

# Abstracts of the 11th Electronic Computational Chemistry Conference

April 2-30, 2007



Robert Q. Topper and Olga Dmitrenko  
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**ECCC 11**  
**THE ELEVENTH COMPUTATIONAL**  
**CHEMISTRY CONFERENCE**  
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**APRIL 2–30, 2007**

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*Cover illustration:* Olga Dmitrenko, **Clever Bird** (2006). Acrylic on canvas panel, 14x11in (36x28cm), private collection, Mariupol, Ukraine. For more information visit <http://www.artabus.com/dmytrenko>.

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## Abstracts of the 11<sup>th</sup> Electronic Computational Chemistry Conference – ECCC11

Robert Q. Topper<sup>1,\*</sup> and Olga Dmitrenko<sup>2</sup>

1. Department of Chemistry, Medical Technology, and Physics, Thomas A. Edison Hall of Science, Monmouth University, West Long Branch NJ 07764-1898 USA E-mail: [rtopper@monmouth.edu](mailto:rtopper@monmouth.edu).
2. Department of Chemistry and Biochemistry, University of Delaware, DE 19716 USA E-mail: [odmitr@udel.edu](mailto:odmitr@udel.edu).

\* Corresponding author. Published June 2008.

The 11<sup>th</sup> Electronic Computational Chemistry Conference, or ECCC11, took place on the Internet throughout the month of April 2007 at <http://eccc.monmouth.edu>. Since its beginnings in November 1994, the ECCC has grown and prospered. It is apparently the longest-running virtual scientific research conference in the world. Another online conference, CONFCHM, began in 1993 and thus predates the ECCC by one year. However, CONFCHM is focused on chemistry education and does not include research. In addition, “the first CONFCHM conference was carried out ...” by means of listserv email, with papers in ASCII text format and GIF graphics being available on a FTP and gopher server.<sup>1</sup> In contrast, the first ECCC made use exclusively of the World Wide Web. At the time the Web was just emerging as a new way for the international community of scientists to share current research. Steven Bachrach (Trinity University) correctly perceived that it was time for a new kind of research-oriented scientific conference that made use of newly emerging online visualization technology, and that was truly international in scope. We have tried to remain true to his original vision.

In the modern era, high-speed access to the Internet is routine and discussion boards, blogs, powerful search engines, and interactive environments are readily available. Given the evolution of things one might think that the ECCC had run its race at last, especially since it is a relatively “low-tech” operation which makes no use of virtual conferencing or other tools one might think essential for an online scientific conference. However, ECCC continues to attract high-quality presentations from around the globe. Following peer review, thirty-six presentations were accepted and presented at ECCC11 from 22 countries or regions: Italy, the Slovak Republic, Taiwan, Egypt, Mauritius, Israel, Austria, India, Poland, Russia, South Korea, Finland, the USA, Mauritius, France, Romania, Croatia, Cuba, Ireland, the UK, Serbia, and Switzerland. There were 246 registered participants in ECCC11.

In recent years the ECCC has enjoyed generous sponsorship by far-seeing companies who are interested in fostering collegial interactions between the members of the

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<sup>1</sup> See <http://www.ched-ccce.org/confchem/past.html> and <http://www.wam.umd.edu/~toh/ChemConference/>. Accessed January 2008.

international community of computational chemists. In particular, we are very grateful to *Scientific Computing and Modeling NV*,<sup>2</sup> *SimBioSys, Inc.*,<sup>3</sup> and *Synergix, Ltd.*<sup>4</sup> for their sponsorship of ECCC11. Their sponsorship allowed the ECCC to recognize two particularly outstanding presentations: “Tunable Hydrogen Bonds and LBHBs” by Timm Lankau and Chin-Hui Yu, and “Quantum-chemical Study on the Mechanism of Irreversible Inhibition of HIV-1 Protease by Epoxide Inhibitors” by Juraj Kóna and Paolo Carloni.

