [2-4], by determining accurate low temperature X-ray crystal structures of selected model substrates. Qualitative structure reactivity relationships will be discussed, and the structural effects associated with asychronous reaction pathways will be discussed.

[1] J. Dunitz, X-Ray Analysis and the Structure of Organic Molecules, Cornell University Press Ltd., London, 1979.

[2] B. R. Pool, J. M. White, Org. Lett. 2000, 2, 3505.

[3] D. Birney, T. K. Lim, J. H. P. Koh, B. R. Pool, J. M. White, J. Am. Chem. Soc. 2002, 124, 5091.

[4] G. Y. Wooi, J. M. White, Org. Biomolec. Chem. 2005, 3, 972.

17:20 oral

The Barrier Height for Automerization Reaction of Cyclobutadiene - The Ab Initio Benchmark Study

Mirjana Eckert-Maksić[1], Mario Vazdar[1], Hans Lischka[2], Zvonimir Maksić[1]

1. *Rudjer Boskovic Institute, Bijenicka cesta 54, Zagreb HR-10000, Croatia* **2.** *Institute for Theoretical Chemistry, University of Vienna, Waehringerstrasse 17, Vienna A-1090, Austria*

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The double bond flipping interconversion reaction between the two equivalent ground state structures of cyclobutadiene (CBD) is examined by the multireference average quadratic-coupled cluster (MR-AQCC) approach, which is capable of optimizing the structural parameters of the ground, transition and excited states on an equal footing. The barrier height involving both the electronic and zero-point vibrational energy contributions is 6.3 kcal/mol, which places theoretical benchmark result in the middle of the range of the measured values (1.6 - 10 kcal/mol) [1]. The adiabatic singlet-triplet energy gap between the $^1B_{1g}$ transition state (TS) and the first $^3A_{2g}$ triplet state is calculated to be 7.4 kcal/mol. A low interconversion barrier height and a small $\Delta E(^3A_{2g}$, TS) gap seem to bear some relevance on the highly pronounced reactivity of CBD together with a large angular strain. It is shown that tetracyano substitution of the CBD lowers the barrier of the automerization reaction, which will be briefly discussed.

[1] a) D. W. Whitman, B. K. Carpenter, J. Am. Chem. Soc. 1982, 104, 6473. b) B. K. Carpenter, J. Am. Chem. Soc. 1983, 105, 1700.

17:40 oral

Omega Polynomial and its Use in Nanostructures Description

Mircea V. Diudea, Simona Cigher, Aniela E. Vizitiu, Margareta S. Florescu, Peter E. John

Babes-Bolyai University, Arany Janos 11, Cluj-Napoca 400028, Romania

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In this talk a new counting polynomial [1], called "Omega", is presented. It was recently defined by Diudea, on the ground of *quasi-orthogonal* cut "*qoc*" edge stripes [2, 3]. Three topological descriptors: (1) *CI* (Cluj-Ilmenau), eventually equal to the well-known *PI* index, in planar, bipartite graphs; (2) - defined on all the normalized derivatives of the above polynomial and (3) the coefficient of the first power term, called n_p are exemplified and used in nanostructures (e.g., fullerenes, nanotubes and tori) description. Good ability of these descriptors in predicting the heat of formation and strain energy in small fullerenes or the resonance energy in planar benzenoids was found [4, 5]. Omega polynomial is useful in describing the topology of tubular nanostructures [6].

[1] M. V. Diudea, Omega Polynomial, Carpath. J. Math. 2005 (accepted).

[2] P. E. John, A. E. Vizitiu, S. Cigher, M. V. Diudea, CI Index in Tubular Nanostructures, MATCH Commun. Math. Comput. Chem. 2006 (accepted).

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[4] E. Vizitiu, M. V. Diudea, Correlating ability of descriptors derived from the Omega polynomial, Studia Univ. Babes-Bolyai 2006 (accepted).

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[6] A. E. Vizitiu, S. Cigher, M. V. Diudea, M. S. Florescu, Omega Polynomial in ((4,8)3) tubular nanostructures, MATCHCommun. Math. Comput. Chem. 2006 (accepted).

18:00 oral

Synthesis and Anti-microbial Activities of Thiazolidin-4-one Derivatives

Kanchugarakoppal S. Rangappa[1], Kamaiah Jayalakshmi[1], Chandagirikoppal V. Kavitha[1], Siddaiah Chandra Nayaka[2], Basappa Basappa[1], Hirihalli C. Devarajegowda[3], Javaregowda Shashidhara Prasad[3]

1. *University of Mysore (UOM), Manasagangothri, Mysore, Bangalore 570005, India* **2.** *Department of Studies in Applied Botany, Seed Pathology and Biotechnology, Mysore 570006, India* **3.** *University of Mysore Physics, Manasagangotri, Mysore 570006, India*

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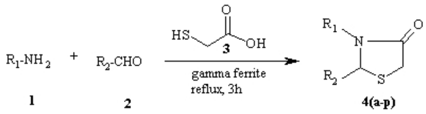
Development of novel therapeutics for the treatment of microbial infection has become a clinical imperative. Synthetic combinatorial libraries made up of hundreds to millions of small organic molecules have been successfully developed and used to discover new antimicrobial leads. In this connection, a series of thiazolidin-4-one derivatives are synthesized by one pot, three-component condensation of amine, aldehyde and thioglycolic acid using γ-ferrite as a catalyst, an effective adsorbent for water molecule (dehydrating agent). The synthesized compounds were characterized by spectral and elemental analyses. The anti-microbial studies of the above mentioned nucleus gave a concordant inhibitory results, where the polycyclic aromatics and the electron withdrawing substituents at both the 3rd and 4th position of the phenyl group. Antimicrobial data of thiazolidin-4-ones against mycotoxigenic isolates of F. verticillioides, A. alternata, A. flavus, A. ochraceous and p. chrysogenum and bacterial isolates of X. oryzae Pv oryzae, C. michigensis Pv michigensis, E. coli, S. aureus and B. subtilis indicate that all the compounds show moderate to strong inhibitory activities compared to streptomycin and nystatin. The X-ray crystallographic details of the compound 2-(4-chlorophenyl)-3-(4-phthalimide)-1,3- thiazolidin-4-one 4a reveals that it crystallizes in monoclicnic system, the space group is p21/a .T=293(2) K and the final R factor is 6.6%.



Where R$_1$ = 4-phthalimide (**4a**); 5-phthalide (**4b**); 4-methyl phenyl **4**(**c**); 4-methoxy phenyl **4**(**d**);
4-methyl phenyl (**4e**); 4-methoxy phenyl**4**(**f**); 4-chloro phenyl **4**(**g**); 4-nitro phenyl **4**(**h**);
4-methyl phenyl (**4i**); 2-naphthyl (**4j**); 4-methyl phenyl **4**(**k**); 4-methoxy phenyl **4**(**l**);
4-chloro phenyl (**4m**); 4-nitro phenyl (**4n**); 2-naphthyl (**4o**); 4-methoxy phenyl **4**(**p**).

R$_2$ = 4-chloro phenyl**4**(**a**); 4-chloro phenyl **4**(**b**); 4-bromo phenyl**4**(**c**);
2-butyl-4-chloro-1H-imidazolyl (**4d**); 2-butyl-4-chloro-1H-imidazolyl**4**(**e**);
4-biphenyl (**4f**); 4-biphenyl **4**(**g**); 4-biphenyl **4**(**h**); 4-biphenyl**4**(**i**); 4-biphenyl**4**(**j**);
9-anthranyl (**4k**); 9-anthranyl**4**(**l**); 9-anthranyl**4**(**m**); 9-anthranyl**4**(**n**); 9-anthranyl**4**(**o**);
4-(N,N-dimethyl amino)phenyl **4**(**p**).

Wednesday, 23 August

Oral Session V

Wednesday morning, 23 August, 11:30
Chair: Zvonimir Maksić

11:30 oral

Reduction of SO$_2$ on Carbons. Reactivity of the Intermediates and Mechanisms of Insertion of Organic Moities on the Carbon Matrix

Eduardo Humeres[1], Karen M. De Castro[1], Regina F. Moreira[1], Wido H. Schreiner[2], Moisés Canle L[3], Isabel Fernández[3], Arturo Santaballa[3], Abil E. Aliev[4], Maria de Gloria B. Peruch[1]

1. *Universidade Federal de Santa Catarina (UFSC), Campus Universitario, Florianopolis 88040-900, Brazil* **2.** *Universidade Federal de Parana (UFPR), Campus Universitario, Curitiba 00000-000, Brazil* **3.** *Universidade da Coruña (UDC), Alejandro de la Sota, Coruña 15008, Spain* **4.** *University College London (UCL), 20 Gordon Street, London WC1H, United Kingdom*

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The reduction of SO$_2$ on different carbons, proceeded through the same stoichiometric reaction [1], with increase of the S content and correspond to the reactive intermediates [2]. The sulfur was bound to carbon as 1,3,2-dioxathiolane and/or 1,2-oxathiene 2-oxide, that decompose producing an episulfide and/or disulfide, and CO$_2$. Theoretical calculations supported the formation of the intermediates [3]. Consecutive reactions of insertion of S form a trisulfide that extrudes S$_2$ regenerating **1** and stablish a transport mechanism [4].

In this work we have studied the reactivity of the intermediates. The reaction of graphite + SO$_2$ at 630 °C showed the formation of the same intermediates as on activated carbon. When modified activated carbon obtained at 630 °C was heated at 900 °C, it was observed that the oxidized sulfur dissapeared with formation of free sulfur. The thiolysis, aminolysis and reaction of alkyl halide with modified activated carbon ocurred with insertion of the organic moiety and extrusion of SO$_2$ as shown by the XPS and NMR spectra. Laser photolysis at 266 nm in t-butanol, showed the insertion of t-butoxide in the matrix, with extrusion of a sulfur-centered radical. These results provide additional evidences on the mechanism of reduction of SO$_2$ on carbons, the chemical nature of the intermediates and offer a new method to modify the physical and chemical properties of the carbon matrix by insertion of an organic moiety.

[1] E. Humeres, R. F. P. M. Moreira, M. G. B. Peruch, Carbon 2002, 40, 751-760.

[2] E. Humeres, M. G. B. Peruch, R. F. P. M. Moreira, W. Schreiner, J. Phys. Org. Chem. 2003, 16, 824-830.

[3] J. R. Pliego, S. M. Resende, E. Humeres, Chem. Phys. 2005, 314, 127-133.

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11:50 oral

Boron and Boron-Nitrogen Analoga of Organic Reactive Intermediates

Holger F. Bettinger

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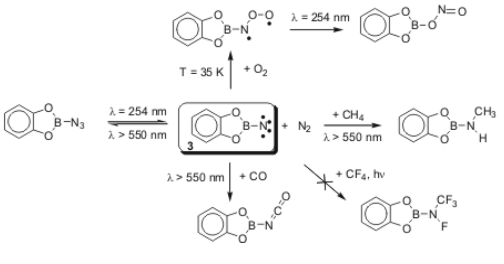
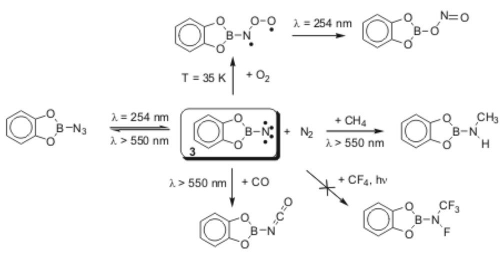
The boron analogues of carbenes, borenes or borylenes, are highly reactive and have hardly been characterized by direct spectroscopic techniques. We here report on the first generation and spectroscopic characterization of phenylborylene (1) from Bisazidophenylborane (2) und on some of its photochemically initiated reactions in inert gas matrixes.



Furthermore, we describe the first spectroscopic characterization of a borylnitrene (3), a BN analogue of vinylidene R$_2$CC, and its thermal and photochemical reactivity in matrixes.



12:10 oral

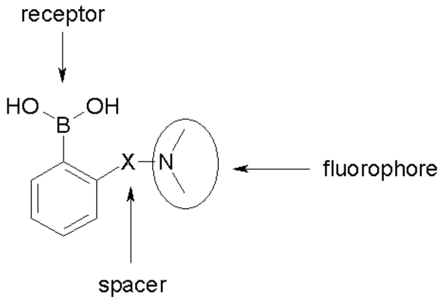
Structure of ortho-Substituted Arylboronic Acids - a Key to Sugar Receptor Activity

Andrzej Sporzyński[1], Agnieszka Lewandowska[1], Beata T. Stepien2, Michal K. Cyranski[2]

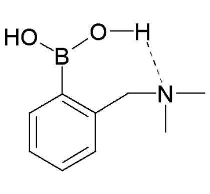
1. *Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, Warszawa 00-664, Poland* **2.** *Warsaw University, Faculty of Chemistry, Pasteura 1, Warszawa 02-093, Poland*

E-mail: spor@ch.pw.edu.pl

Arylboronic acids are widely used as carbohydrate receptors [1, 2]. Their activity is based on the selective formation of esters with polyols. A typical fluorescent receptor consists of a fluorophore linked by a spacer to the receptor containing $B(OH)_2$ group. Frequently used compounds are ortho-substituted boronic acids:



Intramolecular interactions play a key role in the mechanism of the fluorescence activity of such compounds. For the compounds with nitrogen atom in the beta position there is a possibility of intramolecular hydrogen bond formation (structure I) or N→B donor-acceptor interaction (structure II) [3, 4]:



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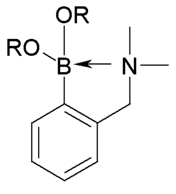

II

The examples of the both types of the structures in solid state, as well as the spectroscopic characterization in solution will be discussed.

[1] T. D. James, S. Shinkai, Top. Curr. Chem. 2002, 218, 159.

[2] J. F. Callan, A. P. de Silva, D. C. Magri, Tetrahedron 2005, 61, 8551.

[3] L. Zhu, S. H. Shabbir, M. Gray, V. M. Lynch, S. Sorey, E. V. Anslyn, J. Am. Chem. Soc. 2006, 128, 1222.

[4] A. Sporzyński, A. Lewandowska, B. T. Stępień, M. K. Cyrański, to be published.

12:30 oral

Prediction of Solid-Gas and Solid-Solid Reactions with Molecular Crystals

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More than 1000 quantitative gas-solid and solid-solid reactions in more than 25 reaction types all across chemistry have been exploratory developed in Oldenburg since 1985 and the waste-free preparative use also at the kg scale became possible due to the experimental three-step "phase-rebuilding mechanism" as deduced from our nanotechnological investigations (AFM, SNOM, GID, Nanoscratching). None of these reactions were foreseen by highly acclaimed Schmidt's "topochemistry" hypothesis that strangely claims "minimal atomic and molecular movements" for isomerizations and photoreactions despite very poor predictive power (e.g. too short distances might be impeding, etc). Conversely, long-range anisotropic molecular migrations have been secured by all of the various nanotechniques used. This applies yet to all reaction types among the different solid-state reaction techniques. Only truly topotactic reactions without geometric change do not require molecular migrations as secured by AFM down to the molecular level. The reason for the molecular migrations is the necessity for release of the enormous pressure that is created by the geometric change of the molecules upon chemical reaction within the crystal bulk. Such release requires the presence of cleavage planes or channels or voids in the crystal: no reactivity is found in their absence. Therefore (unlike very few exceptional topotactic reactions without geometric change) reactivity predictions cannot be based on distances of reacting centers but they must analyze the crystal packing on the basis of the crystal structures. This provides the answers to the anisotropy of the reactions with single crystals. The shapes of cleavage planes and channels (11 basic types) will be classified, limiting cases pointed out. The influence of gaseous or solid reagents is comprehended by their molecular size. All three steps in the solid-state mechanism (1. phase rebuilding, 2. phase transformation, 3. crystal disintegration) must occur in proper solid-state reactions. The strict application of this mechanistic knowledge indicates how the gas-solid and stoichiometric solid-solid reactions have to be performed to give 100% yield in a short time due to favorable kinetics, or how they should be engineered if the steps 2 and/or 3 provide difficulties. Local melting can be detected by AFM. It stops reaction in most cases, as melt reactions require much higher temperatures. But cooling down below eutectics will enable then.

12:50 oral

Childish Benzene Games. What Else Can We Learn in Silico?

Wojciech Grochala[1,2], Adam Sokolowski[1]

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In memoriam Andy C. Albrecht [1]

We have previously noticed [2] that a strikingly simple rule interrelates the values of A (A stands for the equilibrium bond length), for four isomolecular species at their equilibrium geometries: a singlet ground state of a neutral closed shell molecule, M^S, its first excited triplet state, $M^{T\cdot\cdot}$, a doublet ground state of its radical-cation, $M^{\cdot+}$, and a doublet ground state of its radical-anion, $M^{\cdot-}$. The rule predicts that $A^{T\cdot\cdot} = A^{\cdot+} + A^{\cdot-} - A^S$, i.e. that property of a triplet state is a 'hybrid' of properties of the remaining species. This relationship has been explained using formalism of Fukui function [3]. Using QM computations accounting to some extent for electronic correlation (DFT and MP2), we now provide evidence [4] that 'hybrid' rule works well also for other properties A, such as Mulliken charges, spin densities on atoms, or force constants. The relationship holds well for alternant hydrocarbons (antiaromatic as cyclobutadiene or 4.2.2.-bicyklooktatetraene, and aromatic such as benzene or naphthalene), while it fails for non-alternant hydrocarbons (antiaromatic as 3.3.2.-bicyklooktatetraene and aromatic as azulene). The Jahn-Teller distortion ratio (R_{long}/R_{short}) in polyatomic species is predicted with excellent accuracy, based on bond lengths derived from the 'hybrid' relationship, for all quasi-equivalent JT minima (benzene: quinoid & antiquinoid). The hybrid relationship also applies to inorganic molecules with π electron system (N_2, P_2, As_2, B_4), while it falls short for systems where sigma orbitals are responsible for geometry distortion upon electronic excitation or an electron addition/removal from M^S (CO, BF, $Pd(FH)_6^{2+}$, H_2). The rule holds only if no major breakdowns of molecular symmetry are allowed. It might possibly be used to provide reasonable initial guess of molecular geometry and electron density during demanding geometry optimizations for organic radical anions.

[1] W. Grochala, Andreas Albrecht's Tribute Symposium, Cornell University, Ithaca, NY, USA, June 2004.

[2] W. Grochala et al., J. Phys. Chem. A 2000, 104, 2195-2203.

[3] P. W. Ayers, R. G. Parr, J. Phys. Chem. A 2000, 104, 2211-2220.

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Oral Session VI

Wednesday afternoon, 23 August, 17:00

Chair: Omar A. El Seoud

17:00 oral

Modulation of Current by a Single Localized Electron Through Linear Organic Nanostructures Self-Assembled on Silicon.

Gino A. DiLabio

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Electrical transport through molecules has been much studied since it was proposed that individual molecules might behave like basic electronic devices, and intriguing single-molecule electronic effects have been demonstrated. But because transport properties are sensitive to structural variations on the atomic scale, further progress calls for detailed knowledge of how the functional properties of molecules depend on structural features. In this talk, I will describe some of our efforts to control organic linear nanostructure formation on silicon surfaces. I will then describe results from scanning tunneling microscopy and quantum mechanical modeling that show that the electrostatic field emanating from a fixed point charge regulates the conductivity of nearby organic nanostructures.

References:

[1] P. G. Piva, G. A. DiLabio, J. L. Pitters, J. Zikovsky, M. Rezeq, S. Dogel, W. A. Hofer, R. A. Wolkow, Nature 2005, 435, 658-661.

[2] G. A. DiLabio, P. G. Piva, P. Kruse, R. A. Wolkow, J. Am. Chem. Soc. 2004, 126, 16048-16050.

17:20 oral

Iron-Catalyzed Michael Reactions - From Experiment to Theory and Back

Jens Christoffers

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The catalysis of Michael reactions by $FeCl_3 \cdot 6\ H_2O$ is an environmentally sound alternative to classical base catalysis [1]. A number of β-diketones and β-oxo esters are cleanly converted with methyl vinyl ketone to the corresponding Michael reaction products within a few hours at ambient temperature with quantitative yields being achieved in most cases. The reaction can be performed solvent free and without any need for anhydrous or inert condi-tions. Due to quantitative chemoselectivity, work-up and purification are very simple. Iron com-pounds are readily available, and with respect to economical and environmental considerations, it is the transition metal catalyst of choice. Starting materials are converted stoi-chio-metrically and atom-economically without any need of reagents or even solvents and without generation of any by-product.

We have investigated the mechanism of this process by X-ray absorption and Raman spectroscopy [2], ESI-MS spectrometry as well as kinetic studies and DFT-calculations [3]. Actually, a strong anion-dependence of the catalytic activity was predicted by our spec-tro-scopic and theoretical studies which led to the development of a new catalyst system being about 10 times more active than $FeCl_3 \cdot 6\ H_2O$.

[1] a) J. Christoffers, Chem. Comm. 1997, 943-944. b) J. Christoffers, Org. Synth. 2000, 78, 249-253. c) Review: J. Christoffers, Synlett 2001, 723-732.

[2] M. Bauer, T. Kauf, J. Christoffers, H. Bertagnolli, Phys. Chem. Chem. Phys. 2005, 7, 2664-2670.

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17:40	oral

Acidochromism and Solvatochromism of the Fluorescence of Oligo(phenylenevinylene)s with Multiple Basic Sites

Heiner Detert

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Pyridines and related hetarenes have been used as electron-deficient subunits in conjugated oligomers and polymers, with applications ranging from electronic materials to supramolecular chemistry. Key features of these rings are the high electon affinity and the ability to interact with protons, Lewis acids and alkylating agents. As part of our interest in donor/acceptor substituted conjugated oligomers we use these heterocycles as acceptors in oligo(phenylenevinylene)s. The quadrupolar electronic structure results in a strongly solvent-depending fluorescence. Additionally, due to the basic heterocycles, the electronic spectra of these chromophores are sensitive to hydrogen bonding. Protonation alters both, absorption and emission spectra. Moreover, the position of the basic centre relative to the conjugated system is controlling the impact of solvent dipoles and, even more pronounced, of protons on the electronic spectra. Depending on the relative basicities of the different sites, multiple changes in the electronic spectra result from increasing concentration or pK_A . These soluble dyes are interesting for sensor technology since different ways of interaction with the environment may result in two different ways of molecular answers (absorption/fluorescence). Furthermore, as these aza-OPVs are characterized by a quadrupolar electronic structure, they are also attractive as two-photon absorbing dyes.

Friday, 25 August

Oral Session VII

Friday morning, 25 August, 11:30
Chair: Shunichi Fukuzumi

11:30	oral

Effects of Atom Pairs O and S on the Structure and Stability of Zwitterionic Tetrahedral Intermediate in the Aminolysis of Esters

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The aminolysis reactions of aryl *S*-carbamate and *O*-carbamate with arylamines in acetonitrile have been studied. Rates are much faster than the corresponding reactions of aryl *O*-carbamates. The rate increase from *O*-carbamte to *S*-carbamate is greater than that expected from substitution of thiophenoxide for phenoxide leaving group in the stepwise aminolysis reactions of esters. This large rate increase and the similar change in the aminolysis rates that are reported to occur from aryl ethyl carbamate to aryl ethylthiocarbamate lead us to conclude that the aminolysis of *S*-carbamate proceeds by a concerted mechanism in contrast to a stepwise process for *O*-carbamate. The reaction parameter, the negative ρ_{xz} values and violation of the reactivity-selectivity principle support the proposed mechanism. The reactivity parameter, the large β_x values obtained are considered to indicate a large degree of bond making in the transition state, which is consistent with the relatively large kinetic effects observed. The effects of atom pairs O and S on the structure and stability of putative zwitterionic tetrahedral intermediates in the aminolysis of esters have been calculated using DFT method. The suggested model explicits that the solvation of the zwitterionic tetrahedral intermediates occurs for each of the four types of acetates by n = 0, 1, 3, 4, and 5 water molecules. The stability of the zwitterionic intermediates increases in the order (O,O) < (O,S) < (S,O) <(S,S). This stability order is that expected from a frontier energy gap control of the second order perturbation energy of vicinal charge transfer interaction. In this type of the second order perturbation energy control a thiol S (-S-) has a greater charge transfer to the *C=O (or *C=S) orbital than an alcoholic oxygen (-O-). The result shows there are clear distinction between sp^2 and sp^3 carbon zwitterions; for the former case, the reorganization energies are much lower than those for the latter case, i.e., the hydrogen bonding energies of the explicit H_2Os are not sufficient to rehybridyze the carbonyl carbon center from sp^2 to sp^3, which requires successively less and less energy in the order, (O,O) > (O,S) > (S,O) >(S,S). In contrast, the increase in the solvation energy is linear with the number of water molecules, n. The calculated values show again that it increases with the same order as that of the stability order: (O,O = -6.7), (O,S=-7.1), (S,O=-7.9) and (S,S=-8.3 kcal/mol).

References:

[1] D. D. Sung, C. K. Kim, K. A. Lee, C. K. Sohn, H. K. Oh, I. Lee, J. Phys. Chem. A. 2005, 109, 2978.

11:50 oral

Mass Spectrometric and in Situ ESR Vis-NIR Spectro-electrochemical Investigations of the Mechanism of the C_{60} Electropolymerization in the Presence of Dioxygen in Aprotic Solvents

Piotr Pieta[1,2], Andreas Petr[2], Wlodzimierz Kutner[1], Lothar Dunsch[2]

1. *Polish Academy of Sciences, Institute of Physical Chemistry, Kasprzaka 44/52, Warszawa 01-224, Poland* **2.** *Leibniz-Institute for Solid State and Materials Research, P.O.Box 270116, Dresden D-01171, Germany*

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A mechanism of the C_{60} fullerene electropolymerization in the presence of dioxygen, O_2, in 0.1 M tetrabutylammonium perchlorate, in the toluene : acetonitrile (4 : 1, *v* : *v*) mixed solvent solution, was investigated by comparing mass spectrometric (MS) as well as simultaneous cyclic voltammetric (CV), electron spin resonance (ESR) and Vis-NIR spectroscopic behavior of products of both one- and two-electron reduction of C_{60} in the absence and presence of O_2. For the first cathodic CV peak corresponding to the C_{60}/C_{60}^{-} electroreduction, the spectro-electrochemical behavior in the presence of O_2 was similar to that in its absence. That is, a Vis-NIR band at 1080 nm characteristic of C_{60}^{-} appeared if the potential was held at -0.445 V vs. Ag/Ag^{+} psuedo-reference electrode, i.e., at the first cathodic peak, indicating that C_{60}^{-} was electrogenerated. This anion did not chemically react with O_2 present in solution as there was only one strong MS peak with *m/z* of 720 characteristic of C_{60} accompanied by weak peaks with *m/z* of 736 and 739 to 741 indicative of small amounts of $C_{60}O$ and, presumably, $C_{60}OH_4$. Instead, an electron transfer from C_{60}^{-} to O_2 yielding superoxide, $O_2^{\bullet -}$, was demonstrated by using in situ ESR spectroelectrochemistry combined with the spin-trap technique.

At more negative potentials, i.e., those at which C_{60} is electroreduced to C_{60}^{2-} and O_2 to $O_2^{\bullet -}$, the 1080-nm band vanished in the Vis-NIR spectrum and no new band emerged like if the electrogenerated C_{60}^{2-} was consumed in some following reaction resulting in a Vis-NIR inactive product. The ESR signal of the product with the g = 2.0007 value suggested the formation of some C_{60} derivatives. Beside the main peak at *m/z* of 720 in the MS spectrum of the product, several additional peaks in the *m/z* range 739 to 760 appeared indicating that $C_{60}O^{\bullet -}$ and $C_{60}O_2^{\bullet -}$ were generated and, then, protonated. Moreover, several peaks in the *m/z* range 1297 to 1465 were observed. A peak with *m/z* of 1441.187 may indicate the formation of the [2 + 2] dimer, C_{120}. This peak is accompanied by a series of peaks corresponding to dimers, which last C_n (n = 1, 2) or C_{2n} (n = 2-5) carbon atoms. Apparently, C_{60} can spontaneously dimerize after electroreduction of C_{60} and O_2 to C_{60}^{2-} and $O_2^{\bullet -}$, respectively. Importantly, no oxygen atom was built in the dimeric structure although superoxide radical promoted this dimerization.

12:10 oral

Studies on Flash Vacuum Thermolysis of Thiones of Selected N-, O-, and S-heterocycles

Tomasz Drewnowski[1,2], Anna Chrostowska[1], Said Khayar[1], Alain Dargelos[1], Stanisław Leśniak[2], Grzegorz Mlostoń[2]

1. *Laboratoire de Chimie Théorique et Physico-Chimie Moléculaire, UMR 5624, Pau 64013, France* **2.** *Department of Organic and Applied Chemistry, University of Łódź, Narutowicza 68, Łódź 90-136, Poland*

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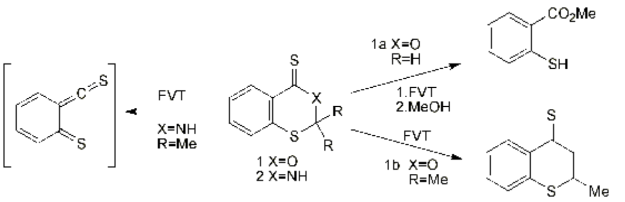
α-Oxo-ketenes have been shown to be very useful intermediates in organic synthesis and their physico-chemical properties were studied from theoretical as well as experimental points of view [1]. In contrast, relatively little is known about their sulfur analogous [2], which should be interesting in the thio-heterocyclic synthesis. We focused our attention on the thermal decomposition of thiones of selected N-, O-, and S- heterocycles under FVP-conditions. In the case of six-membered 4*H*-3,1-benzoxatthiin-4-thione **1** the course of the reaction depends mainly on the substitution pattern at C(2). For the non-substituted derivative **1a**, the reaction led to the unstable product, which upon treatment with MeOH was converted quantitatively into methyl *ortho*-mercaptobenzoate.



An analogous reaction with the 2,2-dimethyl derivative **1b** yielded 2-methylthiochromen-4-thione as an exclusive product. A mixture of three different compounds was identified as a result of benzo[*e*][1,3]thiazine-4-thione **2** thermolysis. Two of them are supposed to be formed by dimerization of initially generated 6-(thioxomethylene)cyclohexsa-2,4-dienthione. UV-Photoelectron Spectroscopy (PES) in conjunction with quantum calculations were applied to provide fundamental information about the structures and bonding of highly reactive intermediates formed during these transformations and to elucidate the reaction pathways in the gas phase.

[1] a) C. Wentrup, W. Heilmayer, G. Kollenz, Synthesis 1994, 1219. b) G. I. Yranzo, J. Elguero, R. Flammang, C. Wentrup, Eur. J. Org. Chem. 2001, 2209.

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Posters

Programme

Tuesday, 22 August

Poster Session I
Tuesday evening, 22 August, 19:30
Chair: Philip Coppens

19:30 poster I-1

Kinetic Study of the Benzenethiolysis of S-Methyl Aryl Thiocarbonates

Margarita Aliaga, Enrique A. Castro, José G. Santos

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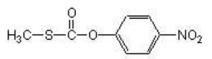
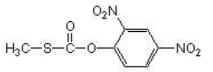
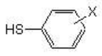
The reactions of S-methyl 4-nitrophenyl thiocarbonate (SMNPTC) and S-methyl 2,4-dinitrophenyl thiocarbonate (SMDNPTC) with a homogeneous series of benzenethiolate anions are subjected to a kinetic investigation in water, 25.0° C, ionic strength 0.2 M (KCl). Under benzenethiolate excess over the substrate all these reactions obey pseudo-first-order kinetics and are first order in the nucleophile.



SMNPTC



SMDNPTC



Benzenethiols

The Brönsted-type plots for the nucleophilic rate constants are linear, with slopes β = 0.55 and β = 0.70 for the reaction of SMNPTC, and SMDNPTC respectively with benzenethiols suggesting a concerted mechanism [1].

SMDNPTC is more reactive than SMNPTC toward benzenethiolate ions due to a carbonyl carbon more positively charged and a better leaving group.

A comparison of these results with those for the concerted phenolysis of the same substrates indicates that benzenethiolates are better nucleophiles toward thiocarbonates than isobasic phenoxides [2].

M.A. thanks CONICYT of Chile (AT-24050119) for doctoral fellowships.

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[2] E. A. Castro, P. Pavez, J. G. Santos, J. Org. Chem. 2003, 68, 3640-3645.

19:30 poster I-2

Regio- and Diastereoselective Diels-Alder Reaction of Chiral Tolylsulfinildienols

Ramiro Araya-Maturana, Iriux Almodovar, Tomás Delgado-Castro, Gerald Zapata-Torres

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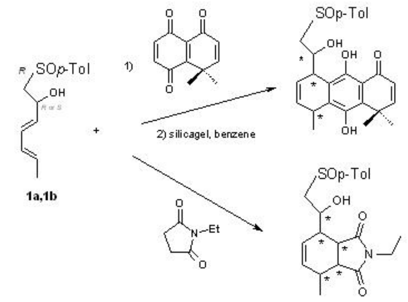
The Diels-Alder reaction of chiral 1-*p*-tolylsulfinyl-3,5-heptadien-2-ols (**1a, 1b**) with 8,8-dimethylnaphtalene-l,4,5(8*H*)-trione (**2**) and *N*-ethylmaleimide (**3**) were studied (**Scheme 1**). The reactions with dienophile **2** take place with high regioselectivity in accord with published results about regioselective reaction with hexadienol [1]. At room temperature these reactions also show high pi-facial selectivity. Instead the cycloaddition with dienophile **3** is unselective in absence of catalyst. However, high yield and high π-facial selectivity was obtained using basic alumina. The structures of transition states of dienophile **2** with both dienols were calculated, the energy differences between them are in good agreement with experimental ratio of products. Interestingly, intermolecular hydrogen bonding is the responsible of the selectivity in one case and intramolecular hydrogen bonding in the other.



Scheme 1

[1] R. Araya-Maturana, B. K. Cassels, T. Delgado-Castro, J. A. Valderrama, B. Weiss-López, Tetrahedron 1999, 55, 637-648.

Acknowledgment
FONDECYT grant 1030916 is gratefully acknowledged. I. A. thanks DAAD for a fellowship.

19:30 poster I-3

Radio Crystallographic Study of Titanium Sesquioxyde at High Temperature and in Vacuum

Afir Arezki

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High-temperature X-ray diffractometry is used to study Ti_2O_3 rhombohedral oxide formed by reduction of titanium dioxide, under vacuum and in the presence of graphite or metallic titanium.The sesquioxide is characterised by a homogeneous field of very low oxygen pressure, both boundary phases appearing independently from one another between 1073K and 1988K. The c/a = 2.660 value for $Ti_{2-x}O_3$ oxidized form of the equivalent hexagonal cell reaches c/a = 2.735 for Ti_2O_3 reduced form, which does not undergo quenching (c/a = 2.640 at 293K).

19:30	poster	I-4

The Interactions of Hydrotrioxides (ROOOH) with Pyridine N-Oxides

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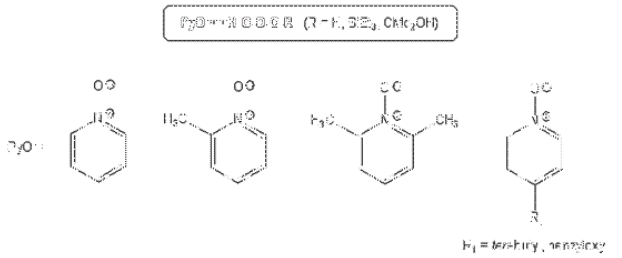
Low-temperature ozonation (-78 °C) of saturated organic compounds, i.e., alcohols, ethers, acetals, hydrocarbons, and organometallic hydrides leads to the corresponding hydrotrioxides (ROOOH), and dihydrogen trioxide (HOOOH) as unstable intermediates [1, 2]. These polyoxides have been well characterized by ^{1}H, ^{13}C, ^{17}O and ^{29}Si NMR, and by IR spectroscopic methods [3]. Furthermore, the structure of HOOOH has recently been determined by microwave spectroscopy [4]. According to the theoretical studies, they form dimeric as well as polymeric structures in »inert«, i.e., non-basic solvents, such as dichloromethane, toluene, chloroform, and benzene. However, basic solvents (acetone, methyl acetate and *tert*-butyl methyl ether) are able to complex with such aggregates and, if basic enough, disrupt the hydrogen bonds to form hydrogen-bonded complexes with ROOOH (HOOOH).

Pyridine *N*-oxides are efficient hydrogen bond acceptors [5], forming complexes with various hydrogen bond donors, such as water, (carboxylic) acids, peroxy acids, alcohols, phenols, and silanols. Therefore, they should also be able to form strong hydrogen-bonded complexes with hydrotrioxides, thus affecting their stability and reactivity. Namely the hydrotrioxides were estimated to be more acidic than their homologues, i.e., hydroperoxides and alcohols [2]. The interactions between various pairs of hydrotrioxides and pyridine *N*-oxides were studied by means of ^{1}H NMR spectroscopy. The change in kinetic and activation parameters for the decomposition of ROOOH-pyridine *N*-oxides complexes will be discussed and plausible binding modes will be presented. A comparison between pyridine *N*-oxides, phosphine oxides, and arsine oxides as suitable hydrogen bond acceptors will also be outlined.



[1] B. Plesničar, J. Cerkovnik, T. Tekavec, J. Koller, Chem. Eur. J. 2000, 6, 809.

[2] B. Plesničar, Acta Chim. Slov. 2005, 52, 1.

[3] J. Cerkovnik, T. Tuttle, E. Kraka, N. Lendero, B. Plesničar, D. Cremer, J. Am. Chem. Soc. 2006, 128, 4090.

[4] K. Suma, Y. Sumiyoshi, Y. Endo, J. Am. Chem. Soc. 2005, 127, 14998.

[5] C. Laurence, M. Berthelot, Perspect. Drug Discov. Des. 2000, 18, 39.

19:30	poster	I-5

Nucleophilicities of Triflinate-Stabilized Carbanions

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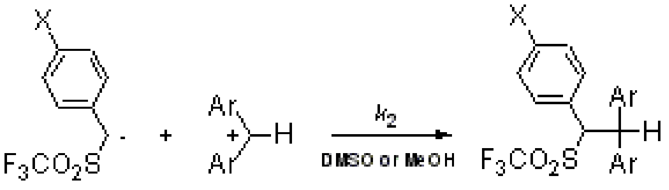
The trifluoromethylsulfonyl group is known to be one of the strongest electron accepting groups. Systematic investigations by Terrier and Wakselman [1] have shown that the CF_3SO_2 group increases CH-acidity more in dipolar aprotic solvents than in water or methanol.

In this work we have investigated the nucleophilicities of triflinate-substituted benzyl anions by determining the rate constants of the reactions of carbanions **1** with benzhydrylium ions **2** which have been employed as reference electrophiles.



1 **2** **3**

Plots of the second-order rate constants of these reactions versus the electrophilicity parameters E of the benzhydrylium ions gave the nucleophilicity parameters *N* and *s* of these carbanions as defined by eq. 1.

log k_2 (20°C) = s ($N + E$) (1) [2]

Figure 1, which compares the *N* parameters of triflinate stabilized carbanions with those of other types of carbanions, shows a close similarity of the *N*-parameters of triflinate and nitro substituted benzyl anions.

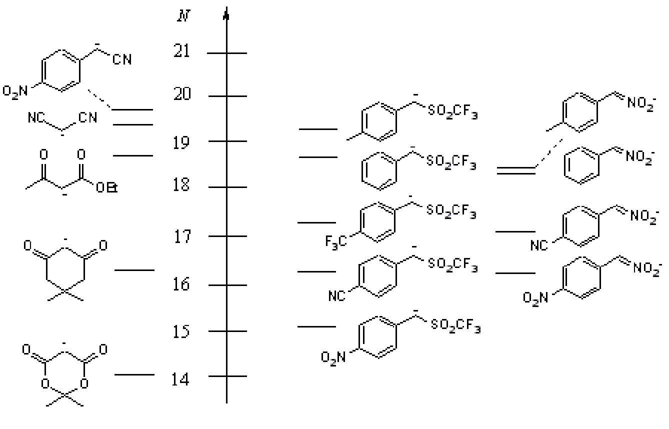


Figure 1. Nucleophilicities of different type of carbanions in DMSO.

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19:30 poster I-6

Mass Fragmentation Pattern of Some Pyrazolo[1,5-a]pyrimidine Derivatives

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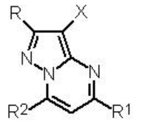
The fragmentation upon electron impact of the title compounds of general formula **1** has been investigated.

The primary fragmentation of pyrazolo[1,5-a]pyrimidine and its derivatives includes two important processes:

- expulsion of acrylonitrile or its derivative that originates from the decomposition of the pyrimidine ring,

- less characteristic loss of CH_2CN radical that occurs by the scission of the pyrazole ring.

The influence of substituents bonded to the pyrimidine and pyrazole rings of the pyrazolopyrimidines on the fragmentation pathways is discussed as well as the stability of these heterocyclic moieties toward ring cleavage.



R = H, Me, Ph
R1, R2 = H, Me, Cl, OH
X = H, NO_2

1

19:30 poster I-7

QSPR for Ionic Liquids by Recursive Neural Networks

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Ionic liquids (ILs) are innovative solvents for organic synthesis. They are low-melting salts (m.p.<100°C) obtained by the combination of large organic cations with inorganic anions. The large number of conceivable ILs (est. $>10^{14}$) doesn't make practically feasible to synthesize every of them and to investigate their properties, so, it would be really helpful if one could correlate the physical-chemical properties of already synthesized ILs with their molecular structure.

Recently, a new QSAR/QSPR method based on Neural Networks for structures, *i. e.* Recursive Neural Networks (RecNNs), has been introduced for the prediction of molecular properties. This model has been successfully applied to the prediction of the pharmacological activity of a series of substituted benzodiazepines [1] and of the physical-chemical properties of molecules [2] and polymers [3]. The RecNN deals with prediction tasks for compounds that can be represented in a structured domain. The network learn directly from the molecular structures, combining the flexibility and general advantages of neural network models with the representational power of structured domains. This approach overcomes the common difficulties and limitation deriving from the traditional representation with molecular descriptors. .

In the present work, a RecNN model has been applied to the analysis of the melting point of 126 substituted pyridinium bromides. The molecules have been represented as tree structures by selecting a limited set of constituent atomic groups and representation rules. Different representations are discussed. The descriptive and predictive abilities of our RecNN model have been tested and compared with those of traditional multiparameter descriptor approaches [4]. Preliminary results show a very good learning capacity of the networks and a promising prediction capacity.

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19:30 poster I-8

Weak Interactions in N-triazinylammonium Tetrafluoroborate Salts as a Reason for Interesting Supramolecular Architecture

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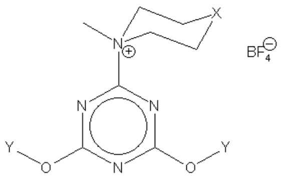
Formation of the amide or ester bond is a crucial step in synthesis of numerous organic molecules, particularly peptides. The most valuable methods involve the coupling reagents activating carboxylic function directly in the reaction media. After two decades of domination of benzotriazole based chemistry, a new type of coupling reagents has been proposed [1, 2].

According to this, several of N-triazyloammonium tetrafluoroborate salts has been studied by X-ray diffraction method.



X = O, CH$_2$ Y = Me, Bz

Each of the determined structures is packed and highly stabilized by many weak hydrogen bonds appearing between fluorine atom and C-H motives. The interplay of different weak intermolecular interactions: π-stacking, C-H· · ·F, C-H· · ·N and C-H· · ·O weak hydrogen bonds determine the supramolecular architecture of these compounds. Chains, grids and three dimensional networks occur in particular structures.

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This work has been supported by European Social Fund and Polish State in the frame of "Mechanizm WIDDOK" programme (contract number Z/2.10/II/2.6/04/05/U/2/06).

19:30 poster I-9

Nucleophilicities of Amines and Amino Acids

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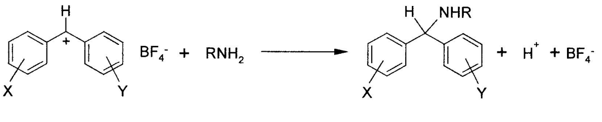
Rate constants for the reactions of amines and amino acids with substituted benzhydrylium ions have been determined photometrically [1]. The correlation equation $\log k_{20\,°C} = s(N + E)$, where s and N are nucleophile specific parameters and E is an electrophile specific parameter has been used to determine the nucleophilicity parameters N of various amines and amino acids in aqueous solution and to compare them with N of other nucleophiles [2]. It is found that diethylamine and pyrrolidine have widely differing nucleophilicities despite of comparable Brønsted basicities. Moreover it is shown that α-effect amines [3] like semicarbazide, hydroxylamine or hydrazine do not show enhanced reactivity toward benzhydrylium ions in water. These reactivity parameters are suggested as guidelines for the nucleophilic reactivities of these important molecules in biological and organic chemistry.



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19:30 poster I-10

Spin-Spin ^nJ(CC) Coupling Computations for Optimized Geometries of Rotamers of Enaminoketone System: a DFT Approach.

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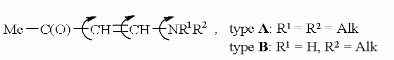
The subject of our interest is the influence of molecular geometry on carbon-carbon spin-spin couplings. As models we have chosen enaminoketones of a general formula:

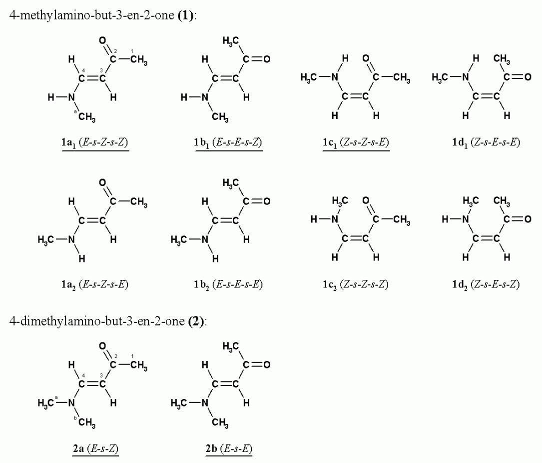


$$\mathrm{Me{-}C(O){-}CH{=}CH{-}NR^1R^2}, \quad \text{type } \mathbf{A}\text{: } R^1 = R^2 = \text{Alk}; \quad \text{type } \mathbf{B}\text{: } R^1 = \text{H},\ R^2 = \text{Alk}$$

which can exist in the form of configurational *E* and *Z* (around a C=C bond) and conformational *s-Z/s-E* (relating to C-C(O) and C-N bonds) isomers. As a result, a single compound of type B can potentially encompass eight, mutually interconverting stereoisomeric forms providing a wealth of conformational structures. The equilibrium between them strongly depends on the bulkiness of alkyl substituents, polarity of solvent and temperature.

Computational methods are very helpful in this kind of structural investigations. Especially *density functional theory* (DFT), in particular with the Becke-3-parameter-Lee-Yang-Parr (B3LYP) hybrid functional, has been shown to be a promising method for the calculation of indirect nuclear spin-spin coupling constants.

In the present communication configurational and conformational studies of two enaminoketones: *4-methylamino-but-3-en-2-one*(**1**) and *4-dimethylamino-but-3-en-2-one*(**2**) have been performed with using of the DFT method and experimental measurements (the INADEQUATE technique) [1]. We attempt to answer the important practical question of how well theoretical values predict experimental spin-spin coupling constants in our model compounds.



Scheme: Possible conformations of enaminoketones studied. Full geometry optimization and spin-spin couplings calculations were carried out using the *Gaussian03* facilities [2] at the DFT[B3LYP/6-311++G(2d,p)//B3LYP/6-311++G(2d,p)] level. Only the underlined species were observed in experimental measurements.

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19:30 poster I-11

Significance of Intermolecular S...C(π) Interaction Involving M-S and -C=O Centers in Crystal Structures of Metal Thiolate Complexes

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A plethora of noncovalent interactions account for a number of known binding and structural motifs in biological systems, synthetic catalysis and supramolecular chemistry. In this regard hydrogen bonding plays a dominant role, but many other less conventional noncovalent forces like the CH…π, cation…π, and anion…π interactions, π...π aromatic stacking, halogen bonding or chalcogen-chalcogen interactions have been identified and extensively explored recently. Nevertheless, some structural and functional aspects of biomolecular or catalytic functions remain an active problem which partly results from the fact that less obvious specific forces involving different chemical entities are only rarely encountered.

In recent years we have demonstrated that in the solid state dialkylaluminum chelate complexes have a tendency to form [R$_2$Al(μ-O,O)]$_2$-type adducts with five-coordinate metal centers. As an extension of our previous investigations directed toward relationship between donor-acceptor bonds, hydrogen bonding and other non-covalent interactions we report herein on the structural studies of alkylaluminum compounds derived from methyl thiosalicylate. The structural analysis revealed that the intermolecular S···C(π) interaction between the Al-S thiolate units and the π-surface of the ester functionality can compete with the putative sulfur-aluminum hypercoordinate bond.

There are already more than 100 crystal structures deposited in the CSD and surprisingly the S···C(π) interaction as well its role on the supramolecular structure of various complexes has not been recognized in any case by the original authors.

To the best of our knowledge, this is the first report on the competition of the intermolecular nπ* interaction, involving the thiolate sulfur atom and the electrophilic carbon atom of the ester functionality.