It appears to us that there are several reasons why the ECCC continues to thrive and to remain relevant. First and foremost, the conference is completely **free** (all of the organizers and staff are volunteers). This makes the ECCC accessible to everyone regardless of their nation’s (or personal) economic status. Because it is completely online, even scientists who find it difficult to obtain a visa can participate.

In addition, the conference is **asynchronous**, so as to allow full participation by everyone. No one is at a disadvantage because they happen to be in a time zone shifted by twelve hours from Eastern Standard Time. All authors around the globe can participate equally in the ECCC.

Also, all abstracts are subjected to **rigorous peer review and editorial oversight**. The peer review is steered by a Scientific Organizing Committee (SOC) which bears great responsibility for ensuring that the proposed research is both timely and original. We gratefully recognize the other members of the ECCC11 SOC for their important contributions in this regard: Noah W. Allen (University of North Carolina-Asheville, USA); Thomas R. Cundari (University of North Texas, USA); Walter M. F. Fabian (Karl-Franzens Universität Graz, Austria); John McKelvey, (McKelvey Computational Chemistry, USA); Sudhakar V. Pamidighantam (National Center for Supercomputing Applications, USA); and Jens Spanget-Larsen (Roskilde University, Denmark).

A special **interactive week**, during which all participants must answer questions within 24 hours or risk withdrawal of their abstract, ensures that presenters “stand by their poster.” Finally, the conference is closely **monitored** to ensure that all discussions are relevant to the presentation in question and proper decorum is observed. The members of the SOC helped to monitor the conference and lead the online discussions. These discussions have always been insightful, constructive, and collaborative in their nature. We hope that this will continue for many years to come.

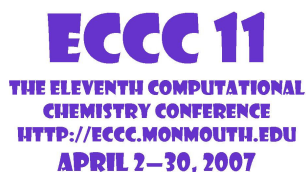
ECCC11 could not have been completed without the hard work of the members of the Scientific Organizing Committee. We are also grateful to Brian Talley and Evelyn Hampton for their assistance in the development, maintenance and monitoring of the ECCC11 website.

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<sup>2</sup> <http://www.scm.com/> .

<sup>3</sup> <http://www.simbiosys.ca> .

<sup>4</sup> <http://www.molecular-conceptor.com> .



## Abstracts of the Eleventh Electronic Computational Chemistry Conference

### ECCC11 Outstanding Research Contribution Award Winner

Award sponsored by SimBioSym and Scientific Computing and Modeling.

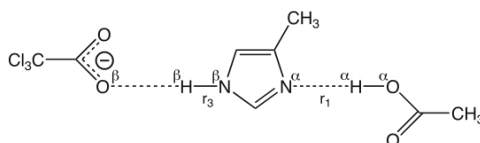
#### 35. Tunable Hydrogen Bonds and LBHBs

Timm Lankau\*, Chin-Hui Yu

Department of Chemistry, National Tsing Hua University, 101 Kuang Fu Road, Section 2, 30013 HsinChu, Taiwan

\* corresponding author: lankau@oxygen.chem.nthu.edu.tw

The proton affinity ( $PA$ ) of the  $[Tca-HMim]^-$  ion (Tca: Trichloroacetic acetate ion, HMim: 4-Methyl-1*H*-imidazole, structure **1**) depends on the position of  $H^\beta$  in the  $\beta$ -hydrogen bond [1].



This property of the  $[Tca-HMim]^-$  ion is caused by a charge transfer from the  $Tca^-$  ion to the imidazole system as  $H^\beta$  moves from  $N^\beta$  to  $O^\beta$  [2] and can be used to tune  $\Delta PA = PA_1 - PA_{Ac^-}$  of the  $\alpha$ -hydrogen bond in the  $[Tca-HMim-HAc]^-$  ion (structure **2**) without changing the interface of the  $\alpha$ -hydrogen bond. Starting from B3LYP/D95+(d,p) calculations, we will use structure **2** to re-examine the  $\Delta PA = 0$  assumption for the formation of low barrier hydrogen bonds (LBHB). The  $\alpha$ -LBHB is formed for  $\Delta PA \neq 0$ , as observed for other hetero-nuclear LBHBs too, which indicates a general weakness of the  $\Delta PA = 0$  postulate. However, the observed linear relationship between  $PA_1$  and the  $\alpha$ -hydrogen bond energy allows us to propose an alternative model for the formation of LBHBs basing on individual hydrogen bonding energies ( $E_{Hbond}$ ) [3]. These calculations show further that an intrinsic hydrogen bond with  $\Delta PA = 0$  can be observed only for one value of the  $N^\alpha O^\alpha$  bond distance ( $d_{N^\alpha O^\alpha}$ ) [4]. The formation of LBHBs has therefore an energetic component ( $E_{Hbond}$ ) as well as a geometric one ( $d_{N^\alpha O^\alpha}$ ), which can be observed only in hetero-nuclear LBHBs with their intrinsic chemical asymmetry. The electronic presentation will be used to review our results and thereby to show the close link between LBHBs and ordinary hydrogen bonds.

[1] T. Lankau, C.-H. Yu Chem. Phys. Lett. 425 (2006) 264-267.

[2] T. Lankau, C.-H. Yu submitted to Phys. Chem. Chem. Phys.

[3] T. Lankau, C.-H. Yu Phys. Chem. Chem. Phys. 9 (2007) 299-310.

[4] T. Lankau, C.-H. Yu Chem. Phys. Lett. 433 (2007) 275-278.

**ECCC11 Outstanding e-Presentation Award Winner**

Award sponsored by SimBioSys and Synergix.

**4. Quantum-chemical Study on the Mechanism of Irreversible Inhibition of HIV-1 Protease by Epoxide Inhibitors**Juraj Kóna,<sup>1,2,\*</sup> and Paolo Carloni<sup>1</sup><sup>1</sup> International School for Advanced Studies (SISSA) and Democritos Modeling Center for Research in Atomistic Simulation (INFM), via Beirut 2-4, 34014 Trieste, Italy<sup>2</sup> Institute of Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-845 38 Bratislava, Slovak Republic

\*Corresponding author. Email: chemkona@savba.sk or kona@sisa.it

Two possible mechanisms of irreversible inhibition of HIV-1 protease by epoxide inhibitors were investigated on an active-site model using ab initio (MP2) and hybrid DFT methods (B3LYP). The calculations predict the inhibition as an acid catalyzed nucleophilic substitution reaction proceeded by a concerted S<sub>N</sub>2 mechanism. A mechanism with a direct proton transfer from the catalytic aspartic dyad onto the epoxide ring shown to be preferred compared to one with the proton transfer from the acid catalyst bridged by a catalytic water. Based on the geometry of a transition state, structural data important for the design of irreversible epoxide inhibitors of HIV-1 protease were defined.

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**Presentations****1. A DFT Study of Antitumor Drugs I. QSAR Study for 2-(4-aminophenyl) Benzothiazoles**Rifaat Hilal<sup>1</sup> and Shabaan. A. K. Elroby<sup>2,\*</sup><sup>1</sup> Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt<sup>2</sup> Department of Chemistry, Faculty of Science, University of Beni-Suef, Beni-Suef, Egypt

\* corresponding author: Sha\_kamel@yahoo.com

Quantitative structure-activity relationships (QSAR) have been established for two sets of the antitumor drugs 2-(4-aminophenyl)benzothiazoles (APBT). Constitutional, geometrical, topological, electronic descriptors (computed at B3LYP/6-31G\*\* level) and some empirical descriptors related to the hypophilicity were computed and analyzed. Multiple regression analysis leads to a set of equations that reflect the weight of each of the studied descriptors. The most relevant of these descriptors were grouped, and a new multiple regressions have been carried out and arrived at the final QSAR models. A validation set of 11 2-(4-aminophenyl)benzothiazoles (APBT) were selected, and their activities were computed using the proposed QSAR model. The correlation between the predicted and observed activities is excellent.