19:30 poster I-12

Reproducibility and Transferability of Topological Data: Experimental Charge Density Study of Two Modifications of L-alanyl-L-tyrosyl-L-alanine

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Bader's theory of Atoms in Molecules [1] allows the derivation of bonding, non bonding and atomic properties from the topological analysis of an electron density distribution. One key concept of Bader's theory is the transferability of submolecular or atomic electronic properties providing a tool to enter these fragments as building blocks for the additive generation of electron densities of macromolecules which are otherwise obtainable only in exceptional cases.

This study is an experimental verification of reproducibility and transferability in the oligopeptide field. We entered into comparative charge density studies of tripeptides of the type L-Ala-Xxx-L-Ala, where Xxx was to be varied among the 20 naturally accuring amino acids. We present a comparison of the experimental charge densities of two modifications of L-Ala-L-Tyr-L-Ala with different solvent molecules in the crystal lattice, water for modification **1** and ethanol for modification **2**.

From the conventional - spherical - structure analyses [2] it was found that the molecular structures in the two modifications were very similar and that even the intermolecular interactions in terms of hydrogen bonds were in most cases comparable with only few exceptions in the contacts to the different solvent molecules. Hence this study represents a favorable case where the reproducibility of the charge density of a given molecule in different crystal structures but widely comparable crystalline environment can be studies. In addition, concerning transferability, the atomic and bond topological properties of the main peptide chain can be compared to the corresponding values of tri-L-alanine [3].

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19:30 poster I-13

Synthesis and Crystal Structure of N-alkyl derivatives of 7-chloro-5-chloropropyl-9-methyl-5,10-dihydro-4,5,6,10-tetraaza-dibenzo[a,d]cyclohepten-11-one

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The N-alkyl derivatives of 7-chloro-5- chlopropyl-9-methyl-5, 10-dihydro-4, 5,6,10-tetraaza-dibenzo [a, d] cyclohepten-11-one have been synthesized and characterized by X-ray diffraction analysis. The azepine ring in all the structures adopts a boat conformation and the overall molecular shape of the fused ring is that of a butterfly. The cyclopropyl ring in all the structures is orthogonal to the fused ring system. The structures exhibit intermolecular hydrogen bonds of the type C-H…O, C-H…Cl. and C-H…Br. The starting material "7-chloro-5-chclopropyl-9-methyl-5, 10-dihydro-4, 5,6,10-tetraaza-dibenzo [a, d] cyclohepten-11-one" is an intermediate of a potent anti-HIV drug Nevirapine. Implications of the derivatives of the intermediate and their biological activities of the molecules with the structure-activity relationships are under progress.

19:30 poster I-14

VGSR Synthesis and UV-PES Characterization of Kinetically Unstabilized Arsaalkenes

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1. *Laboratoire de Chimie Théorique et Physico-Chimie Moléculaire, UMR 5624, Pau 64013, France* **2.** *Laboratoire des Fluides Complexes, Universite de Pau (UPPA), UMR 5150, Pau 64013, France* **3.** *Sciences Chimiques de Rennes, UMR 6226, CNRS-ENSCR, Rennes 35700, France*

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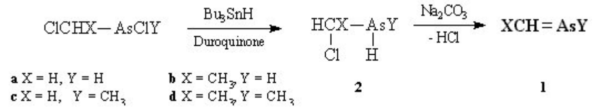
The synthesis of the simplest heterocompounds bearing a multiple carbon-heteroatom bond is a permanent challenge since most of them are not kinetically stable and only the carbon-oxygen double bond (aldehydes and ketones) and carbon-nitrogen triple bond derivatives (nitriles) are kinetically stabilized. As part of our systematic investigation of the heavier group 15 element hetero-analogues of alkenes [1-3] and alkynes [1], our attention is focused on low-coordinate arsenic derivatives, particularly interesting by their physicochemical properties and especially for their photoelectron spectral data, which allow to determine the energy of the orbitals involved in the carbon-heteroatom bond. Limited information exists concerning the electronic structures of weakly hindered species, and most of what is available is derived from theoretical studies [4]. The aim of this work is to study the structural and electronic properties of these highly reactive - simplest arsaalkenes **1a-d** formed by dehydrohalogenation of the corresponding α-chloroarsines **2a-d** in vacuum gas solid reaction (VGSR) conditions. In order to estimate the effect of the methyl substitution on carbon-arsenic double bond, UV photoelectron spectroscopic characterization has been applied. Theoretical calculations (B3LYP/6-311G(d,p); OVGF/6-311G(d,p)) of the ionisation potentials for these molecules have been carried out to assist in the reliable assignment of the experimental data.



$$\mathrm{ClCHX{-}AsClY} \xrightarrow[\text{Duroquinone}]{\mathrm{Bu_3SnH}} \mathrm{H}\underset{\mathrm{Cl}}{\mathrm{C}}\mathrm{X{-}}\underset{\mathrm{H}}{\mathrm{As}}\mathrm{Y} \xrightarrow[\mathrm{-\,HCl}]{\mathrm{Na_2CO_3}} \mathbf{XCH{=}AsY}$$

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19:30 poster I-15

Charge Transfer Complexes Formation Between Benzoanthracenones and Amines

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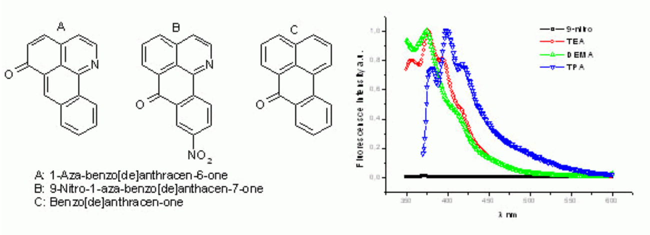
The compounds of the scheme shown below practically do not present appreciable fluorescence in solution. However, an enhancement of fluorescence is notable in the presence of amines, being even observed the appearance from a blue coloration at high amine concentrations suggesting the formation of charge transfer complex, CTC.



The CTC formation that resulted from the transfer of an electron from the amine to the benzoanthracenones was studied by fluorescent titration by plotting I°/(I - I°) v/s 1/[amine]. The complex formation constants were reported with different amines. We accurately reproduced the experimental absorption spectra of the CTC by applying Molecular Mechanics methods to generate the CTC starting from the radical ions of the amine and the benzoanthracenone followed by ZINDO/S-PM3 and semi-empirical calculations.

Aknowledgment to FONDECYT, Proyecto N°1030963, Proyecto Facultad-CEPEDEQ-2003 y a DI Universidad de Chile.

19:30 poster I-16

Spectroscopic Characterization of Radicals Species from 2,3-dihydro-oxoisoaporphines Generated by Flash Photolysis and Pulse Radiolysis

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Photoreduction of 2,3-dihydro-oxoisoaporphine dye (A) by amines occurs *via* a stepwise mechanism of electron-proton-electron transfer that leads to the metastable N-hydrogen 2,3-dihydro-oxoisoaporphine anion ($A\text{-}NH^-$), eventually. During photoreduction that occurs from the triplet manifold of the oxoisoaporphine (^3A), a radical anion ($A^{\cdot-}$) and neutral-hydrogenated radical ($A\text{-}NH^{\cdot}$) derived from the 2,3-dihydro-oxoisoaporphine are postulated as intermediate products. Quantum mechanical semi-empirical PM3 and ZINDO/S calculations for the transient species formed during the flash photolysis of 2,3-dihydro-oxoisoaporphine in the presence of amines reproduce adequately the experimental time-resolved absorption spectra of the triplet-triplet and that of neutral hydrogenated radical ($A\text{-}NH^{\cdot}$) with maxima located at 450 and 390 nm, respectively. However, the ZINDO/S/PM3 spectral calculations performed for the isolated oxoisoaporphine radical anion $A^{-\cdot}$ predict the strongest transitions above 600 nm. Therefore, a transient absorption observed in flash photolysis experiments, with maximum located near 490 nm, for all of the systems studied, was assigned to a radical ion pair between the radical anion of the oxoisoaporphine, $A^{\cdot-}$ and the radical cation of the respective amine. This tentative assignment was confirmed further by Molecular Mechanics and ZINDO/S calculations. Calculated spectrum generates the strongest transition near the experimentally observed absorption maximum at 490 nm.

The validity of prediction of the strongest transitions for the isolated oxoisoaporphine radical anion $A^{\cdot-}$ was separately confirmed in complementary pulse radiolysis experiments. The oxoisoaporphine radical anion ($A^{\cdot-}$) was generated in methanol and acetonitrile solutions by the reaction of e^-_{solv} with 2,3-dihydro-oxoisoaporphine dye. The product of this reaction is characterized by a spectral absorption band with l_{max} located at 605-610 nm. This observation further supports formation of a radical ion pair complex in the first step of the photoreduction.

We thank to FONDECYT, Project N°1030963, 7060244 and to DI University of Chile

19:30 poster I-17

Structural Analysis of Psoralens and Their Analogues

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Psoralens are naturally occurring linear furocoumarins and are used with long-wave UV light as an effective treatment for skin ailments such as psoriasis [1]. They intercalate into double stranded nucleic acids and in the presence of 365-nm UV light, undergo a photochemical reaction with the pyrimidine residues to form photoadducts. It has been experimentally confirmed that preferred base for the process is thymine [2].

Eight crystal and molecular structures of psoralens and their derivatives (both linear and angular, see Fig. 1) were determined by X-ray diffraction experiment. The extent of π-electron (de)localization in the rings depending on the topological environment was analyzed with use of geometry-based descriptor HOMA [3] and magnetism-based descriptor NICS [4]. For the latter, model analogues were optimized at B3LYP/6-311+G** level of theory. The comparison of the total energies led to the conclusion the isomers may differ at most by c.a. 18 kcal/mol, what is rationalized on the base of their topology.

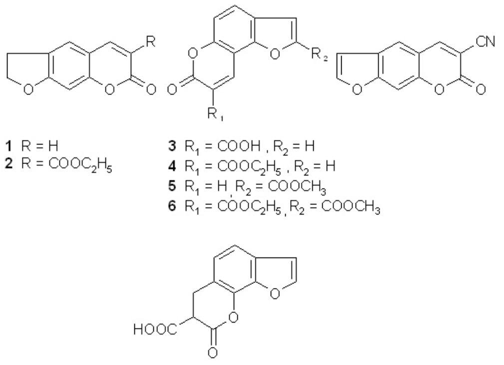

Figure 1

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19:30 poster I-18

Do the N-H...F and S-H...F Interactions Fnfluence on C-H...N and C-H...S Hydrogen Bonds?

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We have found weak C-H...S and C-H...N hydrogen bonds in crystal structures of 1,3-thiazolidine derivatives, which we investigated both experimentally as well as theoretically [1, 2]. To get deeper insight into the nature of such interactions, we performed additional studies on simple modeling complexes [3]. Molecules of CH_4, C_2H_4 and C_2H_2 were selected as proton donors and NH_3 and H_2S molecules were selected as acceptors. We carried out ab initio calculations (SCF, MP2) using different basis set, up to MP2/aug-cc-pVQZ//MP2/aug-cc-pVDZ level of approximation. We used MP2/6-311++G(d,p) and MP2/aug-cc-pVDZ wave functions in order to find and to characterize BCPs in terms of electron densities and their Laplacians. The Bader Theory [4] was applied for such analysis.

The aim of this work was the investigation of the complexes of fluorine derivatives of previously cited methane, ethene and acetylene with the ammonia and hydrogen sulfide molecules.

Molecular graphs for the complexes $C_2H_2F_2$ with H_2S and $C_2H_2F_2$ with NH_3, respectively.

We were wonder if the same tendencies as before are in force here, i.e. if the hybridization effect is also observed [3, 6] and if similarly as for C(sp^3)-H...O interactions the blue-shifting H-bonds are observed for C(sp^3)-H...Y (Y=N, S) [5, 6].

However in same cases formation of N-H...F and S-H...F interactions occurs and it is of interest whether thay can affect the strength or geometrical parameters of earlier discussed C-H...N and C-H...S hydrogen bonds.

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Support have been provided by grant No. 505/675 2005 (University of Łódź). Use of computational resources of the Cracow Supercomputing Center is also acknowledged (grant No KBN/ SGI2800/UŁódzki/082/2002).

19:30 poster I-19

Charge Density Studies of Tetraazamacrocyclic Complexes of Copper(II) and Nickel(II)

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In this contribution will present details of charge density studies of some model tetraazamacrocyclic complexes of copper(II) and nickel(II). These are starting building blocks which we use to make some new face-to-face hetero- and homo-dinuclear complexes containing interacting metal ions in identical tetraazamacrocyclic environment. As a next step we use such bismacrocylic complexes and benzocrown ethers to make homo- and hetero-[2]catenanes.. We are interested in interactions between the metal centers which can be fine-tuned and monitored by magnetic and electrochemical measurements. We observe an interesting effect in a transition-metal heterodinuclear catenane - a translocation of the crown unit back and forth between two different metal centers in response to an external stimulus- an applied potential. Unfortunately, not all of these compounds crystallize and diffract X-rays well enough to perform reliable multipole refinement so this work will be restricted only to some model macrocyclic complexes (Figure 1 below).

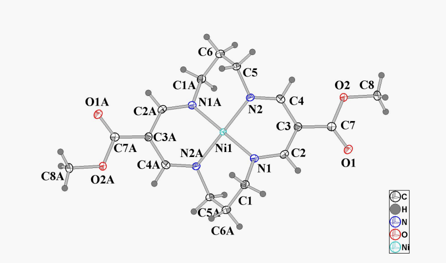

Figure 1. Tetraazamacrocyclic complex of Ni(II).

19:30 poster I-20

Macromolecular Interaction Energies from a Theoretical Databank of Transferable Aspherical Pseudoatoms

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A comprehensive version of the SUNY-Buffalo theoretical databank (SBDB) of aspherical atoms will be presented and its first application to protein/ligand interaction energies will be discussed [1].
The databank consists of all atom-types encountered in peptides, proteins and some other biologically relevant molecules. Each atom-type results from averaging over a family of chemically unique

pseudoatoms, taking into account both first and second neighbors. A new atom type is spawned when one of the parameters for a member of the family deviate more than one standard deviation of the sample. The algorithm for atom-type definition assures that close transferability is obeyed, and will be presented.

It was shown that the databank gives an excellent reproduction of the electron density in a number of amino acids when compared with those calculated with conventional ab initio methods at the B3LYP/6-31G** level, while requiring only a small fraction of the computational time [2]. The databank reproduces electrostatic interaction energies of glycine dimers with an accuracy ~3 kJ per mole [3].

In the present study the SBDB is applied to the interactions between the PDZ domain of the scaffolding protein syntenin and a number of peptides, for which accurate structures are available [4, 5]. It shows the importance of the P_0 and P_{-2} residues of the peptide in establishing the interaction, whereas the P_{-1} residue plays a smaller role, as recognized earlier [6]. Unexpectedly, the charged P_{-3} residue contributes significantly also. Furthermore preliminary results of energy calculations relevant to the inhibition of the neuraminidase enzyme from the influenza virus will be presented.

The SBDB has obvious applications in the refinement of macromolecular crystal structures.

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19:30 poster I-21

Synthesis and Excited State Properties of a [60]Fullerene Derivative Bearing a Star-Shaped Multi-Photon Absorption Chromophore

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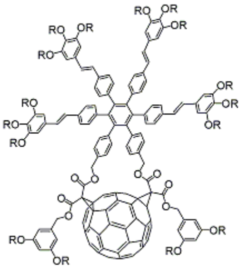
The past several years have seen a considerable interest in the development of photochemical molecular devices based on the combination of C_{60} with π-conjugated oligomers. In particular, such hybrid systems have shown interesting excited state properties and have found applications in the field of solar energy conversion. Whereas the photophysical properties of a wide range of fullerene-(π-conjugated oligomer) dyads have been reported so far, research focused on related assemblies combining C_{60} and conjugated oligomers with strong multi-photon absorption (MPA) cross sections has been probed to a lesser degree. Such hybrid systems are however potentially interesting since they should be capable of generating singlet oxygen upon multi-photon absorption followed by energy transfer to the fullerene sensitizing unit. This could broaden the applicability of C_{60} derivatives in photodynamic therapy which is currently highly limited by both the weak linear and the low induced absorptions of fullerene-based sensitizers in the 650-750 nm region. As part of our research on compounds combining C_{60} with π-conjugated oligomers, we now report the synthesis and the excited state properties of compound **1** assembling C_{60} with a new MPA chromophore. In the design of the MPA dye, we have selected a star-shaped system. Actually, whereas the optimization of MPA like TPA compounds has largely focused on one-dimensional structures, it has been recently shown that increased dimensionality and branched structures lead to highly effective multiphoton absorption.



1 R = $C_{12}H_{25}$

19:30 poster I-22

Synthesis of Calix[4]arene-Based Tetraphosphonic Acid and its Complexing Properties Towards Aminoacids Derivatives in Water

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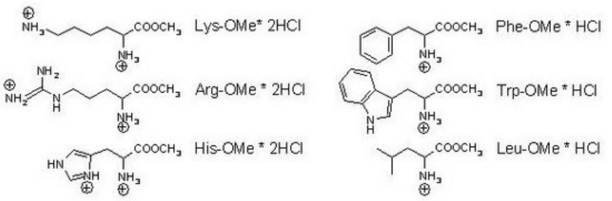
Since water is solution where most biochemical processes take place, searching of new systems interacting selectively in this environment is important. Furthermore, phosphonic acids are used as active moieties within medicines. Understanding of their role and potential as components of neurotransmitters and hormones antagonists and also enzymes and receptors inhibitors [1] is becoming clearer. As we know that the receptor-ligand recognition processes rely on mutual structural relationship of both interacted molecules and that hydrophobic effect is becoming important phenomena in polar solvents, we have obtained a synthetic calixarene-based receptors **1**, **2** which possess four phosphonic acids groups as well as hydrophobic cavity. Complexation processes of the amines, aminoalkohols [2] and aminoacids methyl esters by the compound **1** in water were examined. Herein we demonstrate the synthesis and inclusion properties of the tetraphosphorylated calix[4]arene **2** towards six aminoacids methyl esters, which are shown below. The complexes formation processes and their stoichiometry were studied by ^1H NMR spectroscopy in phosphate buffered deuterated water at pD 7.3. Chemical shifts induced by association process indicate selective inclusion these of the methyl ester aminoacids molecules which have ammonium, guanidinium or imidazolium group at the end of side chain. Possible modes of formed complexes will be discussed.

1. R = $CH_3CH_2CH_2$
2. R = H



Acknowledgements: This work is supported by KBN (grant 3 T09A 141 29).

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19:30	poster	I-23

Properties of the Diazo Group (-N=N-) Modified by Oxidation

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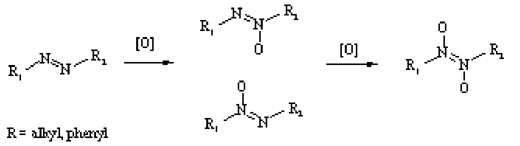
The oxidation of the diazo group (-N=N-) leads to the azoxy and azodioxy compounds [1] as shown below:



The functional groups -NN(O)-, -(O)NN- and -N(O)N(O)- differ in their properties as substituents. To quantify the extent of the changes of electronic structure of the diazo group upon oxidation we have applied a method of estimation the resonance substituent constance (σ^- values), which based on the variation of the aromatic character of 8-substituted heptafulvene [2]. While the electronic character of the -NN(O)-, -(O)NN- groups is rather similar to the diazo group (σ^- = 1.08, 1.00 and 1.02, respectively), the azodioxy group is significantly more electron-accepting substituent (with σ^- = 1.20). The analysis is based on the *ab initio* optimized geometries at DFT B3LYP/6-311+G** level of theory. Since the diazo- and azoxy-groups are isoelectronic with the nitroso and nitro groups, the comparative study of their influence on π-electron delocalization of benzene was performed.

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19:30	poster	I-24

Centipedolide A: Isolation, Structure and Absolute Configuration

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The sesquiterpene lactone Centipedolide A has been isolated from *Centipeda minima* (L.) A. Braun. & Aschers, a perennial herb which is commonly distributed in Siberia, Korea, China, India, Malaysia and Australia. In traditional Chinese medicine the herb is recommended as antiallergic, antitussive, and expectorant agent for the treatment of cold, nasal allergy and asthma. Structure elucidation and determination of the relative configuration of this new sesquiterpene lactone, Centipedolide A, has been accomplished by NMR spectroscopy and X-ray crystallography. The absolute configuration of Centipedolide A could be unambiguously established by a comparison of its experimental CD spectrum with that computed by time-dependent density functional theory .

19:30	poster	I-25

Cyclization of α-Diazonitriles to 5-Halo-1,2,3-triazoles. A Combined Experimental and Computational Study

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5-Halo-1,2,3-triazoles - important heterocycles in biochemistry and pharmacy - can be synthezised by reaction of α-diazonitriles with hydrogen halides. The effect of substituents on the ease of this cyclization reaction is investigated experimentally and computationally. Computed enthalpies of activation are in good agreement with experimental data: $\Delta H^{\neq}_{calc}$ = 21 kcal/mol; $\Delta H^{\neq}_{exp}$ = 21 kcal/mol for 2-cyano-2-diazoacetamide. Considerably larger enthalpies of activation are calculated for 2-diazo-4,4,4-trifluoro-3-oxo-butyronitrile and 2-diazomalononitrile, $\Delta H^{\neq}_{calc} \geq 30$ kcal/mol; no cyclization of these diazo compounds to the triazole is observed experimentally. The reaction proceeds in two steps: first, in the rate determining step, a hydrogen halide adduct is formed; the second step consists in the cyclization of these intermediates to the triazoles. Calculated enthalpies of activation for this second step are < 10 kcal/mol. The first step can be interpreted as a strongly asynchronous [2+2] cycloaddition of the hydrogen halide onto the triple bond of the nitrile group and the second one as a pseudopericyclic heteroelectrocyclization reaction. The overall reaction is strongly exothermic, ΔH^{react}_{calc} = -15 kcal/mol.

19:30 poster I-26

Bromine-Lithium Exchange in 1,2-Dibromobenzene and the Intermediacy of 1,2-Dilithiobenzene

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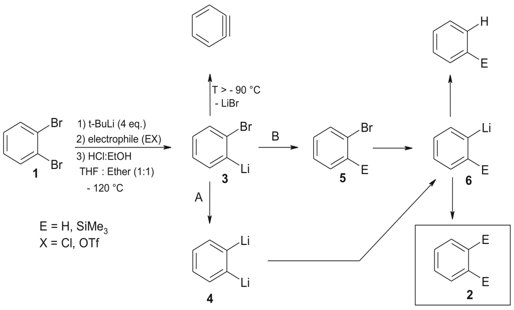
Halogen-metal exchange in *ortho*-dibromobenzene **1** using four equivalents of *tert*-butyl lithium (t-BuLi) in Et$_2$O:THF (1:1) at -120° C was observed to yield *ortho*-difunctionalized benzenes **2** after quenching with an excess of electrophiles based on analysis by GC/MS.

Two reaction pathways are conceivable. The thermally unstable *ortho*-lithiobromobenzene **3** formed in the first exchange step could again be lithiated to give *ortho*-dilithiobenzene **4** (path A)**.** Our trapping studies with electrophiles of differing reactivities show that a successive exchange-functionalisation mechanism (path B) through **5** and **6** is operating.



19:30 poster I-27

Evaluation of Proton Affinity, Gas Phase Basicity and Heat of Formation for 2-Pirrolidinone and γ-Butyrolactone by Isodesmic Reactions: Comparison Between Composite and DFT Methods

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The knowledge about the intrinsic thermochemical properties such as heat of formation (ΔHf), gas-phase basicity (GB), and proton affinity (PA) is one of the keys points to understand the molecular reactivity. Protonated species are central to many chemical processes, such as acid-base phenomena, chemical ionization mass spectrometry, electrospray ionization mass spectrometry, surface chemistry and many other aspects of biophysics such as protein conformation. The ability to calculate thermochemistry properties by using theoretical methods would be advantageous, particularly when experimental measures are difficult to perform. The development of composite ab initio methods has made a great advancement in computational thermochemistry, but a high precision is difficult to obtain even using these methods. In the present study, the heat of formation of 2-pirrolidinone and γ-butirolactone was calculated by three isodesmic reactions, using the chemical models G3, G2, G2(MP2), CBS-Q, CBS-4, CBS-QB3, and DFT methods (B3LYP, B3P86, mPW1PW, PW91PW91, PBE1PBE, and B98) with the 6-31G(d), 6-31+G(d), 6-31G(d,p), 6-31+G(d,p), 6-31++G(d), and cc-pVDZ basis sets. Our results indicate that DFT methods present the most accurate heat of formation for γ-butirolactone. On the other hand, for 2-pyrrolydinone, G2 and G2(MP2) present the best agreement with experimental heat of formation. The proton affinity and basicity of the γ-butirolactone were obtained and compared with the experimental values, described in the literature (PA = 200.8 kcal.mol^{-1} and GB = 193.1 kcal.mol^{-1}). The smallest errors were obtained by using the models B3LYP/6-31+G(d,p), B3LYP/6-31++G(d,p), G2, G2(MP2) and CBS-Q.

19:30 poster I-28

Mechanism of the Reation of N-nitrososulfonamides with Alkali-metal Ethoxides

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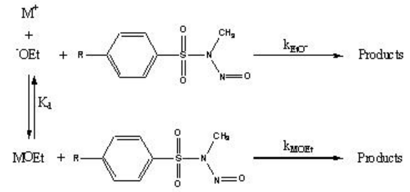
The ethanolysis reaction of several substituted N-methylbenzenesulfonamides (R = **4-MeO**, **4-Me**, **4-H** and **4-Cl**) with different alkaly-metal ethoxides in ethanol a 25°C has been studied. The reactions were also carried out in the presence of the complexing agents 18-crown-6-ether and pentaglyme, with a view to probing the electronic effects of substituents on the uncatalyzed reaction, and to aid in the description of the structure of the transition state in these process.



The kinetic data for the reaction are discussed in terms of the scheme which assigns concurrent kinetic activity to free ethoxide and metal alcoxide, to obtain the second-order rate coefficients for the reaction of the metal ion-ethoxide pairs, k_{MOEt}. From this scheme; the following equation can be obtained:

$$k_{obs} = k_{EtO^-}\left[EtO^-\right]_{st} + k_{MOEt}\left[MOEt\right]_{st}$$

The rate constant for the reaction of free ethoxide (k_{EtO^-}) could be obtained by measuring the rate of reaction with ethoxide in the presence of excess complexing agents.

To discuss the mechanism of the reaction Hammett plots were constructed using σ^+ constants. The result of the Hammett correlation supports a stepwise mechanism involving rate-limiting formation of a pentacoordinate intermediate.

19:30 poster I-29

Bond Indices in Dihydrogen Bonds

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A molecular orbital multicenter bond index $I_{ABC\ldots K}$ has proven to be useful in discriminating between strong and usual hydrogen bonds [1]. It has been the subject of more general treatments through the formalism of General Population Analysis [2] and applied successfully to electron delocalization and aromaticity [3]. It is here used, for the first time, in the description of dihydrogen bonds.

$$I_{ABC\ldots K} = \eta \sum_{\alpha\in A}\sum_{\beta\in B}\sum_{\gamma\in C}\cdots\sum_{\kappa\in K}\sum_{i}\Gamma_i\left[(PS)_{\alpha\beta}(PS)_{\beta\gamma}\cdots(PS)_{\kappa\alpha}\right]$$

where P is the charge-bond order matrix, S the overlap matrix, η a normalization constant and the permutation operator Γ*i* interchanges basis functions labels.

The indices are calculated for: i) dimers of FH and XH_n (X = Li, Na, Be, Mg); ii) the complexes appearing in Ref. [5]; iii) the BH_3NH_3 dimer [6]. While they correlate satisfactorily with the binding energy, their relation to the blue-shift is not equally clear.

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19:30 poster I-30

Designing Neutral Coordination Networks Using Cyclopentadienyl Cobaltacarborane Supramolecular Synthons: an Exercise in Crystal Engineering

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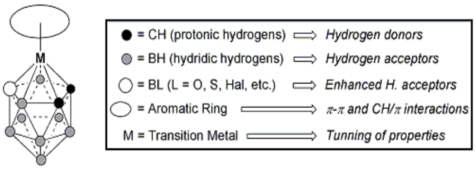
The understanding and control of non-bonding intra- and intermolecular forces and of the supramolecular self-assembly process is a prerequisite for the progress of crystal engineering [1]. In recent years, crystal engineers have begun to explore the potential of weak interactions other than classical hydrogen bonds as directors of molecular association such as C-H···Y (Y = N, O, halogen), π-π, halogen-halogen, and C-H···π [2]. Our initial results in this area include the first example of self-assembly of a mercaptaruthenacarborane complex by an unconventional cooperative effect, including a new dihydrogen bond (S-H···H-B) and its combination with a C-H···S hydrogen bond in crystalline closo-[3-Ru(η^6-C_6H_6)-8-HS-1,2-$C_2B_9H_{10}$] [3]. The latter cooperative chain can be explained by the enhanced (hydrogen)acceptor properties of the B-SH group due to its low acidity (compared with the acidity of a related C-SH group). Thus, we expect that other classical hydrogen bond acceptors will also become better acceptors when attached to boron. The primary aim of this work is to explore further this idea in combination with established ideas in transition metal complexes and in hydrogen bonding as a strategy for metallacarborane crystal engineering. We will show how supramolecular structure of a given cobaltacarborane complex can be controlled by selecting the appropriate substituents. In the absence of substituents, polymorphism is also found in these compounds.



closo-[3-M-1,2-$C_2B_9H_{11}$] (**metallacarborane**)

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19:30 poster I-31

The HERON Reaction - Origin, Theoretical Background and Prevalence

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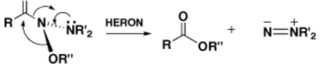
Heteroatom Rearrangements On Nitrogen (HERON) reactions were first identified in the early nineties and named at the second HERON Island Conference on reactive intermediates and unusual molecules. The earliest examples involved decomposition of *N*-alkoxy-*N*-aminoamides to esters and 1,1-diazenes [1], the outcome of the instability of these highly pyramidalised bisheteroatom-substituted amides.



First published as a named reaction in 1995 [2], it is now listed in 13th edition of the Merck Index. Since that time, a number of other examples of this rearrangement have been identified including thermal decomposition of *N,N'*-diacyl-*N,N'*-dialkoxyamides to esters [3], rearrangement of *N*-alkoxy-*N*-azidoamides, which is an excellent source of highly hindered esters [4], reactions of azodicarboxylates with oxygen nucleophiles and, more recently, reactions of the mutagens, *N*-acyloxy-*N*-alkoxyamides, in the gas phase during ESI-MS and upon thermolysis in solution. The rearrangement now has a firm theoretical basis from B3LYP/6-31G* calculations [3, 4] and X-ray analysis of HERON precursors has confirmed the highly atypical properties of "HERON" amides, which have sp^3 hybridised nitrogens [5]. The reaction was recently the subject of a Can. J. Chem. review [6].

This paper will describe the origin of the reaction, its theoretical basis and ensuing the applications.

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19:30 poster I-32

The Dissociation Enthalpy of the (N-O) Bond in Methyl-2-methylquinoxaline-3-carboxylate 1-N-oxide

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Quinoxaline derivatives play an important role in the development of new therapeutic agents, due to their relevant antibacterial, antiviral or antifungal activities. The oxidation of one or both nitrogen atoms of the heterocyclic ring increases the diversity of their biological properties, since their potential to act as oxidizing agents leads to a large variety of therapeutic applications, as for example the hypoxia-selective activity evidenced by some quinoxaline di-*N*-oxides.

Over the last decade, experimental and theoretical energetic studies have been expanded to several quinoxaline 1,4-di-*N*-oxides, in order to evaluate the influence of the chemical vicinity on the dissociation enthalpies of the N-O bonds. However, experimental studies for quinoxaline 1-*N*-oxide derivatives have not been described so far, mainly due to the difficulty in obtaining convenient amounts of highly pure samples of those compounds.

The present work reports the first experimental thermochemical study of a mono-*N*-oxide quinoxaline, the methyl 2-methylquinoxaline-3-carboxylate 1-*N*-oxide. The values of the enthalpy of formation, in the condensed state, and of the enthalpy of sublimation, measured by static bomb calorimetry and Calvet microcalorimetry, respectively, are combined to derive the standard molar enthalpy of dissociation of the N-O bond, in the gaseous state, for this compound. The experimental results for the compounds in the gas-phase are also compared with computational results obtained at the DFT level of theory.

Thanks are due to FCT and to FEDER for financial support to the research project (POCTI / 44471 / QUI / 2002). J.R.B.G. and A.R.M. thank FCT for the award of their research scholarships. Thanks are also due to the University of Porto for funding through the programme "Investigação Científica na Pré-graduação" and supported by Caixa Geral de Depósitos.

19:30 poster I-33

Quartet Ground State Nitrene Radicals

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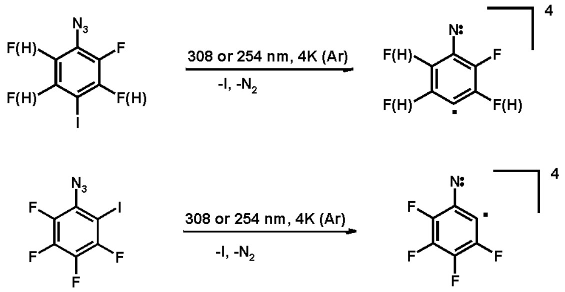
Novel organic high-spin molecules [1] with quartet ground state in which elements of a carbene and a nitrene are linked by a common delocalized π electron were photochemically generated from fluorinated 4- and 2-iodo-azidobenzenes and spectroscolpically characterized in argon matrices at 4 K and 15 K. The observed IR spectra are in excellent agreement with the calculated spectra of the corresponding quartet nitrene radicals 2, 3]. The EPR spectra are in excellent agreement with with the simulation of high-spin quartet species. The zero field parameters were obtained by simulation of the experimental EPR spectra.



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19:30 poster I-34

Problems Associated with Settings for ab initio Calculations of Torsional Barriers with Gaussian 03

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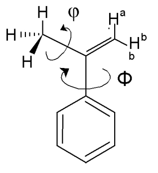
We introduced the use of chemical shifts of geminal protons (H^a and H^b) of vinyl or isopropenyl substituents as experimental and theoretical probe of ring current induced anisotropies of aromatic systems [1].

HF, MP2 and DFT B3LYP calculations of rotational barriers of the vinyl substituents led for energies and GIAO NMR shieldings to problems around saddle points in the presence of freely rotating methyl groups observed for isopropenyl benzene (**1**) and for 2-methylstyrene (**2**).



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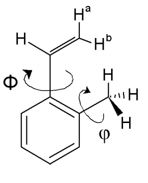

2

Difficulties have been observed: 1) for NIMAG-values, 2) with adjustment of extrapolation curves by spline functions for energies and 3) for plots of NMR shieldings while fully optimising the geometry for the complete range of rotation (Φ) between the vinylic substituent and the phenyl system in steps of 15°. The calculation of a two-dimensional energy hypersurface in dependence on the torsional angle Φ and on the rotation of the methyl group φ (with 48 points for **1** and 104 points for **2** in steps of 15° in each dimension) shows how the rotational barrier behaves around the saddle points. The "true" rotational barrier may be extracted as the minimum path on this surface. The observed difficulty can be avoided by optimisations with use of the key words CalcAll (leading to evaluation of the Hessian matrix for each optimisation cycle) or by use of VeryTight (setting extremely tight optimisation convergence criteria). The torsional dependence of experimental and GIAO calculated chemical shifts for the geminal protons H^a and H^b have been compared to predictions by use of our APUDI model [2].

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19:30 poster I-35

The Influence of Structure on the Autoxidation of Hydrazones

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Hydrazones are easily oxidised by molecular oxygen, yielding α-azohydroperoxides [1, 2]. The rate determining reaction in a propagation step appears to be the abstraction of hydrogen atom from the NH group [1]. Our measurements show that it was of comparable magnitude to those of hydrogen atom abstraction from 1,3- and 1,4-dihydrobenzene with rate constants of about 10^3 $M^{-1}s^{-1}$ [3].

In order to measure the rate of binding of molecular oxygen to the hydrazonyl radical, cyclopropylcarbinyl radical clocks [4] were synthesized. We found out that the rate constant of the addition of oxygen is of the order of 10^9 $M^{-1}s^{-1}$.

The overall rates of autoxidation were measured by means of ^{1}H NMR and UV-Vis spectroscopy in solutions, saturated with oxygen (pseudo-first order conditions). Good correlation between Hammett s and *log*k_{rel} was obtained, giving r values of -2.0 and -1.0 for substituents on the arylhydrazone and arylketone moiety, respectively. Pseudo-first order rate constants were about 10^{-3} s^{-1} for the autoxidation of arylhydrazones of aliphatic ketones, about 10^{-5} s^{-1} for aromatic aldehydes and ketones and 10^{-7} s^{-1} for nitro-substituted substrates and phenylhydrazones of conjugated ketones and aldehydes. The latter also inhibit the autoxidation of the more reactive hydrazones.

Quantumchemical DFT calculations demonstrated that the energies of hydrogen abstraction with hydroperoxy radicals are in the range of +4 to -7 kcal/mol, decrease with the number of alkyl substituents and are the lowest for hydrazones with aryl subtituents. The energies of activation appear to be relatively low, below 10 kcal/mol, also dependent on the number and structure of the substituents.

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19:30 poster I-36

The Competition Between P=O···X (X = I, Br) Interaction and P=O···H Hydrogen Bond in Iodine- and Bromine Compounds Containing an O,C,O-coordinating Pincer-Type Ligand

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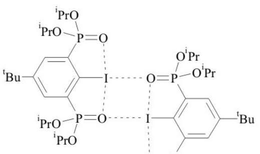
The O,C,O-coordinating pincer-type ligands $\{2,6[P(O)(OR)_2]_2$-4-*t*-Bu-$C_6H_2\}^-$ (R = *i*-Pr; Et) were successfully applied for the synthesis of a series of hypercoordinated organosilicon, organotin, and organolead compounds [1]. For the bromine derivative $\{2,6[P(O)(OR)_2]_2$-4-*t*-Bu-$C_6H_2Br\}$, P=O···H-$C_{(aromatic)}$ bonds were formed and no P=O···Br-C interactions were observed [2], although interactions of this type are reported in the literature. We anticipated that the replacement of *ypso* hydrogen in the case of $\{2,6[P(O)(OR)_2]_2$-4-*t*-Bu-$C_6H_3\}$ with iodine may lead to the novel iodine derivative with P=O···I-C interactions due to much softer character and higher tendency for the formation of hypervalent complexes of I^+ in comparison with Br^+. Finally, the examples of C-I···O=P interactions are relatively rare, despite secondary I···O bonds represent an essential feature of structural chemistry of hypervalent iodine and has also been recognized as an important noncovalent interaction that can be exploited for the rational design of supramolecular structures.



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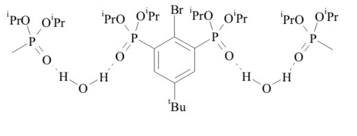

II

The iodine derivative $[\{2,6[P(O)(Oi\text{-}Pr)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}I]_2$ (**I**) and, for the sake of comparison, bromine derivative $\{2,6[P(O)(Oi\text{-}Pr)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}Br$ (**II**) were synthesized in the reaction of the organolithium derivative $\{2,6[P(O)(Oi\text{-}Pr)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}Li$ with ICl and Br_2, respectively. The analysis of the crystal structure of **I** revealed the novel coordination mode of iodine with both inter- and intramolecular C-I···O=P weak interactions that lead to the formation of dimeric structure. It must be noticed that linear character of O···I-C bridges reminds linear hypervalent I_3^- molecule with I-I-I close to 180°. In contrast, in bromine derivative **II** monomeric units form polymer chain via strong P=O···HOH···O=P hydrogen bonds that efficiently compete in this case with potential C-Br···O=P interactions.

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19:30 poster I-37

Preparation and Characterization of Novel Grafted Azopolymers Containing Disperse Orange-3, Disperse Orange-13, Disperse Yellow-7 and Disperse Red-13.

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Acryloyl chloride (AC) was grafted into commercial polyethylene films (PE) by g-irradiation, in order to obtain precursor grafted polymers. Disperse orange-3, disperse orange-13, disperse yellow-7 and disperse red-13 were incorporated to these polymers by esterification. The obtained azo-polymers films were characterized by FTIR spectroscopy and their thermal and optical properties were studied by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and absorption spectroscopy. These polymers exhibited a good thermal stability with T_{10} values between 460-500^{o}C. The melting point of the polymers was very similar to that of the non-grafted PE. Obtained azopolymers exhibited a maximum absorption wavelength in the range 381-501 nm depending on the incorporated azo-dye. The surface of the azo-polymer films was studied by atomic force microscopy (AFM) and the particle size was determined.

19:30 poster I-38

Linear and Non-linear Optical Properties of 2,5-disubstituted Pyrroles Supported by a Catalyst-free SiO_2 Sonogel Matrix

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A modification of the Schulte-Reisch reaction was employed to obtain several 2,5-disubstituted pyrroles: 1,2,5-triphenylpyrrole, 1-(p-metoxiphenyl)- 2,5-diphenylpyrrole and 1-(p-nitrophenyl)-2,5-diphenylpyrrole were obtained by amine addition to diacetylenes. This procedure is versatile and applicable for the synthesis of a wide variety of pyrrole derivatives. Pyrrole ring with multiple aromatic ring substitutions have applications as electroluminiscent devices. Pyrroles were dissolved at different concentrations in tetrahidrofurane (THF) and were optimally embedded into a catalyst-free SiO_2 sonogel network. By this method, solid state hybrid samples suitable for optical characterization were obtained. Due to the high porosity exhibited by the sonogel samples, several lightly and heavily doped composites were obtained. The adequate purity level displayed by the sonogel route allowed us to perform optimal optical characterizations of these hybrids, in order to evaluate their photo-physical properties and potential applications in photonic sciences. In this work, we present a comparative absorption-, Raman- and PL-spectroscopy studies of these novel composites. Since the SiO_2 sonogel network exhibit an amorphous structure, therefore we performed a comparative cubic nonlinear optical study of these composites according to the third harmonic generation (THG) and the Z-Scan techniques.

19:30 poster I-39

Synthesis and Stabilities of 3-Indolyl-substituted Methyl Cations

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On the polarizability of azulene ring, very stable 1-azulenyl-substituted methyl cations have been reported [1]. We also found that the 3-indolyl group stabilizes the carbocations [2]. Herein, we present the synthesis and properties of a series of indole analogues of triphenylmethyl cation. (1-Alkyl-3-indolyl)diphenylmethyl cations **1a**,**b**, bis(1-alkyl-3-indolyl)phenylmethyl cations, **2a**,**b**, and tris(1-alkyl-3-indolyl)methyl cations **3a**,**b** were prepared by DDQ oxidation of the corresponding methane derivatives. The pK_{R^+} values were determined spectrophotometrically and shown in Fig. 1.

From these values, it was found that the 3-indolyl group highly stabilize cations by an extended conjugation effect among the central cation and the indolyl rings in comparison with triphenylmethyl cation [3].

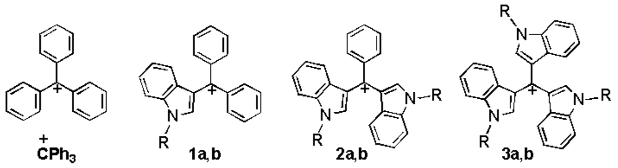

Fig. 1

	$\overset{+}{C}Ph_3$	R		1	2	3
pK_{R^+}	- 6.4	a	CH_3	2.9	9.8	13.5
		b	CH_2CH_3	2.9	9.8	13.7

The Hammett analysis of pK_{R^+} values of (*p*-substituted aryl)bis(1-methyl-3-indolyl)methyl cations is also discussed.

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19:30 poster I-40

Thermotropic Azomethine-Based Liquid Crystals for Plastic Electronics

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In this communication, we will report the synthesis and detailed chemical ($^1H/^{13}C$ NMR, Elemental Analysis, FTIR-ATR, and SEC), thermal (WAXD-SAXS, DSC, POM, polarized FTIR-ATR), and optical (UV-Vis and PL) characterizations of two types (see Fig.1) of π-conjugated organic semi-conductors (OSCs) for the field of organic/plastic (opto)electronics: Thermotropic liquid crystalline (LC) bis(azomethine) OSCs (LCBAZx) vs. ionically self-assembled thermotropic LC bis(azomethine)-alkylsulfonic acid supermolecules (ISALCBAZx) in which the side-groups (i.e. functionalized sulfonic acids (FSA): $C_{10}H_{21}SO_3H$) are connected to the LCBAZ's π-conjugated backbone by a non-covalent (ionic-type (acid-base): protonation of the CH=N units by SO_3H groups of the FSA derivative used in this study) interaction. We will demonstrate that some (8 over 16) of the members of this concise library of LC OSCs behave as thermostable "greenish emitters" leading to an overall tuning of the maximum of their emission bands over 42nm. Finally, based on detailed thermal (sequence of phase transitions: glass transitions, crystallization-melting, ordering-disordering of (smectic+nematic) mesophases, and isotropization) vs. optical (UV-Vis & PL) characterizations, we will discuss how the complex LC behavior of these "smart" LCBAZx/ISALCBAZx organic semi-conductors is impacting their optoelectronic properties.

Fig.1(Left vs. middle vs. right panels): Chemical structures of **LCBAZx** molecules and of **ISALCBAZx** supramolecules. **POM** microphotographs of **LCBAZ6** (schlieren: SmC) and of **ISALBAZ6** (Schlieren: SmX) at 162°C and 87°C, respectively.

19:30 poster I-41

A Novel Blue Light Emitting Materials Based on the Triphenylamine Core

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In this communication, we will report the synthesis and detailed chemical and optical (UV-Vis and PL) characterizations and also a molecular dynamic calculations of two types of p-conjugated organic compounds having triphenylamine moieties for the field of optoelectronics: azomethine organic compounds *vs.* ionically self-organized azomethine-Bronsted acid supramolecules in which the side-groups (i.e. functionalized sulfonic acids (methanesulfonic acid: MSA or camphorosulfonic acid: CSA) or phenols (m-cresol: MC or p-chlorophenol: PClPh) are connected to the azomethine backbone by non-covalent ionic-type (acid-base: protonation of the CH=N units by the SO_3H groups of the MSA or CSA or by H-bond formation of MC or PClPh derivative used in this study) interactions. Photoluminescence of the model compound was observed at 460 nm in chloroform solution and intensity of the emission band was found to be concentration dependent-increased with dilution from 10^{-3}mol/l to 10^{-5}mol/l and then decreased. The protonation of the azomethine cause little blue shift of the emission band along with huge increase of the photoluminescence intensity. The similar relations were also observed for polymer synthesized from the 4,4'-diformyltriphenylamine and 4,4'-oxydianiline. The polymer formed transparent, flexible foil and emitted light at 468 nm being good material for blue light emitting diodes.

19:30 poster I-42

Azobenzene-Functionalized Polymers as Potential Materials for Fabrication of Nanostructures

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Azobenzene-functionalized polymers have been extensively explored for their potential use in photonics, optoelectronics, and optical signal processing [1]. All of these applications are based on the photoisomerization of the azobenzene groups attached to the polymer chains and photoinduced anisotropy upon irradiation with polarized laser light. This process leads also to surface relief grating (SRG) formation of depth ranging from a few nanometers up to the micrometer scale [2]. Thus the SRG formation can be used to fabrication of different periodic nanostructures. The formation process was found to be dependent on both the experimental conditions such as light intensity, its polarization and incidence angle and polymer structure i.e. azobenzene unit substitution [3, 4]. The aim of the present work is to study the surface relief grating formation ability in some azobenzene-functionalized polyimides. A series of well-defined soluble polyimides containing azobenzene group have been synthesised and prepared in the form of thin films. Two-wave mixing technique with Ar^{+} laser line (l = 514.5 nm) has been employed to inscribe the gratings in these polymers for two *s-s* and *s-p* polarisation configurations of the writing beams. Atomic Force Microscopy imaging has been used to monitor the obtained structures.

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19:30 poster I-43

Optical Studies of Aromatic Polyazomethine Thin Films

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Aromatic polyazomethine belong to conjugated polymers with extended π-system having alternately CH=N group and benzene ring in the main chain. Since many years these polymers have been of interest due to their thermal stability and promising electro-, photoluminescent and nonlinear optical properties [1-3]. A series of four aromatic polyazomethine thin films have been obtained by thermal vacuum evaporation onto quartz substrates via polycondensation process. As initial monomers terephaldehyde (TPA) and four different amines i.e.: paraphenylene-diamine (PPDA); 7,2-diamino-fluorene; 1,1'-biphenyl-3,3',4,4' tetramine; 3-amino-4-(1-naphthyldiazenyl) phenylamine (fat brown RR) were used. The absorption spectra of investigated films cover the range from 200 to 2500 nm (6.2 - 0.496 eV) and reveal a few absorption bands. The feature at about 2.8 eV is attributed to transition between delocalized states with the electron-phonon interaction involved. The vibronic progression was deconvoluted with modified Fourier self-deconvolution and Finite Response Operator (FIRO) method. The bands in the range 3.8 - 4.9 eV are mainly attributed to the localized to delocalized states (and vice versa) transitions and Frenkel-type exciton formation. For all investigated films, the strongest absorption band, seen at 5.48 - 6.2 eV, is due to transitions between localized states. Changes of the position and intensity of the bands for different polyazomethine films are connected with the conformation of polymer chain. The energy gap of investigated films, following the relation typical for amorphous semiconductors (like in [4]), was found to change from 2.05 to 2.4 eV and is expected to be dependent on polyazomethine chain structure and the length of conjugated parts. These optical investigations seems to be useful to better understand electronic structure of different aromatic polyazomethine thin films as new optoelectronic materials.