**2. Theoretical Study of the Trans and Gauche Rotamers of 1,2-Dihalogenodisilanes (XSiH<sub>2</sub>SiH<sub>2</sub>X; X=F, Cl, Br, I)**

Ponnadurai Ramasami\*

Department of Chemistry, University of Mauritius, Réduit, Republic of Mauritius.

\*Corresponding author. Email: p.ramasami@uom.ac.mu

1,2-Dihalogenoethanes are known to exist in an equilibrium mixture of two rotational isomers namely the trans and gauche rotamers. 1,2-Dihalogenoethanes have been studied to a large extent theoretically, but the analogous 1,2-dihalogenodisilanes have not been comparably studied. To address this deficiency and in continuation with our work involving conformational analysis of 1,2-disubstituted ethanes, 1,2-dihalogenodisilanes (XSiH<sub>2</sub>SiH<sub>2</sub>X; X=F, Cl, Br, I) have been studied in the gas phase using theoretical methods. The methods used are MP2 and DFT/B3LYP and the basis



set used is 6-311++G(d,p) for all atoms except that 6-311G(d,p) has been used for iodine atom. G2/MP2 calculation has also carried out using the MP2 optimised structure for the title compounds except for 1,2-diiododisilane. All structures have been fully optimised and the optimised geometries, dipole moments, moments of inertia, energies (electronic and zero-point correction) and rotational constants are reported. HOMO-LUMO gap for each rotamer is also reported. The optimised structures have been used for calculations of vibrational frequencies and these frequencies are reported with appropriate assignments. The results indicate that for these 1,2-dihalogenodisilanes, the trans rotamer is more stable than the gauche rotamer and unlike 1,2-difluoroethane, the gauche effect is not observed for the analogous 1,2-difluorodisilane. The energy difference between the trans and gauche rotamers increases with the size of the halogen atom and the MP2 energy differences are 0.85 kJ/mol (X=F), 1.91 kJ/mol (X=Cl), 2.43 kJ/mol (X=Br) and 3.64 kJ/mol (X=I). These energy differences are smaller compared to their analogous 1,2-dihalogenoethanes. The experimental and computational literature for the title compounds are limited and therefore the results of this work will be useful for reference.

### 3. Hydrogen Bonds in Liquid Protonated Water

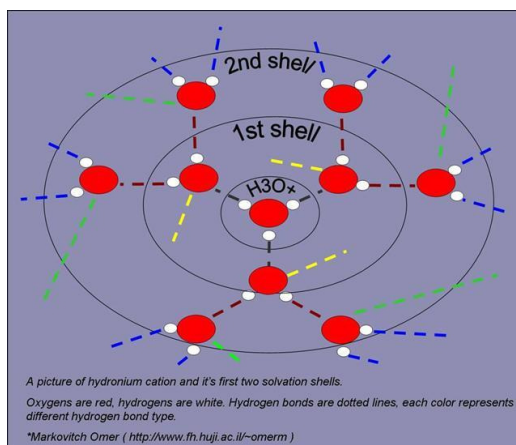
Omer Markovitch\* and Noam Agmon

Department of Physical Chemistry and the Fritz Haber Research Center, The Hebrew University, Jerusalem 91904, Israel

\*Corresponding author: omermar@fh.huji.ac.il or <http://www.fh.huji.ac.il/~omerm>

Hydrogen bonding (*HBond*) for the hydronium and its first two solvation shells have been studied at temperatures ranging from 260K to 330K using second generation MS-EVB<sup>[1]</sup> (multi state empirical valence bond).

We have developed a robust method to determine HBond strengths and employed it to calculate enthalpies and free energies for five types of HBonds formed by water ligands in the first two solvation shells of the  $\text{H}_3\text{O}^+$  ion (figure 1).