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19:30 poster I-44

Transition Between Concerted and Stepwise Mechanisms of the Reductive Bond Cleavage of 1-Chloro-10-methyltribenzotriquinacene

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Tribenzotriquinacenes belong to centropolyindanes, unusual polycyclic hydrocarbons, which are promising building blocs for molecular architecture [1]. However, their physicochemical properties are studied only scarcely. The title compound, **RCl**, undergoes the C-Cl bond cleavage induced by the electron transfer from electrodes [2] and because of its structure (a saturated carbon atom in the C-Cl bond and peripheral benzene rings) it looks interesting for investigations of a transition between the concerted (1) and stepwise (2) mechanisms of a reductive cleavage.

$RCl + e \rightarrow R^{\bullet} + Cl^{-}$ (1)

$RCl + e = RCl^{\bullet -}$ (2a)

$RClR^{\bullet -} \rightarrow R^{\bullet} + Cl^{-}$ (2b)

Factors deciding on such transition were intensively examined [3]. In the present work a transition of a mechanism is analyzed for results obtained at the same conditions in different solvents. In benzonitrile at glassy carbon or mercury electrodes the stepwise process was found with the reversible electron transfer (2a) followed by the bond cleavage (2b) and the resulting radical $R^{\bullet}$ undergoes the disproportionation giving a two electrons transfer for the overall process. In acetonitrile and *N,N*-dimethylformamide (DMF) the one electron process was established, indicating the H atom abstraction by the radical $R^{\bullet}$ from solvent molecules. A detail analysis of potential dependence of the apparent transfer coefficient $\alpha = (RT/F)\, d\ln k/dE$, obtained from convoluted voltammetric curves in DMF and CH_3CN, indicates the concerted process. According to the theory of the dissociative electron transfer [3] a slope $d\alpha/dE = 12.06/\Delta G_o^{\ddagger}$ is inversely proportional to the intrinsic activation barrier, $\Delta G_o^{\ddagger}$. A low slope $d\alpha/dE = 0.14\ V^{-1}$ found for the concerted process is in agreement with the high intrinsic activation barrier, which includes a contribution form the bond dissociation energy (ca. 2.9 eV [2]). The transition from the stepwise process in C_6H_5CN to the concerted one in DMF and CH_3CN can be explained by an acceleration of the bond cleavage in the radical anion (2b) due to a stronger solvation of the final product Cl$^-$ by CH$_3$CN and DMF.

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19:30 poster I-45

Interaction of Hydroperoxides with Natural and Synthetic Antioxidants Catalized by Cationic Surfactants

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Cationic surfactants (**S**) were found to protect lipids in O/W emulsions from oxidation in some extent [1]. However, in reverse systems, micelles and microemulsions of W/O type, cationic surfactants such as alkyltrimethyl ammonium halides, alkylpyridinium salts, cause accelerated oxidation of hydrocarbons and lipids. Hydroperoxides (ROOH), which are the primary oxidation products, were found to be more surface-active than initial hydrocarbons or lipids. So, in nonpolar organic media, hydroperoxides form joint reverse micelles with **S**, in which ROOH decompose into free radicals with a greater rate in comparison with the bulk decomposition. It resulted in the increase of oxidation rate.

Because the most of known antioxidants (AO) include a polar group (phenolic, sulfuric, or amine) in their molecules, and physical location of AO changes in the presence of **S** as well as that of ROOH, this partitioning can dramatically influence AO effectiveness. The behavior of various natural (α-tocopherol, quercetin, -carotene) and synthetic (hydrogenated quinolines, nitroxyl radical, dimer 2,2′-bis[2-(*p*-dimethylaminophenyl)indane-1,3-dione]) antioxidants in the presence of hydroperoxides (derived from cumene and limonene oxidation) and cationic surfactants, which differ in their polar heads, counter ions, and hydrophobic parts, has been studied. Analysis of the AO consumption kinetics and AO transformation products had shown that there are two routes for AO consumption which are accelerated in the presence of cationic **S**: i) interaction with free radicals, derived from ROOH decomposition, catalyzed by **S**; ii) direct interaction with ROOH activated in joint micelles. The latter rout is not valid for completely hydrophobic β-carotene. Kinetic parameters characterizing the reaction rates and catalytic effects of **S** have been estimated.

Financial support of this work by the Russian Foundation for Basic Research (grant No 04-03-32569) and Scientific School (No 5236.2006.3) is gratefully acknowledged.

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19:30 poster I-46

Bis-(cycloamidin-2-yl)alkanes as the Proton Trap

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Bis-cyclic amidines are interesting tectones for crystal engineering of molecular solid [1-4], so the study of the efficient procedure for their synthesis is still important. We tried to optimize the synthesis ofbis-(cycloamidin-2-yl)alkanes **1-6** [5-11] using the modification of the thio-Pinner's method. This procedure, usually applied in the synthesis of mono-cyclic amidines, proceeds via in situ activation of a nitrile by sulfur containing catalyst and the subsequent reaction with aliphatic diamine. We used alkanedinitriles and tionatig agents such as S_8, P_4S_{10}, Lawesson Reagent, and $Na_2S\cdot 9H_2O$, obtaining the highest yields 86-97% for S_8 and P_4S_{10}.

We observed that the strong conjugation between imino double bond and the electron pair on the amino nitrogen limited the reactivity of these compounds. These strong bases with several reagents exclusively give the diprotonated form possessing four N-H protons and anionic equivalents. Even in the reaction with bromine bis-(cycloamidin-2-yl)alkanes force the reduction-oxidation processes to form the tribromide salts **7**, **8, 9** with highly ordered, predicted molecular networks in the solid state. The tribromide salt **7** is used as a new convenient source of bromine in aromatic substitution reactions.

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19:30 poster I-47

Heterocyclizations of N-[(2-nitroaryl)methylene]arenamines to (2-aryl-2H-indazol-3-yl)ryl amines via Indium/iodine-mediated Reaction

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Indium metal has recently drawn increasing attention because of environmental issues and the ease of reactions [1]. Of our special interest was the possibility of utilizing indium promoted reaction for the preparation of various nitrogen containing heterocycles as an extension of our study on reductive cyclizations of 2-nitroarenes [2]. Thus, we examined various reaction conditions using indium to develop efficient and new heterocylization reactions, and found that indium/iodine-mediated reactions could successfully transform 2-nitroaroyls to 2,1-benzisoxazoles in MeOH. However, reductive reactions of *N*-[(2-nitroaryl)methylene]benzenamines in the presence of indium/iodine in MeOH, mixtures of 2,1-benzisoxazoles and indazoles were produced. Indazole formation was in some way unexpected. As indazoles have attracted much attention for their pharmaceutical activities, such as anti-tumor and anti-HIV, the reductive reactions of *N*-[(2-nitroaryl)methylene]benzenamines reinvestigated at the point of the indazole formation. Consequently, we found that *N*-[(2-nitrophenyl)methylene]benzenamine in the presence of indium, iodine, and excess amount of aniline was mainly cyclized to (2-phenyl-2*H*-indazol-3-yl)phenylamine in THF solution. In general, reductive cyclizations of various *N*-[(2-nitroaryl)methylene]arenamines were successful using excess amount of corresponding aniline derivatives, which are the subunit of substrate, *i.e.* bold of Ar-CH=N-Ar (method A). However, substituents of 2- and 3-position of indazoles were mainly dependent upon the nature of added anilines regardless of the nature of subunit of starting substrate. Consequently, reaction of (2-phenyl-2*H*-indazol-3-yl)phenylamine in the presence of indium, iodine, and excess amount of *p*-toluidine produced [2-(4-methylphenyl)-2*H*-indazol-3-yl]-4-methylphenylamine (Method B). Herein, we report synthetic and mechanistic consideration for the indium/iodine-mediated heterocyclizations of 2-nitro-substituted iminobenzenes to indazoles.

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19:30 poster I-48

Acedan-Derived Two-Photon Probe for Cytosolic Mg^{2+} Measurement in a Living Cell

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We report an acedan-derived two-photon (TP) probe (1-AM) that can accurately measure the cytosolic magnesium in a living Hep3B cell. To determine intracellular magnesium concentration, a variety of membrane-permeable one-photon fluorescence (OPF) probes has been developed and some of them are commercially available. One of the major drawbacks of such probes is that the excitation wavelengths are in the range of 350-560 nm, which can cause damage to the substrates. To avoid such problem, two-photon microscopy (TPM) employing two NIR photons for the excitation has been developed. The advantages of TPM include reduced photodamage and photobleaching, and enhanced resolution due to the improved penetration depth, small absorption coefficient of light in tissue, and lower tissue auto-fluorescence. Recently, TP probes sensitive to the metal ions, pH, and fluoride ion have been developed. However, they have been studied in organic solvents or model membranes and membrane-permeable TP probe that is useful for TPM is rare.

19:30 poster I-49

Aqua Magnesium(II) Phthalocyanine Bis(diethylamine) Solvate

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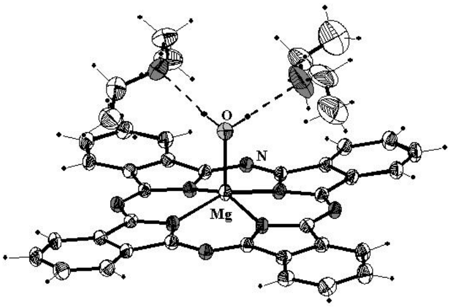
Magnesium phthalocyanine (MgPc) and its MgPcL and $MgPcL_2$ coordination complexes (4+1 and 4+2) with N and O donor ligands deserve attention first of all because of similarity with chlorophyll, thus being its synthetic models. Due to their electrochemical properties they find application in solar energy conversion, are used as pigments in optical disks, laser printers and display devices. Particular interest in aquamagnesium phthalocyanine ('X-phase') is concerned with its solid-state intence near-IR absorption band, which origin is not completely clear up to now. Two of the works dedicated to the problem give different explanation: first assigns $MgPc(H_2O)_2$ composition to the 'X-phase' and suggests that the near-IR absorption arises from extinction coupling effects [1], second analyses crystal structures of triclinic and monoclinic modifications of $MgPc(H_2O)$, of which only triclinic one exhibits near-IR absorption. Similarity of the structures of triclinic $MgPc(H_2O)$ and β-MgPc, which also exhibits the phenomenon of near-IR absorption, suggests that the origin could be found in formation of face-to-face π-π stacked dimers [2].



Violet crystals of the title compound were obtained by recrystallization of MgPc from diethylamine solution, sealed in glass ampoule, at 50 ºC during 12 hours. The compound is stable up to 140 ºC, where it loses simultaneously both diethylamine solvate molecules, at 195 ºC it loses water molecules and transforms to the β-MgPc. Structure of MgPc(H$_2$O)·2Et$_2$NH is built of MgPc(H$_2$O) moieties, stacked in dimers by back-to-back fashion. These dimers pack together via very weak hydrogen-bond interactions of C-H...N type into infinite planes perpendicular to c-axis direction at 0 and ½ height of the unit cell. Two diethylamine moieties are in the outer coordination sphere, attached to water molecule by O-H...N H-bonds (1.94(2), 1.97(2) Å and 172(2), 167(2)º for H...N distances and O-H...N angles, respectively). N-H protons are not involved in any H-bond formation. The ethyl groups exhibit high thermal librations. Mg atom deviates from N4-isoindole plane by 0.494(2) Å, some 0.04 Å more than in two polymorphs of MgPc(H$_2$O). The Mg-O distance (1.993(2) Å) and four Mg-N distances (2.038(2)-2.040(2) Å) are comparable with the appropriate values in the MgPc(H$_2$O). Saucer-shaped geometry would be an expected one for 4+1 coordinated MgPc moiety, but it is considerably distorted by flattering through repulsive π-π interactions between two Pc rings, which are overlapped along isoindole-N axis.

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19:30	poster	I-50

Structural Consequences of the Formation of Intramolecular Hydrogen Bonding

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Hydrogen bonding is a kind of molecular interactions very important in biological systems due to high ability of structures formation and simultaneously a large flexibility which results in high efficiency in molecular recognition and replication processes. Intra molecular hydrogen bonds reveal enhanced thermodynamic and structural stability, which makes them very useful model systems in study of the nature of hydrogen bonding. Some specific features of these bent hydrogen bonds appear, not only interactions decrease, but also substantial lowering of the intensity of stretching n(X-H) vibrations is observed. It is a result of vector character of dipole moment derivatives of basic and acidic parts of a bridge. The bond length increments resulting from chelate ring formation show a pattern of ortho quinoid resonance structure, even in molecules with weak p electron coupling between acidic and basic components of the system (Mannich bases). A procedure of estimation of the energy of intramolecular hydrogen bond is not solved problem, yet. A model is proposed on the basis of thermodynamic cycle. The energetic consequences of steric effects can be estimated within this model, which increase of estimated energy of hydrogen bond on about 2.5 kcal/mol. These effects are compared with related in the systems with direct electron coupling between acid and base (Schiff bases, also important from the practical point of view). It is stated, that the steric effects in these rigid molecules, are higher about three times than in Mannich bases. The amount of keto resonance form in description of the structure of hydrogen bonded, open and zwitterionic forms, in Schiff bases, is estimated. It is shown, that only after the opening the chelate rings of zwitterionic form gives the predominance of keto structures.

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Wednesday, 23 August

Poster Session II

Wednesday evening, 23 August, 19:30
Chair: Philip Coppens

19:30	poster	II-1

Car-Parrinello Molecular Dynamics Study of Mannich type compound (4,5-dimethyl-2(N,N-dimethyl aminomethyl)phenol) in Gas Phase and Solid State

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The intramolecular hydrogen bond properties of Mannich type compound (4,5-dimethyl-2 (N,N-dimethylamino methyl)phenol) [1] have been investigated. Density Functional Theory (DFT) based *ab initio* molecular dynamics simulations were performed according to method proposed by Car and Parrinello [2]. The calculations were performed in gas phase and solid state in order to study the environmental influence on proton dynamics in the molecule studied. The proton potential functions for several snapshots from the MD have been analyzed by solving the vibrational Schroedinger equation of the selected O-H mode [3]. According to the obtained simulation results, intramolecular hydrogen bond properties of the studied compound are strongly influenced by the type of the environment.

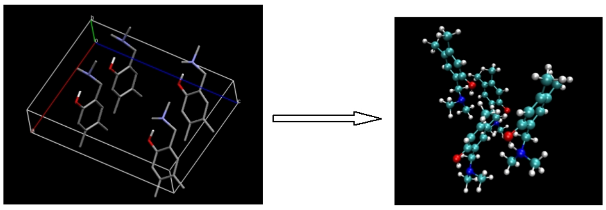

Figure: The model of 4,5-dimethyl-2(N,N-dimethylaminemethyl) phenol in solid state. The Figure was prepared using Mercury and VMD programs [4,5]

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Acknowledgements:

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19:30 poster II-2

Novel Bisstyryl Dyes Containing 18-crown-6 moieties: Synthesis, Complexation with Ammonium Substrates and [2+2]-photocycloaddition

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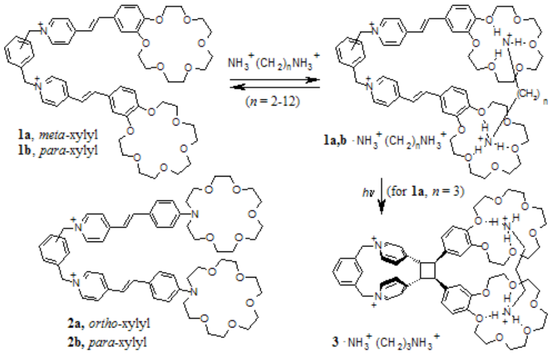
New bis(18-crown-6) and bis(aza-18-crown-6) bisstyryl dyes of pyridine series **1a,b** and **2a,b** containing a xylyl spacer were synthesized and their spectral and binding properties with ammonium compounds were studied by spectroscopic methods.

Homoditopic receptors **1a,b** have strong absorption at 410 nm and form stable pseudocyclic 1 : 1 complexes ($\lg K \geq 5.5$) with $NH_3^+(CH_2)_nNH_3^+$ (n = 2-10, 12) resulting in hypsochromic shift of their absorbance by upto 27 nm. Irradiation with visible light leads to stereospecific reaction of [2+2]-photocycloaddition (PCA) in the pseudocyclic complexes of **1a** with formation of cyclobutan derivative **3**. Contrarily, receptors **2a,b** (λ_{max}=490 nm) were found to form only non-cyclic 1 : 1 complexes with diammonium compounds.



Financial support from the Russian Foundation for Basic Research, the Russian Academy of Sciences and the Ministry of Education and Science of Russia is gratefully acknowledged.

19:30 poster II-3

Nanoparticles of Palladium in Polyacetylene or Polyaniline Matrix and Their Activity in Model Hydrogenation Reaction

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In recent years a certain group of polymers with conjugated system of carbon bonds, has attracted the interest in academic and applied research. This is due to the electrical conductivity of those polymers. Its value may vary within over 16 orders of magnitude, from conductivity characteristic of isolators to that of typical metals in process called "doping".

These polymers, called also "synthetic metals", have found many technical applications, such as: rechargeable batteries without heavy metals, antistatic coatings, chemical sensors, light emitting diodes, etc. [1, 2].

Conducting polymers, when properly doped, can be attractive as a host for the catalyst particles since this medium provides an efficient route for the shutting of electronic charge to the catalyst centres. It has been shown that Pd modified polyaniline (PANI) or polyacetylene (PA) exhibits interesting catalytic character in highly selective semihydrogenation of alkyne to alkene CC bonds with a preferential (*Z*)-hexene stereoselectivity in olefine production. In such system a polymer has a role of "support" for catalytic material [3, 4].

In present work authors concentrated on PANI and PA doped with palladium as catalysis in hydrogenation reaction of alkynes. Polyaniline was doped with H_2PdCl_4 in H_2O solution and polyacetylene, synthetized by Naarmann method, was doped with $Pd(NO_3)_2$ in acetonitrile solution.

Samples were examined by X-ray photoelectron spectroscopy (XPS), X-ray Diffraction (XRD), scanning electron microscopy (SEM), and infrared (IR). Catalytic activity was examined in semihydrogenation reaction of hexyne-2.

Both materials were catalytically active and selective in the triple to double CC semihydrogenation. Selectivity of triple CC bond transformed into double bond was over 80%.

The nature of catalytic sites depended on polymer and the procedure of polymer doping. According to the XPS and XRD analysis, Pd in polyaniline appeared mainly in $PdCl_4^{2-}$ complex with some minor amount of Pd cluster. The influence of moisture on the Pd doped PANI catalysts have been observed. Most active was the catalyst aged in dry atmosphere, during a long and slow process.

In polyacetylene XPS and XRD analysis show three palladium forms: metallic, clusters, and complex form. Form responsible for high selectivity in model hydrogenation reaction are small clusters (less then 1.0 nm). Even small content of metal form of palladium (less then 10%) lowers selectivity of specimen.

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19:30 poster II-4

Divergent Coordination Mode of Magnesium and Zinc Alkyls Supported by the Multidentate Pyrrolylaldiminato Ligands

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Organomagnesium compounds have many application in both organic and organometallic chemistry. Over recent years the exploitation of magnesium and zinc complexes supported by β-diketiminato, [1] and tropoiminato [2] ligand systems has provided a number of spectacular results.

As part of ongoing structure and reactivity studies involving the RZn(*X,Y*) chelate complexes, we have initiated to examine the solid state and solution structure of alkylzinc and magnesium *N,N'*-chelate complexes based on pyrrolyl ligands. We turned our attention to the bi- and trifunctional pyrrolyladiminato ligands, anticipating that a combination of pyrrole and Schiff base type ligands may provide spectacular results. Additionally, the choice of our target complexes was dictated by the fact that the chemistry of main group metal complexes with bi- and tridentate pyrrolyladiminato ligands remains relatively poorly explored.

Series of zinc and magnesium alkyl complexes supported by pyrrolylaldiminate ligands have been synthesized and structurally characterized. Our studies demonstrate that pyrrolylaldimines are electronically very flexible ligand system. We have found that pyrrolylaldiminate type ligand in magnesium complexes may acts only as σ-N donor ligand, whereas in zinc complexes may acts both: as σ-N donor ligand or the dihapto η^2-π-donor by the 2,3-carbon atoms of the pyrrolyl ring.

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19:30 poster II-5

Metal Silanethiolates with Aminopyridines as Coligands - the Role of N-H···S Bond

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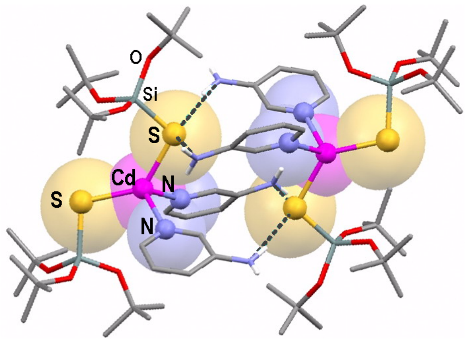
Much attention has been lately devoted to the construction of different crystal architectures. Although several approaches have been tried these involving hydrogen bonds were found especially useful. For metal complexes, however, N-H¨S interactions known for their very important role in biological systems, did not find a widespread use. The structures of ammonium silanethiolates were reported with the charge assisted N-H···S hydrogen bond as a structure forming factor [1]. Now, we have obtained manganese(II) trialkoxysilanethiolate complexes incorporating aminopyridines as coligands and found that their structures reflect the ability of the neutral silanethiolate sulfur atom to serve as the N-H···S bond acceptor as well [2]. Pursuing further our studies we have synthesized a series of new silanethiolate complexes of cadmium(II). In all syntheses $[Cd\{SSi(OBu\mathit{t})_3\}_2]_2$ [3] served as a substrate and 2-, 3- and 4-aminopyridines were chosen as additional ligands. For comparison 4-dimethylaminopyridine was also used. For all colorless crystalline products molecular structure has been determined. Again, the formation of N---H···S hydrogen bonds was observed and their significant influence on the structure of the complexes established. Two complexes may serve as examples. In the case of 2-aminopyridine a complex containing only one molecule of the N-donor ligand was formed $[Cd\{SSi(OBu\mathit{t})_3\}_2(2\text{-}NH_2py)]$ and the amino group has been found to act as a donor of the intramolecular N-H…S bond to one of the thiolate sulfur atoms. The same R(6) motif was found previously in the related manganese(II) containing complex. When less sterically hindered 3-aminopyridine was used not only two N-donor ligands entered the cadmium coordination sphere (compared to only one in the Mn-containing complex) but also bimetallic complex $[Cd\{SSi(OBu^t)_3\}_2(3\text{-}NH_2py)_2]_2$ was formed. Its molecular structure, showing the role of intermolecular N-H···S hydrogen bonds is shown in the picture.



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19:30 poster II-6

Physicochemical Properties of Substituted 9-(Phenoxycarbonyl) Acridinium Cations - an Important Systems Used in Luminescent Assays

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Chemiluminescence capable compounds have been successfully employed in biomedical and environmental analyses for over 20 years [1]. Derivatives of 10-substituted acridinium-9-carboxylic acid phenyl esters are being used as fragments of tracers used in quantitative immunoassays of biological molecules. A family of 10-methyl-9-(phenoxycarbonyl) acridinium salts, di-substituted at the *ortho* positions in the lateral phenyl ring with substituents expressing various electronic effects (CH_3, X), were synthesized with good yields. A catalytic esterification of acridine-9-carboxylic acid chloride followed by the alkylation of endocyclic nitrogen using effective methylating agent such as methyl trifluormethanesulfonate was employed [2]. The acridinium esters were analyzed in terms of purity and chemical identity employing, among others, HPLC chromatography and NMR spectroscopy. In order to establish their usefuleness as fragments of chemiluminescence sensors, luminogenic properties of new derivatives were investigated applying absorption and fluorescence spectroscopy supported by theoretical calculations performed at semi-empirical level. Time-resolved measurements were employed to investigate the parameters of chemiluminescence process accompanying the reaction of the acridinium salts with hydrogen peroxide in basic media. Results enabled to obtain pseudo-first order kinetic constants of CL decay, relative CL efficiencies and the stability of the chemiluminogens in aqueous systems having various pH values. Post-reaction products were analyzed in order to establish the proportions between the "light-path" product, that is, 10-methyl-9-acridinone, and the "dark path" (hydrolysis) product, namely, 10-methylacridinium-9-carboxylic acid cation. The perspectives of practical applications of the new compounds are briefly outlined.