The donor type HBonds strengths increase upon approaching the highly charged protonated center, whereas the acceptor type HBonds weakens. In the second solvation shell the bond strengths are already close to those of pure water<sup>[2, 3]</sup>. The innermost HBonds around the  $\text{H}_3\text{O}^+$  are more than twice stronger compared to those of bulk liquid water. This supports Eigen's vision<sup>[4]</sup> that the hydronium cation is better described as  $\text{H}_9\text{O}_4^+$ , which includes  $\text{H}_3\text{O}^+$  and its first solvation shell. We hope to repeat these calculations using DFT methodologies in the near future.

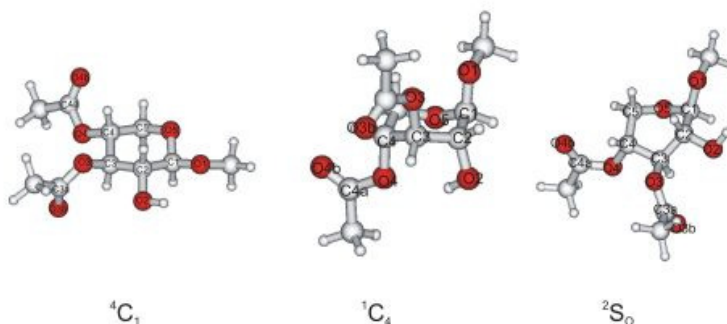
## 5. Computational Study of the Conformational Space of Methyl 3,4-Diacetyl- $\beta$ -D-xylopyranoside: ${}^4C_1$ and ${}^1C_4$ chairs, and Skew-Boats Forms

Sajjad Karamat\* and Walter M.F.Fabian

Institut für Chemie, Karl-Franzens Universität Graz, Heinrichstr: 28, A-8010, Austria

\*Corresponding author: sajjad\_karamat1974@yahoo.com

Ring and substituent rotamers conformations of methyl 3,4-diacetyl- $\beta$ -D-xylopyranoside were studied in the gas phase and in solvents of different polarity ( $\text{CCl}_4$ ,  $\text{CHCl}_3$  and DMSO) by B3LYP density functional theory. The  ${}^4C_1$  chair is the most stable ring form in the gas phase as well as in all solvents, followed by  ${}^1C_4$  and  ${}^2S_0$ . The  ${}^4C_1$  chair is 0.41 and 1.38 kcal/mole ( $\Delta G$ ) lower in energy than  ${}^1C_4$  and  ${}^2S_0$  respectively in the gas phase. The calculated population of ring forms showed significant  ${}^2S_0$  and its population increases with increasing polarity of solvent while reverse is the case for  ${}^4C_1$  and  ${}^1C_4$ . The results proved the importance of free O3-H group for induction of ring flip from  ${}^4C_1$  to  ${}^1C_4$  as in methyl 2, 4-diacetyl- $\beta$ -D-xylopyranoside.



## 6. Novel Applications of Atomic Softness and QSAR Study of Testosterone Derivatives

Srivastava Hemant Kumar\*#, Pasha Farhan Ahmad, Singh Pashupati Prasad

Department of Chemistry M. L. K. (P. G.) College Balrampur, (U. P.), INDIA

Phone- +91-5265-252639, Fax- +91-5263-232708; Email: hemantksri@gmail.com

#Current Address- Department of Medicinal Chemistry and Natural Products, School of Pharmacy, Faculty of Medicine, Ein Kerem Campus, The Hebrew University of Jerusalem, Jerusalem - 91120, ISRAEL.

Klopman atomic softness values  $E_n^+$  at different sites of testosterone derivatives have been evaluated by Klopman equation. Various essential indices of this equation has been calculated by semiempirical PM3 calculations. The testosterone derivatives have been taken from three different sets on the basis of the method used for the measurement of the biological activity. The QSAR study shows that the highest Klopman atomic softness values  $E_n^+$  in combination with quantum chemical descriptors (electrophilicity index, global softness, electronegativity etc.) and the observed biological activity have good relationship also clear from the MLR analysis. The  $r^2$  values are in the range of 0.84 to 0.87 and the predicted activity values are close to observed activity values. On the basis of the QSAR model we can build up theoretical base for demonstrating relative activity of new testosterone derivatives. Klopman atomic softness  $E_n^+$  is applicable for making the qsar models for all three types of biological activities (relative androgenic activity, TeBG affinity and mytrophic to androgenic potency in temporal).