(Study supported by state funds for scientific research under BW/ 8000-5-0280-6).

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19:30 poster II-7

Synthesis and Physical-Chemical Properties of New Diazatricyclo Derivate

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Nitrogen containing heterocyclic compounds (the most widely known are bipyridine and phenanthroline types) act as ligands in coordination with palladium, copper, molybdenum etc. There is a possibility to prepare compounds which are suitable for enantioselective catalysis by implementation of chiral centre to these systems. It seems to be very convenient using of natural raw materials as carriers of chirality [1]. Model of 2-fenylimidazole as a nitrogen containing heterocycle has been chosen. Pinocarvone has been used as the source of chirality. 9,9-Dimethyl-4-phenyl-3,5-diazatricyclo[6.1.1.0$_{2,6}$]deca-2(6),4-diene has become final molecule in this case.

The synthesis has been done by condensation of benzaldehyde with PinDione [2] and ammonium acetate in propan-2-ole. The derivate synthesized has been characterized by the GC/MS, ^1H and ^{13}C NMR spectra and elemental analysis. Optical rotation alfa$_D^{20}$ = -21° (methanol, c = 0,4) has been obtained. The synthesized derivate has been used as a ligand for complexation with copper chloride. Benzene ring could be also replaced by 2-pyridyle ring to improve complexation ability.

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The authors are indebted to the Ministry of Education, Youth and Sports of the Czech Republic for financial support (Research project MSM 0021627501).

19:30 poster II-8

Media Effects on Kinetics of Radical Scavenging by Flavonoids.

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The details of the radical - scavenging mechanism and activity of antioxidants became the subject of the wide interest. One of the most important ways of radical desactivation is Hydrogen Atom Transfer (HAT) from a phenol hydroxyl group to a radical: $PhOH + X^{\cdot}$ --> $PhO^{\cdot} + XH$. For the long time HAT was considered as one step process and, in fact, such opinion is valid for non-polar solvents. However, the surprisingly high values of the rate constant for the reaction of phenols with 2,2-diphenyl-1-picrylhydrazyl radical carried out in alcohols and in other polar solvents lead to the discovery of *Sequential Proton Loss Electron Transfer* mechanism (SPLET) [1]. The first step of SPLET is the phenol deprotonation: $PhOH = PhO^- +$

H^+, then the fast electron transfer from the phenol anion to radical: $PhO^- + X^\cdot$ --> $PhO^\cdot + X^-$, and the last step involves protonation of X^- to form neutral XH molecule. The SPLET mechanism can be clearly observed for the reactions carried out in ionization supporting solvents (notably methanol, ethanol and the mixtures of organic solvents with water) for phenols with low pK_a values and for electron-deficient radicals.

In our studies we described SPLET mechanism for the reactions of 2,2-diphenyl-1-picrylhydrazyl radical with a number of synthetic phenols [1, 2] and natural antioxidants (like curcumin and Vitamin E) [3]. In our presentation the above results of the studies on SPLET / HAT competition will be compared with the recent findings. Currently we study the structure-reactivity relationship for flavonoids and the simple phenols like catechols and resorcinols. The pK_a values measured in water-methanol mixtures (1:1) are correlated with the rate constants for phenol + 2,2-diphenyl-1-picrylhydrazyl reaction in alcohols indicating the crucial role of phenol acidity in the reaction kinetics governed by HAT / SPLET mechanisms. It was demonstrated, that depending on the favoured mechanism, the different hydroxyl groups in flavonoids are the most active sites in flavonoids structure.

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19:30 poster II-9

Coordination Properties of Imidazole Derivatives

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Synthesis of 2-phenylimidazole derivatives and their coordination properties have been studied. 2-Phenylimidazole-4-carbaldehyde has been chosen as starting material in this work. Base catalyzed Knoevenagel condensation [1] of 2-phenylimidazole-4-carbaldehyde with various active methylene group compounds has been used to produce a series of ten 4-substituted 2-phenylimidazole derivatives. Identity and purity of all products has been confirmed by ^1H NMR and ^{13}C NMR spectroscopy, elemental analysis and by GC/MS. Coordination properties of all prepared substances have been tested. The formation of Cu(II) complexes in solution has been studied by UV/VIS spectroscopy. The results have been compared with 2-phenylimidazole and 2-phenylimidazole- 4-carbaldehyde.

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The authors are indebted to the Ministry of Education, Youth and Sports of the Czech Republic for financial support (Research project MSM 0021627501).

19:30 poster II-10

π-Electron Delocalization in Cyclopentadienylaluminum Complexes

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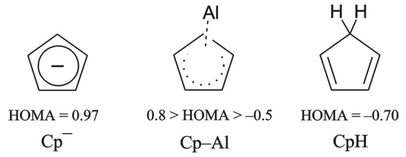
Cyclopentadienylaluminum complexes are of interest due to their practical application in various technological processes as well as their versatile bonding modes with metallic center observed. The analysis of the factors influencing the electronic structure of the cyclopentadienyl ring in aluminum complexes of general formulae Cp_xAlL_y is the subject of this contribution.



The electronic structure of the cyclopentadienyl ligand bonded to metallic center can be regarded as intermediate between the highly aromatic, uncomplexed cyclopentadienyl anion and the structure of the cyclopentadiene, CpH, exhibiting antiaromatic character. Basing on the crystal structure of the newly characterized aluminum complexes and the data deposited in CSD the relationship between the Cp ligand aromaticity (described by HOMA index [1]) and the Cp bond-mode with aluminum will be discussed. The impact of both the negative hyperconjugation and steric effects will be shown. The nature of the effects observed will be supported and explained by DFT calculations (B3LYP/6-311G**) and NBO analysis [2].

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19:30 poster II-11

Sigma Cutoff - and What Lies Behind

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The I/s_I cutoffs are commonly applied at all stages of crystallographic structure solution and refinement, as it is statistically justified to consider insignificant the intensities lower than three s_I. The approach reduces actual dataset to the strong, well defined reflections, yielding better refinement statistics and shorter computational time. However, the weak signals may carry some information, especially in the case of charge density studies, where high resolution and, therefore, weaker reflections are essential for the proper structure refinement, and the number of refined parameters is great.

Expecting that some minute yet important effects may be lost due to the exclusion of weaker reflections, we decided to analyze the influence of applied I/s_I cutoff on the series of multipole charge density refinements, conducted on a couple of datasets with sigma cutoffs of 4, 3, 2, 1 and 0 I/s_I. The general quality of refinements measured by R-factors and residual density extrema improves slightly with the higher sigma cutoff applied. Interesting dependences of r(r) and Lap(r) vs I/s_I cutoff are observed within the estimated errors range.

19:30 poster II-12

Comparative Studies of Oxaphosphinane and Chromone Derivatives. X-ray, DFT, AIM Studies

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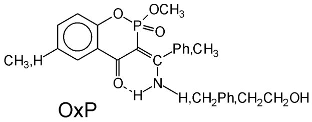
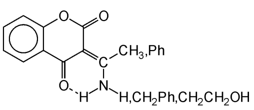
The crystal and molecular structure of seven oxaphosphinin-4-one (OxP) and three chroman (ChD) derivatives have been analyzed by single X-ray diffraction analysis. Benzo-g-pyrone chromone derivatives are another class of biologically important compounds. On the other hand chromone and coumarin derivatives containing phosphorus create a novel group of compounds with biological and alkylating properties. Their in vitro alkylating properties were confirmed in Preussmann test with 4-(4-nitrobenzyl)pyridine (NBP). What is more these compounds exhibit strong cytotoxic effects and also some anticancer activity in vivo. For these reasons X-ray studies were undertaken.

The intramolecular N-H…O resonance assisted hydrogen bond closing extra six-membered ring is observed in all investigated compound. The strongest p-delocalization effect influencing the strength of resonance assisted hydrogen bond seems to exist in **ChD1** structure. This observation was confirmed by SP calculations performed at B3LYP/6-311++G(d,p) level. The topological 'atoms in molecules' (AIM) analysis was also applied. The oxaphosphinane rings adopt half-chair or twist-boat conformations except of OxP2 structure. The P atom connections possess tetrahedral geometry slightly distorted towards trigonal pyramidal with elongated P-C bond. This is typical for such derivatives with one double bond.

The tautomerism of the studied compounds was also examined. The DFT calculations have been performed at B3LYP/6-311++G** level of theory for similar model species. The proton transfer process N-H…O↔N…H-O for some model systems have been studied. The geometrical, energetic and topological parameters were analyzed. Numerous interrelations between them were found. The substituent effect for this class of compounds was also studied.



OxP



ChD

19:30 poster II-13

Thermo-solvatochromism of Merocyanine indicators: Effects of the Hydrophobic Character of the Alkyl Group

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Our previous work on solvatochromism has indicated that probe's pKa and hydrophobic character (indicated by log P) are relevant to solute-solvent interactions. The indicators of widely different properties make evaluation of the relative contribution of these structural properties not viable. In order to remedy this problem, a series of 2,6-dibromo-4-[(e)-2-(1-alkylpyridinium-4-yl)ethenyl]phenolate. For this series, similar pKa´s and variable log P were expected, and indeed determined (pKa = 5.15, and log P = -0.16, 1.12 and 2.71, for R = methyl, n-butyl and n-octyl, respectively). Their solvatochromism was studied at 25 ºC in 34 protic and aprotic solvents. E_T(probe) in kcal/mol correlated linearly with the $E_T(30)$ scale, with slopes of ca. 0.65. In pure solvents, for all indicators, the multi-parameter correlation showed the order of contribution of solvent parameters to E_T(probe): acidity (a) > dipolarity/polarizability (p*) > log P. Thermosolvatochromism was studied in binary mixtures of water with methanol, MeOH, 1-propanol, 1-PrOH, acetonitrile, MeCN, and dimethylsulfoxide, DMSO, respectively. The results were treated according to a model that considers the exchange in the probe solvation micro-sphere of the two pure solvents, and hydrogen bonded species, e.g., MeOH-W. In alcohols, all are preferentially solvated by the organic solvent, and more by the ROH-W species. In MeCN, the probes are more solvated by water and by MeCN-W than by pure MeCN. In DMSO, the probes are more solvated by the pure solvent, whereas the efficiency of DMSO-W in displacing both W and DMSO is lower than the mixed species of the above-mentioned solvents. As expected, E_T(probe) decreases as a function of increasing T, due to the concomitant decrease in solvent structure. The multi-parameter correlation in the above-mentioned alcoholic mixtures was performed and the correlation coefficients showed that the response of E_T(probe) to solvent hydrophobicity increases as a function of increasing the chain length of the probe. We thank FAPESP for financial support and a pre-doctoral research fellowship to C. T. Martins; CNPq for a research productivity fellowship to O. A. El Seoud, and a BIPIC fellowship to M. S. Lima; Paulo A. R. Pires and C. Guizzo for their help.

19:30 poster II-14

Double Aromaticity in Monocyclic Carbon Clusters

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Monocyclic carbon clusters have two kinds of p-molecular orbitals, namely, out-of-plane p-molecular orbitals and in-plane p-molecular orbitals. We studied the double aromaticity/antiaromaticity in monocyclic carbon clusters from the geometry criterion and electron count criterion. The B3LYP method was used to obtain the optimized structures for monocyclic carbon clusters. We found that (1) monocyclic carbon clusters C_{4n+2} are doubly aromatic, (2) C_{4n} are doubly anti-aromatic, and (3) C_{4n+1} and C_{4n+3} are out-of-plane aromatic and in-plane anti-aromatic.

We also calculated the NICS values for the monocyclic carbon clusters to evaluate the aromaticity. The obtained NICS values show that (1) monocyclic carbon clusters C_{4n+2} are aromatic, (2) C_{4n} are anti-aromatic, and (3) C_{4n+1} are anti-aromatic while C_{4n+3} are aromatic .

19:30 poster II-15

Synthesis and Chemical Transformation of Fused Tetrazoles Derivatives from of 2-bromomethyl- and 2-iodomethyl-3,5,6,7-tetrahydrobenzofuran-4-ones

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The 2-bromomethyl-3,5,6,7-tetrahydrobenzofuran-4-ones **1** were subjected to tetrachlorosilane and sodium azide ($SiCl_4$-NaN_3) in acetonitrile to afford tetrahydrotetrazolofuroazepine derivatives. Under similar reaction conditions, the 2-iodomethyl-3,5,6,7-tetrahydrobenzofuran-4-ones affords mixtures of products characterized as tetrahydrotetrazolofuroazepines **2** (major) and the 4-azido-2-iodomethyl-2,3-dihydrobenzofuran derivatives **3**. We have recently described the synthesis and further studies of chemical transformation of 2-bromomethyl- and 2-iodomethyl-3,5,6,7- tetrahydrobenzofuran-4-ones **1** [1].

The results and the mechanism of formation of tetrahydrotetrazolofuroazepines **2** (major) and the 4-azido-2-iodomethyl-2,3-dihydrobenzofuranderivatives **3** is proposed [2].

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19:30 poster II-16

Structure-Lipophilicity Relationships in Series of Quinoline Derivatives

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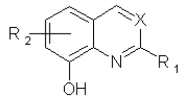
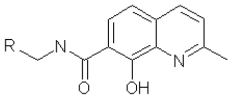
Quinoline derivatives have shown a wide range of biological activities [1]. Derivatives of the 8-hydroxyquinoline were studied as potential HIV-1 integrase inhibitors [2] and as potential antifungal agents [3, 4]. Their herbicidal effects were reported as well [3, 5].

One of the major prerequisites for pharmacological screening and drug development is the prediction of absorption, e.g. the transport of a molecule through cellular membranes. The drugs cross biological barriers most frequently through passive transport, which strongly depends on their lipophilicity. In general lipophilicity is one of the most important physical properties of biologically active compounds. This feature were assigned for combinatorial library of the ring-substituted quinoline derivatives by calculation using commercially available computer programs and by means of the RP-HPLC techniques for the lipophilicity measurement.



X = C, N; R_1= H, CH_3

R_2 = H, Br, NH_2, NO_2, SO_3H



R= -C_6H_5, -C_6H_4-4F, -C6H4-4CH_3, -C6H4-4OCH_3

-$CH_2C_6H_5$, -$CH_2C_6H_4$-4F, -$CH_2CH_2CH_2C_6H_5$

In the present study the correlation between RP-HPLC retention parameter log K (the logarithm of capacity factor K) and log P data calculated in various ways is discussed as well as the relationships between the lipophilicity and the chemical structure of the studied compounds.

The study was supported in part by a grant from KBN Warsaw: 4T09A 088 25.

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19:30 poster II-17

Charge-Transfer and Oxidized States of Boron-Bridged Ferrocene Monomers and Polymers

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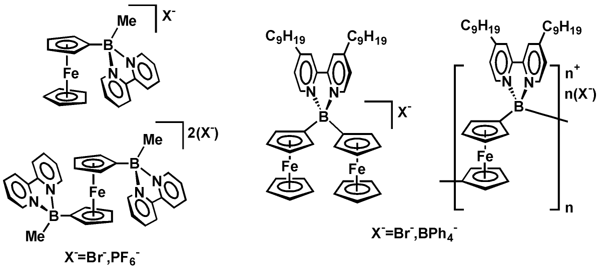
We present recent spectroscopic results on a group of compounds consisting of ferrocene (Fc) donors and 2,2'-bipyridine-based

(B-bpy) acceptors with tetracoordinated boron bridges (see illustration). Such compounds are interesting candidates for materials where doping and/or charge-transfer optical excitation can lead to a variety of interesting electronic interactions, such as (photo-)conductivity, spin-spin interactions and strong correlation phenomena.

For the mono-ferrocene compounds, we analyze the solvent dependence of the visible-range Fc→B-bpy MLCT band (metal-to-ligand charge transfer) using a modified solvatochromism model that takes into account the cationic charge of the solute. This analysis supports the assignment of an MLCT excited state involving almost complete displacement of a unit electronic charge from the Fc donor to the B-bpy acceptor. We have studied the excited-state dynamics of the MLCT state using two-color pump-probe transient absorption spectroscopy, including the effect of solvent polarity on the initial sub-picosecond dynamics and sub-nanosecond back-electron transfer rate.

For the Fc-polymer and di-ferrocene monomer, in addition to the study of the MLCT excited state, we present results of the changes during chemical oxidation of the Fc centers in solution and neat-polymer drop-cast thin films (using iodine, NOPF$_6$). During oxidation of the polymer, a near-infrared absorption band arises (with λ_{max}=1780 nm, $\Delta\nu$=4300 cm^{-1}, ε_{max}=65 M^{-1}cm^{-1}) which we assign to a Fc→Fc$^+$ intervalence charge transfer transition between neighboring Fc/Fc$^+$ groups along the polymer chain. Based on Marcus-Hush theory, this yields an estimate of the effective interaction parameter of α~0.03 between adjacent Fc/Fc+ groups. Hence, in their oxidized state, these polymers possess both a ground-state and MLCT excited-state mechanism for in-chain conductivity.



19:30 poster II-18

Studies on C-H and N-H Pyrazine Acid-Base Properties.

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Heterocyclic compounds with an active methylene moiety are known to have antiinflamatory, anelgetic and large number of other pharmacological activities. In our previously study we confirm that pyrazine derivatives obtained by the nucleophilic substitution of chlorine atom in the pyrazine ring system with active methylene compound, posses above mentioned activity. Some of new pyrazine C-H and N-H acids also demonstrated antithrombotic and antiplatelet activity. Structural analysis of pyrazine acetonitrile derivatives show pyrazinyl-pyrazylidene tautomerism

PyH D Py$^-$ + H$^+$ (K$_1$) PyH + H$^+$ D PyH$_2^+$ (K$_2$)

Because pharmacological properties are often related to acidic-base charcter of compounds it was important to maeasure p*Ka* value for this new class of active biological compound**.** **pKa$_1$** and **pKa$_2$** value were determined by specroscopic and potentiometric methods. Relationship between tautomeric form, **pKa** and structure of several new pyrazine CH- and N-H acids are discussed.

19:30 poster II-19

Sensitivity of Carbon Atom Bonded to a Substituent to its Polar Effects in the ^{13}C NMR Spectra

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Substitution of any organic compound by a certain substituent causes changes of the chemical shifts of carbon atoms up to 3 bonds away. The semiempirical methods, still commonly used for prediction of chemical shifts for various kinds of compounds, are based on the assumption that the substituent induced change in the 13C NMR is an additive property. The chemical shifts of carbon atoms in a compound containing given substituent are calculated by addition of certain constant values to the chemical shifts of carbon atoms in the parent unsubstituted compound. These parameters are characteristic for the substituent and its position with respect to the carbon atom in question. Such aproach implies that for each type of compound and, moreover, for each site of substitution a separate set of parameters has to be used. For given substituent the values of these parameters, even for analogous substitutions site (*e.g.* for the substituted carbon atom) are considerably different.

Any substituent, however, has a definite electron donating or electron withdrawing properties. Thus it seemed reasonable to assume that chemical shifts of carbon atoms in all compounds of certain kind, where polar effects of a substituent are transmitted by analogous sequence of bonds, could be calculated with just one common set of parameters, but these parameters will be multiplied by the factor "a_s" specific for the kind of the compound and the position of substituent with respect to the substituent R, as shown by the equation:

$$\delta\ C(k) = \delta^{o}C(k) + a_s A(R)$$

Above hypothesis was recenly confirmed on the example of six-membered heteroaromatics [1] alicyclic hydrocarbons [2], as well as condensed aromatics, or five-membered heterocycles and alkenes [3].

In this work we have investigated the factors influencig the term a_s for a substituted carbon atom. It was found that its value depends mainly on hybrydization, electron density on this atom and the distortion of the bond angle. In the case of the sp^2 hybridization the a_s value increases with the increase of the electron density characterized by the 13C NMR chemical shift before substitution, whereas for the sp^3 hybridization, opposite, it decreases.

For both hybrydization cases all correlations between the chemical shifts of carbon atoms and their changes involved by substitution are of at least good quality ($r > 0.95$). For bulky substituents, and in the case of occurence of the gamma-effect another relations are observed, as it was previously found [1, 2].

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[2] J. Oszczapowicz, I. Oszczapowicz, J. Phys. Org. Chem. 2005, 818-824.

[3] J. Oszczapowicz, I. Oszczapowicz, in preparation.

19:30 poster II-20

DNA Damage and Lipid Peroxidation in L1210 Cells by Formamidino Derivatives of Doxorubicin

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In the search for new more selective anticancer drugs new derivatives of doxorubicin, containing in the position C-3' of daunosamine moiety formamidino group with morpholine (DXM) or hexamethylenoimine (DXH) rings, have been synthesized. These analogs were compared with their parent doxorubicin (DX) for cytotoxic activity, cellular uptake, DNA damaging properties and lipid peroxidation potential. All experiments were carried out on leukemia L1210 cell line.

The values of DNA single strand breaks, measured by alkaline elution technique are 375.0 ± 41.0 for (DX), 573.0 ± 0.1 for (DXM) and for (DXH) 120.0 ± 10.0 rad-equivalents, DNA-protein crosslinks, quantified by KCl-SDS precipitation are 3.0 ± 0.43, 27.0 ± 0.23 and 77.0 ± 0.16 (crosslinking indices), accordingly. The amounts of anthracyclines uptaken by the cells are 76.0 ± 9.0, 247.0 ± 37.0 and 83.0 ± 6.0 (pmole/10^6cells), as well as lipid peroxidation are 7.10 ± 0,14, 10.60 ± 0,47 and 8.76 ± 0.67 (MDA nmoles/10^6cells), respectively (both estimated by spectrofluorimetric measurements). MDA = maleic dialdehyde.

Obtained results show that biological properties of above mentioned analogs are substantially different from those of the parent doxorubicin. The replacement of the amino group at C-3' position of daunosamine moiety in (DX) by amidino substituent, containing morpholine ring (DXM) resulted in the enhancement of genotoxicity, cellular uptake and slight loss of cytotoxic activity (IC_{50} = 24.0 pM), whereas for (DX) IC_{50} = 18.0 pM. Analog (DXH) exhibited low cytotoxicity (IC_{50} = 91.0 pM) which was attributed to low ability of this drug to produce DNA damage. Both derivatives were more active in the production of lipid peroxidation then their parent drug.

It has to be pointed out that introduction of the formamidino group with morpholine ring into daunosamine moiety resulted in significant enhancement of cellular uptake of anthracyclines, which leads to assumption that (DXM) may be able to overcome the barrier of drug resistance, developed in tumor cells treated with anthracyclines.

19:30 poster II-21

Kinetics and Mechanism of the Nitrosation of Cyclic 1,3-diones by SNO^+

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2-mercaptopyridine reacts rapidly with nitrous acid in mildly acid aqueous solution to give an unstable S-nitroso ion (SNO^+) in a reversible process. SNO^+ is readily detected by two peaks in the UV spectum at 295 and 240 nm. Addition of cyclic 1,3-diones (RH) to an acidified solution of SNO^+ resulted in quantitative nitrosocompound formation and kinetic measurements of the nitrosation of Meldrum´s acid, dimedone and barbituric acid in the presence of MP showed marked catalysis at low MP concentration. At higher MP concentration values, catalysis disappears since there is virtually complete conversion of HNO_2 to SNO^+.

We carried out some experiments to examine the potencial of SNO^+ cations as electrophilic nitrosating species. SNO^+ was generated at acid pH from equimolar amounts of MP and nitrous acid and was used to react with Meldrum´s acid, dimedone and barbituric acid. The reaction kinetics were studied by following the change in absorbance at 240 nm for Meldrum´s acid, at 250 nm for barbituric acid and 305 nm for dimedone due to the nitrosocompound formation using an spectrophotometer fitted with thermostated cell holders. All kinetic experiments were performed with a great excess of the 1,3-diones over SNO^+. The absorbance-time data always fitted the first-order integrated equation, and k_{obs}, the corresponding pseudo-first order rate constant, could be reproduced to within 3%.

If we accept that reaction occurs as indicated by equations (1) and (2), we can calculate a value for K_N and for the bimolecular rate constant (k).

$MP + HNO_2 + H^+$ « $SNO^+ + H_2O$ K_N (1)

$SNO^+ + RH$ ®R-NO + MP+ H^+ k (2)

Meldrum´s acid itself exists primarily in the diketo form, with a very small enol content This contrasts quite markedly with the behaviour of dimedone which exists in aqueous solution primarily as the enol tautomer.

The possibility then exists that electrophilic attack in RH can occur either via the carbanion (enolate) or the enol intermediates.

19:30 poster II-22

Anion Recognition by Artificial Polyamide Receptors

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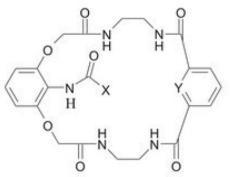
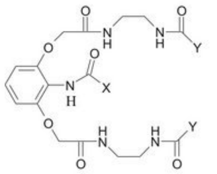
Synthesis and examination of receptors, which are able to bind different kinds of molecules, are one of the main purposes of supramolecular chemistry [1]. Synthesis of anion receptors is an especially demanding task due to larger size, variety of shapes and low charge density of anions comparing to cations. One of the ways to solve these problems is a design of the tweezer-like receptors which are flexible enough to adjust their structure to guests of various sizes and shapes. An interesting application of anion receptors is formation of optical sensors, especially those able to give visible response in the presence of anions [2].

Simple and efficient way of synthesis of both macrocyclic **1** and open-chained **2** tweezer-like molecules will be presented. Modular structure of this type compounds is easy modifiable and allows to incorporate an array of various groups. Compounds bearing nitro groups change color in the presence of anions. Binding properties of obtained receptors were examined by ^{1}H NMR titrations with three typical anions - Cl^-, $PhCOO^-$, and $H_2PO_4^-$. Binding constants, obtained in DMSO by this method, vary from 10 to 10^3.



1: X = Ph, C_6F_5, C_6H_4 p-NO_2, CH_3
Y = CH, N



2: X = Ph C_6F_5, C_6H_4 p-NO_2, CH_3
Y = Ph, C_6F_5, C_6H_4 p-NO_2, C_3H_7

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19:30 poster II-23

Interactions in the Crystal Structure of Guanidinium Hydrogen Oxalate Monohydrate Derived from Experimental Charge Density Distribution

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High-resolution X-ray diffraction data were collected at 80K for guanidinium hydrogen oxalate monohydrate to obtain accurate crystal data and experimental charge density. The measurements were carried out using Nonius KappaCCD diffractometer equipped with Oxford 700 Cryostream Cooler. The studies were performed to explore inter- and intramolecular interactions. The crystal structure is built of layers, parallel to (-101), ~3.2 Å apart, formed by hydrogen oxalate anions, monoprotonated guanidinium cations and water molecules. In the crystal structure hydrogen oxalate anion is surrounded by three monoprotonated guanidinium cations and water molecule. All possible donors are involved in intermolecular hydrogen bonding. The hydrogen bonds are of N-H···O and O-H···O types. The guanidinium cation, with pseudo *3m* symmetry, interacts with the hydrogen oxalate anions and water molecules through relatively strong hydrogen bonds of N-H···O type. The water molecules play exceptional function in the structure holding the layers together through $O(4)_{water}$-H···$O(22)_{oxalate}$ and $O(4)_{water}$-H···$O(21)_{oxalate}$ strong hydrogen bonds. O(22) atom accepts three hydrogen bonds (two N-H···O and one O-H···O type), whereas the remaining oxygen atoms of hydrogen oxalate carbonyl groups, O(11) and O(21), accept two hydrogen bonds of N-H···O type each. O(12) atom of hydroxyl group is a donor of hydrogen bond to oxygen atom O(4) of water molecule. Evaluation of experimental electron density and related properties such as moments and electrostatic potential was performed using Hansen-Coppens multipole formalism [1]. According to Bader's AIM theorem [2] topological analysis charge density led to determine quantitative parameters of the interactions, like value of electron density and Laplacian $\rho(r)$ at the bond critical point's (BCP). Multipole refinement and the analysis of static densities was performed using the XD program suite [3] and all topological interactions (atomic volumes, atomic charges) were evaluated with program TOPXD [4].

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19:30 poster II-24

Gas-Phase Lithium Cation Basicity of Histamine and its Agonist 2-(β-aminoethyl)-pyridine. Chelation Effect

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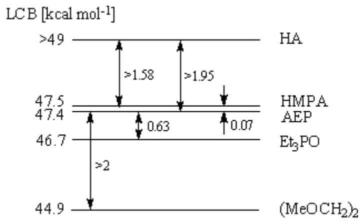
The gas-phase lithium cation basicities (LCBs) were obtained for histamine (HA) and its agonist 2-(β-aminoethyl)-pyridine (AEP) from collision-induced dissociation of lithium adducts (kinetic method) using Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). For measurements, $(MeOCH_2)_2$, Et_3PO and HMPA, the strongest bases in the LCB scale, were used as the reference compounds. The experimental LCB of AEP is between those of Et_3PO and HMPA. The experimental LCB of HA is higher than those of AEP and HMPA by 1.5-2 kcal mol^{-1} indicating that it is out-side of the current LCB scale.



In parallel, quantum-chemical calculations [DFT(B3LYP/6-31G*] were performed for HA, AEP and their lithium adducts using the Gaussian'98 program package. Among twenty two conformations of HA-Li^+ adduct, only one structure is significantly more stable than others. This is also the case for one structure among seven conformations of AEP-Li^+ adduct. These two stable structures have the 'scorpio' conformation, where Li^+ cation is almost equally chelated by two basic nitrogens, the ring N-aza and the chain N-amino. Other HA-Li^+ and AEP-Li^+ conformations have considerably higher energies than the 'scorpio' structures.

The DFT calculated difference between LCB of HA and AEP (4 kcal mol^{-1}) is in agreement with that experimentally obtained (> 2 kcal mol^{-1}). High experimental and theoretical values of LCB for HA and AEP confirm the strong chelation of Li^+ by both ligands in the gas phase. This chelation effect was also observed previously for the proton gas-phase basicity.

Acknowledgments. DFT calculations were carried out at the Interdisciplinary Center for Molecular Modeling (ICM, Warsaw).

19:30 poster II-25

Influence of Copolymers on Radiation Resistance of Polypropylene Blends

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Polypropylene (PP) is the most common commercial polymer of good mechanical and thermal properties however the polymer is degradable upon radiation processing. Irradiation with sterilizing dose of about 25 kGy initiates in polypropylene radicals that lead to undesired processes like chain scission, oxidative degradation or formation of oxygen containing polar groups. The sensitivity of polypropylene may be overcome by introduction of other constituents.

We investigated blends of polypropylene with copolymer poly(ethylene-co-vinyl acetate) (EVA). Samples of the blends were irradiated with electron beam to doses of 25 or 50 kGy. Thermal properties of the blends before and after irradiation were characterized by DSC measurements. Rheological properties were studied by Melt Flow Index (MFI) and apparent viscosity measurements. The behaviour of alkyl radicals in PP and EVA was investigated by EPR technique. The influence of several concentrations of EVA on radiosensitivity of PP/EVA blends was evaluated.

19:30 poster II-26

α-Cyclodextrin Inclusion Complexes with Solvatochromic Pyridiniophenolates

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The interaction of four solvatochromic pyridiniophenolates with α-cyclodextrin was investigated by means of UV-visible and ^{1}H-NMR spectroscopies, and supported theoretically by molecular simulation studies. By inserting different substituents into the hydrophobic cavity of α-CD, we were able to identify the separate contributions of the donor and acceptor moieties of these dyes to their solvatochromic behaviour in water.

^{1}H-NMR evidence suggested that insertion of the less hindered phenoxide group inside the hydrophobic host cavity took place for three complexes. Steric hindrance prevented this in the case of one betaine, leading instead to the encapsulation of an aryl substituent of the pyridinium ring. The fact that in this case no UV-Vis spectral changes were observed points to a negligible influence of this pyridinium substituent to the solvatochromic behaviour of the dye.

We carried out docking of all betaines into the α-CD host, followed by molecular dynamics simulations in water, employing the CHARMM27 force field in a a 20-Å-radius sphere built with TIP3P water molecules. The resulting structures were compared with the experimental data. The theoretical results agreed with the spectroscopic evidence, indicating that UV-Vis spectral changes were observed only when the phenoxide donor lodged inside the more hydrophobic microenvironment of the cyclodextrin host.

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19:30 poster II-27

Quantum Chemical Study of the Hydrolysis of Imines: Structure and Reactivity

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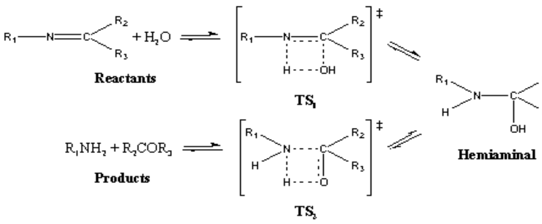
Schiff bases have been widely used as protective group of the amino group in organic synthesis [1]. The hydrolysis of these compounds has been extensively investigated by Jencks and others empirically [2]. However, to our knowledge there have been no computational attempts to model this process in detail.

The molecular mechanism of imines hydrolysis at neutral pH has been theoretically characterized by using DFT at the B3LYP/6-31++G** computing level. The geometry and energy of all relevant stationary points for several simple imines derived from aliphatic amines were calculated. The reaction proceeds via a stepwise mechanism, as empirically observed (see scheme) [2]. The attack of a water molecule on the C=N double bond takes place in the first step, subsequently the so-formed hemiaminal collapses, leading to the parent amine and carbonyl compounds.



The role of water as solvent was analyzed by using discrete and hybrid discrete-polarized continuum (PCM) models. Discrete water molecules were added to describe the solute-solvent interaction in the first solvation layer, while the PCM model was used to assess the effect of bulk water.

Explicit water molecules showed catalytic effect, lowering the reaction barrier, either by net charge stabilization, or directly participating in the transition structures. Calculations involving the PCM model improve the description of the studied reaction in water, stabilizing the localized charges, and, therefore, modifying significantly the corresponding free energy profile. Quantum chemical calculations revealed the role of water in the title reaction, and the characteristics of the process obtained with water clusters and PCM should hold in the reaction in bulk solvent.

The present study opens the door to the detailed analysis of the molecular mechanism of the hydrolysis of Schiff bases.

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19:30 poster II-28

Intermolecular Donor-Acceptor Interactions of B(OH)$_2$ Group in Phenylboronic Acids – Important or Not?

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The arylboronic acids are widely used in organic chemistry for Suzuki coupling reactions but have also many applications in biochemistry and in medicinal chemistry. Similarly as in benzoic acids, the most basic structural motive found in the crystals of phenyl boronic acids are dimers. Since the boronic group (B(OH)$_2$) may be a donor of two hydrogens to hydrogen bonds, usually more complex structures are formed, which offers expanded possibilities in crystal engineering. The formation of complex structures is facilitated by appreciable high rotational flexibility of the group. So far, successful attempts have been made to form heterodimers with aminoacids [1], with other systems containing carboxylate groups [2] and the complexes with pyridine derivatives [3]. Since boron is an electron deficient atom, apart from hydrogen bonds formed by hydroxyl groups, the donor-acceptor interactions should also influence the chemical behavior of the group and are expected to be a potentially important building factor determining the architecture of a crystal. In fact, this kind of interactions has been found in the ortho substituted systems having a nitrogen atom in the beta position N→B [4]. A problem arises whether the donor-acceptor interactions are also decisive in intermolecular interactions. To answer this question, we have traced the crystal structures of phenylboronic acid and its para substitued derivatives, where the substituent significantly differs by van der waals radius and electronegativity: -F, -Cl, -Br and -I. Our attempts to determine the crystal structure of p-flurophenylboronic acid failed since the system transformed to tris(4-fluorophenyl)boroxin. The molecular structures of chloro- and bromo- derivatives are similar to the structure of the parent molecule. The dimers are linked through a hydrogen-bonded network to adjacent pairs which lie almost perpendicular to each other, forming infinitely extended chains, as shown in the figure below. An important stabilising factor are the Cl…Cl and Br…Br interactions which are 3.528 Å and 3.562 Å, respectively. In contrast, the iodo- derivative (which cocrystalises with water molecule) reveals short contact between the iodo substituent and boron atoms and the molecules are perpendicular each other (as shown in the figure). The B…I distance is 3.670 Å and 3.744 Å.

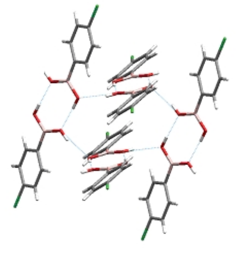

Fig. 1. Crystal structure and packing of p-chlorophenyleneboronic acid

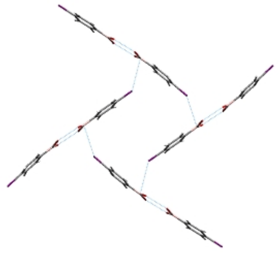

Fig. 2. Crystal structure and packing of p-iodophenyleneboronic acid

A similar arrangement of molecules can be observed in the structure of p-bromophenylboronic acid cocrystalising with ethanol [5]. Taking into account the difference in van der waals radius between I and Br the distance of 3.645 Å and 3.682 Å B…Br appeals, however, for much less efficient donor-acceptor interaction. The analysis based on crystal structures from Cambridge Structural Database leads to the conclusion that in contrast to donor-acceptor intramolecular interactions, the intermolecular ones generally lose the competition with hydrogen bonds formed by hydroxyl groups.

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19:30 poster II-29

The Effects of a Guanine Hole on the Structure and Dynamics of DNA Duplexes. Consequences for Theoretical Estimation of Charge Transfer Parameters

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Control over charge transfer in DNA attracts a great attention since it opens a route to the common usage of the biopolymer in nanoelectronics and might be relevant for understanding its oxidative damage and mutations. Today a consensus exists that guanine radical cation (G^{+}) is a key intermediate in a hole transfer mediated by DNA. A hole, initially created on a guanine, hopes through the DNA stack using other guanine bases as resting states. This mechanism may be described as G-hopping, a series of tunneling steps between G sites separated by AT pairs. The rate of the tunneling charge transfer is proportional to the square of the electronic coupling, Vda, between the donor and acceptor sites. Therefore, the Vda matrix element is a major factor which controls the efficiency of charge transfer in DNA.Thermal fluctuations are known to affect considerably the structure and properties of biomolecules. Recently it was recognized that conformational changes in DNA can produce significant variations in π-stacking of base pairs and thereby modulate the efficiency of charge transfer. However, in theoretical studies on hole transfer one usually uses the geometries of a neutral π-stack neglecting thus any structural effects of a positive charge localized on the one of guanines. Thus, in the present study we estimate the effects of a hole on the structure of DNA duplex (including counter-ions and water molecules) and the corresponding consequences of its structural changes on charge transfer parameters.We employ a combination of molecular dynamics and quantum chemical calculations to compare the propensity to hole transfer for the neutral and positively charged Watson-Crick base pair dimers (WCPs) incorporated into the B-DNA π-stack. Namely, we carried out five nanoseconds MD simulations for two B-DNA double-stranded octamers of the 5'-A1A2G3A4A5G6A7A8-3' sequence. These systems differed with the charge localized to the third guanine that was neutral or positively charged. The MD trajectories were analyzed in terms of effects that the positive charge exerts on the DNA dynamics and, in consequence, on electronic coupling. In particular, the analyzed WCP dimer conformational parameters for the neutral and charged species were compared. Moreover these geometrical characteristics were correlated with the variations of electronic coupling along the MD trajectories.Our main finding indicates that in order to predict reliable values of Vda one cannot neglect the effects of electron hole on the DNA structure. It turned out that accounting for these effects may essentially (by a factor of 2) change the magnitude of computed electronic couplings.Acknowledgements. This work was supported by the: Polish Ministry of Education and Science, grants Nos. Dec.127/02/E-335/S2006 (J.R.) and DS-8372-4-0138-5 (C.C.), (ii) Spanish Ministerio de Educación y Ciencia, Project No. CTQ2005-04563 (A.V.).

19:30 poster II-30

Kinetics and Mechanism of the Pyridinolysis of Thiolbenzoates and Carbonates

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The reactions of 4-nitrophenyl and 2,4- dinitrophenyl 3,5-dinitrothiolbenzoates (**1** and **2** respectively) and of phenyl, 4-methylphenyl and 4-chlorophenyl 2,4-dinitrophenyl carbonates (**3**, **4** and **5**, respectively) with a series of 3- and 4-substituted pyridines are subject to a kinetic study in 44 wt% ethanol-water, at 25 ºC and an ionic strength of 0.2 M. Under excess amine all the reactions show pseudo-first-rate constants and are first order in the pyridine.

The Brønsted-type plots (log k vs pK_a) for the reactions of 1 and 2 are non linear downwards, with the curvature centre at 11.1 and 10.4, respectively. The values of the slopes (β) at low pK_a (ca. 1) and high pK_a (0.1-0.2) are in agreement with a stepwise mechanism, through a zwitterionic tetrahedral intermediate ($T^{\pm}$), and a change in the rate-determining step, from $T^{\pm}$ breakdown (low pK_a) to $T^{\pm}$ formation (high pK_a).

The pyridinolysis of other 4-nitrophenyl and 2,4-dinitrophenyl 4-Y-substituted thiolbenzoates (Y= H, Cl, NO_2) also show curved Brønsted plots, with increasing pK_a^{o} values as Y becomes more electron withdrawing.[1,2]

For the reactions of the carbonates **3**, **4**, and **5** the Brønsted type plots are linear with slopes ca 0.6, consistent with a concerted mechanism.

4-Methylphenyl and 4-chlorophenyl 4-nitrophenyl carbonates react with a series of secondary alicyclic amines (SAA) in water solution by a stepwise mechanism with biphasic Brønsted plots with pK_a^{o} at 10.5 and 10.6 respectively.[3] It is known that both the change to a better nucleofugue in the substrate and a change of SAA to pyridines shift the pK_a^{o} to smaller values.

The absence of break in the Brønsted-type plots at the pK_a range studied (2.4 -11.5) allow to us confirm a concerted mechanism.

We thank FONDECYT of Chile (projects 1020254 and 1060593) for financial support. R.C.A. thanks DIPUC of Pontificia Universidad Católica de Chile for a Doctoral scholarship.

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19:30 poster II-31

Aminolysis of Aryl Chlorodithioformates. A Kinetic Study

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There have been many reports on the kinetics and mechanisms of the solvolysis [1] and aminolysis [2] of chloroformates. Nevertheless, the solvolysis [3] and aminolysis [4] of chlorothioformates and chlorothionoformates has received little attention. Furthermore, except a study on the solvolysis of phenyl chlorodithioformate (PClDTF), to our knowledge there have been no investigations concerning the kinetics of the aminolysis of aryl chlorodithioformates.

In this work we undertake a kinetic investigation on the reactions of secondary alicyclic (SA) amines with PClDTF. A specific objective is to assess the influence of two sulphur atoms on the mechanism and on the reactivity of the substrate. The reactions were studied spectrophotometrically, in water and in ethanol (44 % wt) aqueous solution at 25.0±0.1ºC and ionic strength 0.2 M (maintained with KCl). Pseudo-first-order rate constants (k_{obs}) were found in all cases and the second-order rate constants (k_N) were obtained as slopes of linear plots of k_{obs} vs. free amine concentration, and were pH independent.

The Brønsted-type plots are linear in both solvents, with slopes consistent with a stepwise mechanism with the formation of a zwitterionic tetrahedral intermediate ($T^{\pm}$) as the rate determining step, in accordance with the found for the reactions of the same series of amines with aryl chloroformates [2] and aryl chlorothionoformates [4a].

The rate constant values obtained for the $T^{\pm}$ formation are 3-4 times smaller than those of the same aminolysis of PCITF. This result is explained by the softer nature of the carbonyl group in PClDTF and the fact that SA amines are considered relatively hard bases.

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19:30 poster II-32

From Supramolecular Porphyrin Tweezers to Dynamic $A_nB_mC_lD_k$ Multiporphyrin Arrangements Through Orthogonal Coordination

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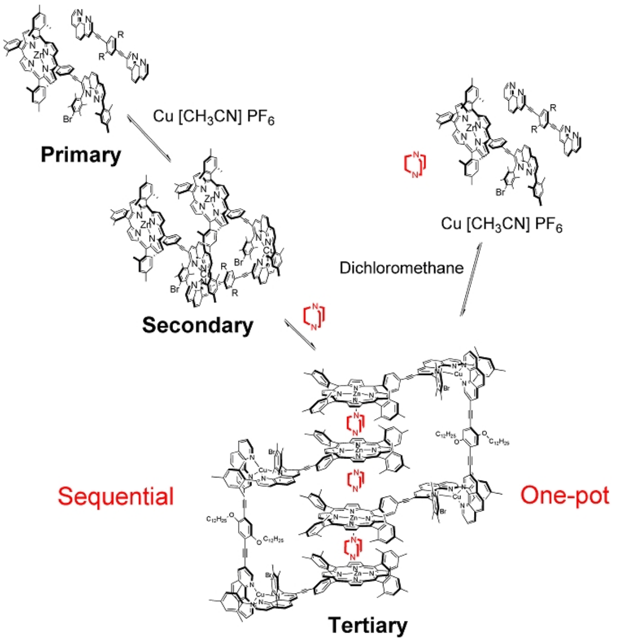
A dynamic supramolecular three-component $A_nB_mC_l$ bis-(zinc porphyrin) tweezer has been prepared quantitatively using the HETPHEN concept. Upon addition of nitrogenous spacers of different length, *i.e.* an extended bipyridine, 4,4'-bipyridine and DABCO, to set up an additional orthogonal binding motif (Zn_{Por}—N_{spacer}), three structurally different, still dynamic four-component $A_nB_mC_lD_k$ assemblies were cleanly formed, as indicated by UV-Vis and NMR titrations as well as by DOSY investigations. The structures were identified as a bridged monotweezer A_2BC_2D, a doubly bridged double-tweezer $A_4B_2C_4D_2$ and a triply bridged double-tweezer $A_4B_2C_4D_3$, the latter resembling a porphyrin stack. Notably, the same structures were equally formed directly from a mixture of the constituents A,B,C and D put together in any sequence if the correct stoichiometry was applied [1].



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19:30 poster II-33

Electrophilicities of Benzylidenebarbituric Acids

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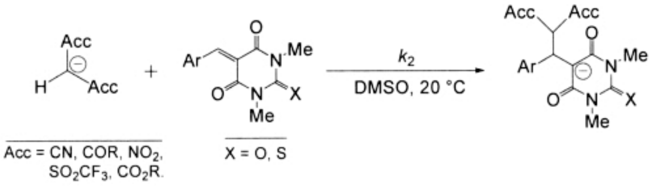
Benzylidenebarbituric acids have been termed "electrically neutral organic Lewis acids" because of their highly polarized double bond [1]. By measuring kinetics of the addition reactions of stabilized carbanions, the electrophilicities of these Michael acceptors could be quantified according to the correlation equation $\log k\ (20\ °C) = s(E + N)$, where s and N are nucleophile-specific parameters and E is an electrophilicity parameter [2].



Scheme 1. Reaction of an acceptor-stabilized carbanion with a benzylidenebarbituric acid.

It is found that the electrophilicities of benzylidenebarbituric acids are in between those of stabilized benzhydrylium ions and quinone methides [3].

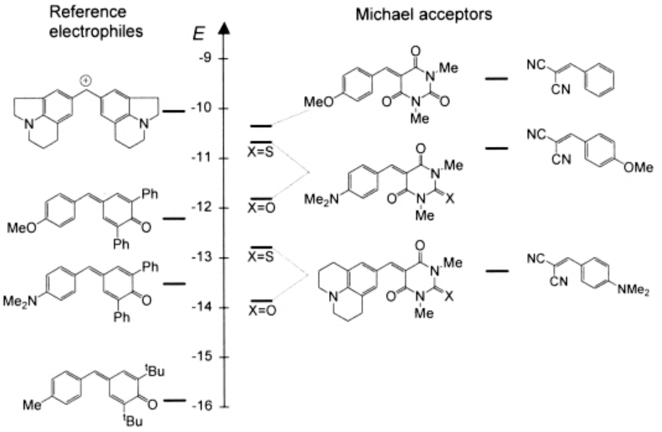


Figure 1. Electrophilicity parameters of benzhydrylium ions and Michael acceptors.

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19:30 poster II-34

Antioxidant Behavior of 2-Amino-5-pyridinols Derived from Vitamin B$_6$

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The increasing interest in the inhibition of radical reactions, which have been associated with lipid oxidation and cell aging processes, inspired computational modeling of novel antioxidants. Based on those computational results, compounds were designed containing an electron rich pyridine ring, followed by a semi-industrial scale synthesis. The key compound, 2-amino-3,4,6-trimethylpyridin-5-ol hydrochloride (1), was obtained from commercially available vitamin B$_6$ in four steps. *N*-Monoalkylated derivatives of 1 were found to possess better radical scavenging properties than corresponding dialkylamino substituted structures. This unexpected behavior was most likely observed due to a steric interaction between the 3-methyl substituent and the relatively bulky 2-dialkylamino group. Multi-gram scale preparation of these monoalkylated compounds was accomplished via *N*,*O*-diacyl derivatization followed by borane-tetrahydrofuran reduction. In addition, some biheterocyclic pyridinols, the best chain-breaking antioxidants known, were also obtained from pyridoxyl hydrochloride. Reactivity of these various vitamin B$_6$ derivatives with peroxyl radicals was investigated in an aqueous environment as well as in an organic medium. A peroxyl radical clock has recently been developed utilizing the competition between β-fragmentations of non-conjugated peroxyl radicals and trapping by a hydrogen atom donor in fatty ester oxidations. Using this system, the rate that these compounds donate hydrogen atoms to peroxyl radicals was measured to determine their scavenging ability. The stoichiometric factors (n) for all molecules tested were close to 2 in benzene, whereas in aqueous buffer in all cases $n < 2$. The relative decrease of n values in the aqueous medium was attributed to the ability of water to favor electron transfer reactions and ability of *p*-aminopyridoxyl radicals to undergo them.

19:30 poster II-35

Synthesis and Reactivity of New Benzimidazolylcarbamates

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The 2-aminobenzimidazole ring system represents the core structure of a number of biologically significant molecules and its derivatives have been found to possess a wide spectrum of biological activity. Particularly, alkyl benzimidazole-2-carbamates show potent fungicide [1] and anti- helmintic activity, [2, 3] being Carbendazim® a good example of a successful market fungicide. Nevertheless, there are, to our knowledge, no studies on aryl benzimidazole-1-carbamates, either in terms of synthesis, bioactivity or chemical reactivity. So, in the sequence of our on- going work about aryl carbamates we decided to synthesize new 2-aminobenzimidazole-1-carbamates (1a-e, 2). Synthesis of new 2-aminobenzimidazole-1-carbamates was accomplished by carbamoylation of 2-aminobenzimidazole using different substituted phenyl chloroformates. The aqueous hydrolysis of the new compounds was examined in the pH range 1-13 at 25^o C. The evaluated kinetic parameters led to the conclusion that up to pH 4 reaction proceeds by a bimolecular attack of water to the N- protonated substrate, *via* an $A_{Ac}2$ mechanism with specific acid catalysis. This is the first time this behaviour is described for carbamates, and can be ascribed to the higher basicity of the benzimidazolyl moiety when compared with the carbonyl oxygen. For higher values of pH, the results are consistent with a $B_{Ac}2$ mechanism with nucleophilic catalysis, but while between pH 4 and pH 7 water acts as the nucleophile, for pH > 7 the hydroxide ion is the acting species.

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19:30 poster II-36

Pt L_2 and L_3 Absorption Studies of Pt-doped Polymers

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A new application of noble metals dispersed in polymer matrices as heterogeneous catalysts has been developed in recent years. By using x-ray absorption methods we have examined electronic states and local structure around Pt ions incorporated in electro-active polymers namely polyaniline (PANI), poly(o-toluidine) (POT), poly(o-methoxyaniline) (POM), polypyrrole (PPY) and an electro-inactive polymer poly(4-vinylpyridine) (PVP). The absorption spectra were measured using synchrotron radiation. Polymers were doped with platinum using appropriate precursor solutions of Pt^{+4} or Pt^{+2} compounds containing chlorine.

The Pt L_3 and Pt L_2 absorption edges in the samples studied contain information on the partial densities of unoccupied 5d electron states around Pt ion according to dipole selection rules. The energy position of the absorption maximum depends on valency of Pt ion and bond ionicity, as well. It was found out that the Pt^{+4} ions were partially reduced by electroactive polymers studied (PANI, POT, POM and PPY). In contrast, the Pt^{+4} ions doped in electro-inactive polymer PVP have not been reduced.

The Fourier analysis of the x-ray extended absorption structures revealed the nearest atomic shells around Pt ions in the sample studied. The main contribution is originated from Pt-Cl bond. The strong amplitude of Pt-Cl bond in case of Pt/PVP sample was evidence that the Pt^{+4} ion is surrounded by 6 chlorine ions. In contrast, the small amplitude of Pt-Cl bond in case of electro-active polymers can be interpreted as caused by active groups of the polymer chain bonded to Pt ions instead of chlorine ligands.

19:30 poster II-37

Molecular Recognition of Nitro- and Cyanoarenes by Podand Diazacoronands

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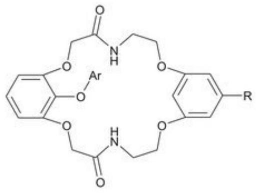
Molecular recognitions, the keystone of supramolecular chemistry [1], depends on a variety of noncovalent interaction. Among them an arene-arene interaction play a fundamental role in the selective complexation of π-neutral guests. The interaction between simple arenes compromise π-acid/base (charge-transfer), van der Walls (dispersive), and polar electrostatic (coulombic) components [2]. The understanding of electron transfer processes is essential for future progress in many diverse fields of science, spinning from biological enzymes [3] via organic synthesis [4] to optoelectronic devices [5].

In this communication we would like to present the synthesis and complexation study of O-benzylated diazacoronands of type **1**.



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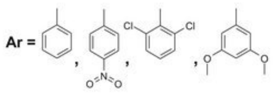

R = H, OMe, $N(Me)_2$

The above-mentioned electron-rich macrocyclic donor compounds with electron-poor acceptor like nitro- and cyanoarenes, forming 1:1 charge-transfer complexes. Their formation was confirmed by NMR and UV-vis spectroscopy as well as X-ray analysis.

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19:30 poster II-38

Dithia- and Dioxadiazuliporphyrin: Facile Generation of Carbaporphyrinoid Cation Radical and Dication

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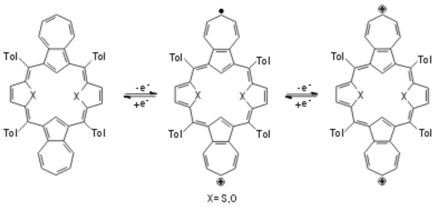
Introduction of an azulene moiety to the porphyrinoid framework is of particular interest because of the unusual electronic properties of this bicyclic system. Exploration of this concept led to the synthesis of azuliporphyrin and its heteroanalogues - systems that exhibit borderline macrocyclic aromaticity and unusual reactivity pathways [1, 2].

The newly designed dithia- and dioxadiazuliporphyrins are nonaromatic porphyrinoids, easily oxidizable to their radical cations and, consequently, to the aromatic dications [3]. Combination of the azulene π system with the porphyrin-like macrocyclic framework results in a redox-switchable chromophore system with a potential for electrochromic and molecular conductivity applications.



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19:30 poster II-39

Thermodynamic Parameters $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ as Probes for the Transition State in the Reaction of N-phenyltriazolinedione with Alkenes in Nucleophilic Solvents.

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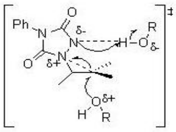
The ene reaction of triazolinediones (TADs), singlet oxygen ($^1O_2$), and nitrosoarene (ArNO) with alkenes bearing allylic hydrogens have attracted much attention over the year from both synthetic and mechanistic points of view. Furthermore, they have recently been reviewed. The reactions proceed via stepwise processes through a three-membered ring intermediate, namely a perepoxide, a diarizinium imide, and an aziridine-N-oxide, as evidence by isotope effect studies. Recently, on the basis of computational results, a biradical intermediate was proposed in the ene reactions of TADs, which was consequently challenged by experimental evidence from stereochemical and stereoisotopic studies. This issue remains open for additional structural studies in the future.

The thermodynamic parameters, $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$, were determined for the interception of an intermediate, with the structural characteristics of an aziridinium imide, by nucleophilic solvents during the reaction of 2-methyl-2-butene with N-phenyltriazolinedione. The experimentally parameters were found to be in favour of an S_N2-'like' transition state and showed strong dependence on the bulkiness of the incoming molecule of the nucleophile solvent.



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19:30 poster II-40

Varying Electronegativity of OH/O$^-$ Groups Depending on the Nature and Strength of H-bonding in Phenol/Phenolate involved in H-bond complexation

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Electronegativity is a frequently used chemical term, describing "the power of an atom in a molecule to attract electrons to itself". Application of the Domenicano et al method of estimating group electronegativity from angular geometry of the ring in monosubstituted benzene derivatives[1] allowed us to find how electronegativity of OH/O$^-$ groups in H-bonded complexes of phenol and phenolate depends on the nature and strength of H-bond. For complexes in which the OH group is only proton donating in the H-bond a linear dependence of the estimated electronegativity on O…O(N) interatomic distance was found for experimental (CSD [2] base retrieved) data. The following rule is observed [3]: the weaker is the H-bond the more electronegative the OH group is. If apart from this kind of interaction the oxygen is proton accepting, then an increase of electronegativity is observed. Modeling (B3LYP/6-311+G**) variation of the strength of H-bond leads to a qualitatively the same picture as the scatter plots for experimental data.

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19:30 poster II-41

Patch-Clamp Study on the Influence of Zinc and Copper Ions on the Activity of Voltage-Gated Potassium Channels Kv1.3

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Potassium channels are integral membrane proteins selectively permeable for potassium ions, which are expressed in all types of cells. The channels are primarily involved in regulation of electrical activity in neurons. Moreover, they are required for many different processes including cell proliferation, volume regulation, apoptosis, insulin sensitivity. The channel activity is modulated by a number of chemical factors, among them are zinc (Zn) and copper ions (Cu). In the present study we applied the electrophysiological technique "patch-clamp" in the "whole-cell" configuration to study the modulatory effect of Zn and Cu on voltage-gated potassium channels Kv1.3 expressed in human lymphocytes. Obtained results provide evidence that both Zn and Cu inhibit the activity of Kv1.3 channels when applied at micromolar concentrations by direct binding to binding sites on the channels. However, the mechanisms of such an inhibition seem to be different. First, because Cu inhibits the channels much more potently than Zn. Second, the binding stoichiometry of Cu and Zn is apparently different from each other. Moreover, the inhibition of Zn is accompanied by a significant shift of voltage-dependence of both activation and inactivation towards positive membrane potentials and by a pronounced slowing of the current activation. In case of Cu-induced inhibition, only a slowing of the current activation was observed. The inhibitory effect of Zn depends on the membrane holding potential and on extracellular potassium concentration - no such dependencies occur in case of the inhibition by Cu. The inhibition by Cu is time-dependent, whereas the Zn-induced inhibition is not. Finally, the inhibitory effects of Cu and Zn are additive. This strongly suggests that the effects occur by different mechanisms. Possible influence of these effects on the function of Kv1.3 channels is discussed.

19:30 poster II-42

Time-Resolved and DFT Study of the Reactions and Mechanisms of M(CO)$_5$ Cyclohexane M=(Cr, Mo, W) with Different Ligands

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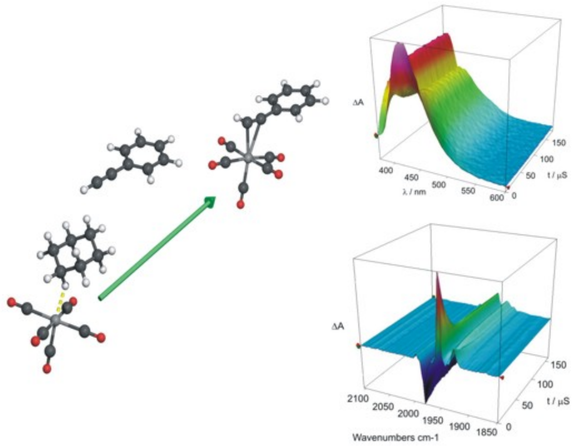
The photolysis of group VIB hexacarbonyl complexes in solution is studied using time-resolved IR and UV techniques. The reactions of the reactive intermediates produced by laser photolysis with small molecules (e.g. N_2, O_2) are investigated both experimentally and by density functional theory. The most probable intermediates are identified by comparison of the calculated IR and UV spectra with the simulated time-resolved spectra of the intermediates. The reaction pathways are calculated and compared to the measured kinetic data. Spectroscopic evidence of a novel weakly bound metal carbonyl-O_2 is presented.



19:30 poster II-43

Photoreactions of 1,8-Anthrylene-ethynylene Acyclic Oligomers

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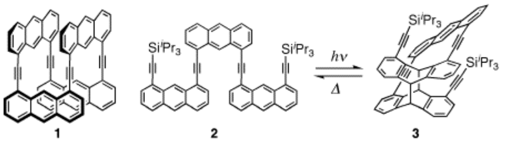
We reported the synthesis of structure of 1,8-anthrylene-ethynylene cyclic tetramer **1**, which featured the diamond prism structure with two pairs of parallel oriented anthracene group [1]. This macrocyclic compound gave no significant products upon UV irradiation because of the structural constrain. Similar photoreactions were carried out with acyclic oligomers to investigate the relation between the conformational mobility and the reactivity.

Trimer **2** was prepared by the Sonogashira coupling between 1,8-diiodoanthracene and singly silylated 1,8-diethynylanthracene. Compound **2** gave a single product Upon UV irradiation (>420 nm) in benzene, where the anthracene groups at the both ends underwent [4+4]photocyclization. Since this product was enantiomerically resolved by chiral HPLC, its structure was established to be the chiral form **3**, which resulted from cyclization in the *anti*-form rather than the *syn*-form. This photo-product was reversibly converted to the original oligomer upon heating it at 180 °C. Details of the reversibly processes, chiroptical properties of enantiopure **3**, and some attempts of photoreactions of an acyclic tetramer will be reported.



[1] S. Toyota, M. Goichi, M. Kotani, Angew. Chem. Int. Ed. 2004, 43, 2248.

19:30 poster II-44

Synthesis and Structures of 1,8-Anthrylene-alkynylene Cyclic Trimers with Strained Frameworks

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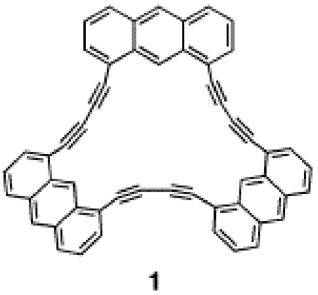
As a new type of π-conjugated oligomers, we synthesized two types of macrocyclic compounds with three 1,8-anthrylene units and acetylene or diacetylene linkers to construct strained frameworks. One is compound **1** with three diacetylene linkers, and the other is compound **2** with one diacetylene and two acetylene linkers, the latter having two isopropyl groups to increase the solubility.

The linear precursors were prepared by the Sonogashira and Eglington coupling reactions, which were then cyclized by the Eglinton coupling to give the desired macrocyclic compounds in 22-34% yield as yellow crystals. X-ray analysis revealed that compound **1** took a nearly C_2 symmetric structure with distorted alkynic carbons (bond angles 166-174°). On the contrary, the ^{1}H NMR signal pattern was symmetric even at -60 °C in CDCl$_3$ because of the facile dynamic processes. The structure of **2** was optimized by the DFT calculation to give a saddle-like structure of C_s symmetry. All bond angles at the sp carbons in **2** are smaller than 170°, and there are significant out-of-plane deformations in the anthracene rings. The ^{13}C NMR signals due to alkynic carbons in these compounds are shifted by 3-8 ppm to the lower field relative to the strain-free cyclic tetramers because of the bending deformations. The UV and fluorescence spectra of these compounds are compared with those of the related oligomers.



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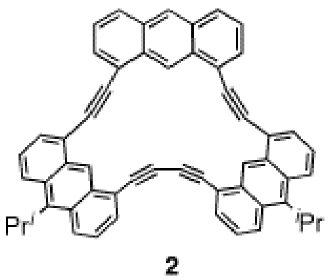

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19:30 poster II-45

Photosolvolysis Mechanism of Phenacyl Mesylate

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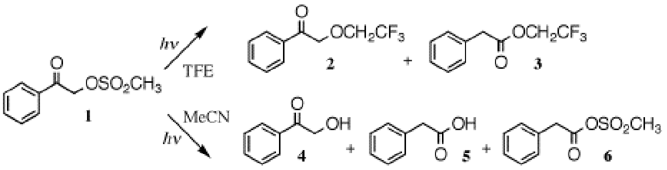
Phenacyl derivatives baring leaving group (L) at its α-position to carbonyl exhibit C-L cleavage upon photoirradiation, followed by neighboring phenyl group migration to result corresponding phenylacetic acid derivatives. The reactions are known as Photo-Favorskii rearrangement, and the reactions of phenacyl compounds including chlorides and phosphates have been studied as synthetic method or photoremoval protecting group. The rearrangements are considered to proceed through some ionic intermediate, since the reactions are favored in polar solvents such as alcoholic or aqueous media, although the existence of reduction products indicates the possibility of the involvement of phenacyl radical intermediate in the mechanism. Thus, the reaction mechanisms are to be subjected to further investigation. To test whether the Photo-Favorskii rearrangement undergoes through an ionic or a radical intermediate, the photosolvolysis of phenacyl mesylate (**1**) were investigated in 2,2,2-trifluoroethanol (TFE) or in acetonitile (MeCN).

The photosolvolysis of **1** in TFE afforded phenacyl trifluoroethyl ether (**2**) and phenylacetic acid trifluoroethyl ester (**3**) in 16.2 and 83.8 % yields, respectively. The former product is derived by the nucleophilic trapping of phenacyl carbocation with solvent, suggesting the photochemical generation of phenacyl carbocation in TFE. The photosolvolysis of **1** in MeCN afforded slight amount (1.4 %) of phenacyl alcohol (**4**) which is formed by the nucleophilic trap of phenacyl carbocation with a trace of water in MeCN. The major products were phenylacetic acid (**5**, 58.8 %), and its methanesulfonyl mixed anhydride (**6**, 33.5 %), which were obtained by the Photo-Favorskii rearrangement, followed by the addition of water or methanesulfonate leaving group.

When 0.01M of N$_3^-$ was added to the photosolvolysis in TFE, the yield of **2** was reduced to 4.8 %, while that of **3** was little affected (84.0 %). The addition of 0.01M (*t*-Bu)$_2$NO as radical trapping reagent, on the other hand, exhibited the considerable decrease in the yield of **3** to 60.5 % and slight decrease in the yield of **2** to 13.2%. The result indicates that the Photo-Favorskii rearrangement proceeds through phenacyl radical intermediate. The effect of added trapping reagent was more remarkable in the photosolvolysis in MeCN, where the addition of (*t*-Bu)$_2$NO completely prohibited the formation of nucleophilic substitution product **4** as well as the Photo-Favorskii rearrangement products **5** and **6**. This remarkable effect of (*t*-Bu)$_2$NO addition indicate that the phenacyl carbocation is formed by the electron transfer within the radical pair generated by the C-L bond homolysis in the photolysis.



19:30 poster II-46

Photoreactivity of β- and γ-Lactams

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Lactam derivatives are among the most important groups of antibiotics. Some of these may undergo photo-initiated reactions, leading to a loss of antibiotic activity or to a modification of their chemical structure [1]. Thus, penicillin derivatives containing a β-lactam structure undergo UV-initiated ring opening of their thiazolidine moiety to yield an imine-thiolate anion. γ-lactams, reported to have substantial antibacterial properties [2], also undergo UV-initiated photodegradation.

We have investigated the mechanisms of the photo-initiated processes for both groups of compounds, *i.e.*: β- and γ-lactams, including the photophysical processes originated from the initially-generated excited states and the photochemical processes leading to the observed photoproducts. The obtained results are presented here.

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19:30 poster II-47

Influence of Transformation of the Amino Group in Anthracyclines into -N=CH-N< or -N=CH-O- Group on Their Biological Properties

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The antitumor drugs of anthracycline group, *e.g.* daunorubicin are widely used in the treatment of variety of human neoplastic diseases. However, their clinical effectiveness is limited mainly by dose-dependent toxicity (particularly cardiotoxicity) and by the increase of resistance of cancer cells.

In the search for new derivatives of anthracyclines of lower toxicity and/or higher cytotoxic activity a series of new analogs in which the amino group bonded to the C-3' carbon atom of the daunosamine moiety was replaced by various -N=CH-N< (amidino) groups [1] or by the oxazoline ring (containing -N=CH-O- group) have been synthesized.

For derivatives of daunorubicin (I-V) their biological properties has been compared to those of the parent drug. It was found that new derivatives display both considerably lower toxicity (the LD_{50} values are 8-21 times higher) and significantly lower cardiotoxicity than those of the parent antibiotic. The cytotoxic activity *in vitro* of amidino derivatives (I-IV) is similar to that of the referential daunorubicin, but for oxazolino derivative (V) is even higher.

Moreover, opposite to daunorubicin, all of them appeared to be able to overcome the barrier of drug resistance of cancer cells. The values of ID_{50} for several sensitive human cancer cell lines and their resistant to anthracyclines sublines are almost identical, whereas these values for the parent drug are 8-650 times higher. The best results were obtained for the oxazolino derivative (V).

These advantageous results indicate that the transformation of the amino group in anthracyclines into amidino group or oxazoline ring appears to be very promising way to find new derivatives, which may be more useful in therapy than the parent daunorubicin on account of their lower toxicity, mainly cardiotoxicity, and an ability to overcome the barrier of drug resistance.

[1] M.Wąsowska, I. Oszczapowicz et al., Anticancer Res. 2005, 25, 2045-2048.

19:30 poster II-48

The Indole-Based Receptors for Anion Recognition

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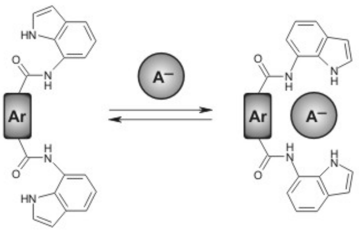
Designing of receptors capable of anion binding by hydrogen bonds continues to be an area of active research. In contrast to many possible hydrogen bond donors, the pyrrole ring does not contain a built-in hydrogen bond acceptor and this unique feature makes the pyrrole moiety an attractive motif in anion recognition [1]. The conjugation with benzene ring leads to increased acidity of the pyrrole *N-H*, hence enhanced anion binding ability. For this reason the incorporation of a benzopyrrole subunit into the anion receptors has become recently a subject of intensive exploration [2]. In this communication we would like to present results of the examination of the indolamine-based receptors.



We prepared aromatic bisamides from indol-7-amine and phenylamine and compared their anion binding properties. The incorporation of the indole moiety into hosts can lead to over five times stronger interaction with anions. The structural analysis of the indole-containing receptors revealed the correlation between their conformational preferences and their affinity towards anions.

[1] J. L. Sessler, S. Camiolo, P. A. Gale, Coord. Chem. Rev. 2003, 240, 17.
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19:30 poster II-49

DFT Studies of Amide-Iminol and Amine-Imine Tautomerism for Cytosine

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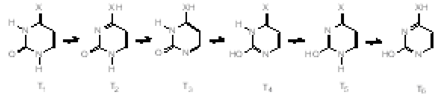
DNA mutations are among the most exciting subject by which many scientists (chemists, biochemists, and biologists) have been attracted during the last 50 years. Although various hypotheses and models were proposed in the literature, the nature and the mechanism of DNA mutations are not quite clear yet. Any changes in the DNA sequence, the key to all genetic information, can generate mutations during the replication or repair processes. Therefore, understanding of DNA mutations is crucial not only to explain but also to predict and consequently to eliminate various diseases affecting human beings.

Prototropic tautomerism (amide-iminol and amine-imine tautomerism in DNA bases) is one of the phenomena responsible for spontaneous point mutations. During tautomeric interconversion, it is sufficient that a proton is transferred from one to the other conjugated site in DNA nitrogen bases that their ability to H-bond formation dramatically changes.

For pyrimidine bases, thymine (X = O) and cytosine (X = NH), their tautomeric preferences seem to be particularly sensitive to various internal and external effects. Since they contain two protons and four functions (two ring nitrogens and two *exo*-groups with heteroatoms), and rotations of the *exo*-groups take place, 13 tautomers-rotamers for thymine and 14 tautomers-rotamers for cytosine may be considered.



To understand how ionization influences tautomeric equilibria and pi-electron delocalization for these pyrimidine bases, in this work quantum-chemical calculations were performed for isolated neutral and ionized tautomeric forms of cytosine using the DFT(B3LYP) method and the 6-311+G(d,p) basis set. Change of tautomeric preferences upon ionization induces the point mutation of DNA.

Acknowledgments. DFT calculations were carried out at the Interdisciplinary Center for Molecular Modeling (ICM, Warsaw).

19:30 poster II-50

Benzylaminoboronic Acids - Synthesis and Characterization

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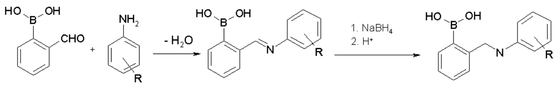
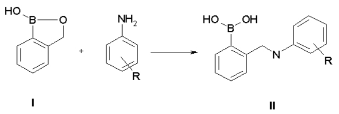
Arylboronic acids with the amino group in ortho position are widely used as carbohydrate receptors [1, 2]. They can be synthesized from o-formylphenylboronic acid by reduction of corresponding Schiff base:



An alternative method is the reaction of benzoxaborole I with amines:



Benzoxaborole I is a stable compound, easy to obtain from o-tolueneboronic acid by bromination and hydrolysis.

The spectroscopic characterization of the products II will be presented.

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[2] J. F. Callan, A. P. de Silva, D. C. Magri, Tetrahedron 2005, 61, 8551.

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Index