## 7. Calculation of spin-spin coupling across an intramolecular Hydrogen bond O-H...N in nucleotide derivatives.

Marek Doskocz,<sup>1\*</sup> Agnieszka Strupinska,<sup>1</sup> Roman Gancarz,<sup>1</sup> and Szczepan Roszak<sup>2</sup>

<sup>1</sup> Department of Medicinal Chemistry and Microbiology, Faculty of Chemistry Wrocław University of Technology, Wyb. Wyspińskiego 27; 50-370 Wrocław, Poland;

<sup>2</sup> Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, Wyb. Wyspińskiego 27; 50-370 Wrocław, Poland.

\*Corresponding author. Email: marek.doskocz@pwr.wroc.pl

In the last few years NMR techniques have become very popular for hydrogen bonding studies. Analyzing NMR spectra allows one to observe coupling constants across a hydrogen bond ( $^{\text{nh}}J_{\text{XY}}$ ) and can be a very helpful method for analysis of the inter and intramolecular interaction, conformational changes, and preferences for compounds. In 1986 Koole and co. reported in the paper "Intramolecular Base-Backbone Association in 8-Bromo-2',3'-O-isopropylideneadenosine on detection of an O(5')-H...N(3) Hydrogen Bond via a Long Range H(5'')-N(3) Spin-Spin Coupling" (J. Am. Chem. Com, 1986, 362). We have calculated NMR parameters chemical shifts for two diastereotopic protons (H5', H5'') and couplings ( $^4J_{\text{NH}}$ ,  $^3J_{\text{NC}}$ ,  $^2J_{\text{NO}}$ ,  $^1J_{\text{NH}}$ ) for this system. Our calculations were done are in good agreement with the predicted coupling and explain observable data. In our calculations we have used DFT methods such as B3LYP and B3PW91 with 6-31G(d,p) and modified IGLO II basis sets. Calculations were performed in solvents: chloroform, benzene, acetonitrile and DMSO (applying the PCM model).

## 8. Systematic Structure-Property Investigation and Ability to Electropolymerization Theoretical Studies of N-alkyl-3,6-bis(2-thiophene)carbazole and N-alkyl-N,N-bis(4-(2-thiophene)phenyl)amine

Krzysztof Idzik<sup>a</sup>, Jacek Doskocz<sup>a\*</sup>, Szczepan Roszak<sup>a</sup>, Jadwiga Soloduch<sup>a</sup>, Sylwia Golba<sup>b</sup>, Mieczysław Lapkowski<sup>b</sup>

<sup>a</sup>Department of Chemistry, Wrocław University of Technology, Wyb. Wyspińskiego 27, 50-370 Wrocław, Poland;

<sup>b</sup>Department of Chemistry, Silesian University of Technology, Strzody 9, 44-100 Gliwice, Poland

\*Corresponding author: jacek.doskocz(et)pwr.wroc.pl

Polymers containing carbazole and aniline moieties in the main chain or side chain have attracted attention because of their unique properties which allow various photonic applications such as photoconductivity, electroluminescence, and photorefractivity of materials. To control the electronic properties of such type of polymers one may introduce thiophene electron-rich heterocycle at the terminal polymerization sites. The differences between HOMO-LUMO gaps, vertical ionization potentials, and distribution of total atomic spin densities of radical cations of the studied molecules could indicate the expected electropolymerization properties. The electronic states of derivatives of these carbazoles and fluorenes were elucidated by molecular orbital calculations using the DFT utilizing B3LYP and the 6-311G(d,p) basis set. The reactivity for coupling reaction of thiophene derivatives are inferred from calculated unpaired electron spin densities of the respective radical cations, and ionization potentials which correspond to energies for generating radical cations during oxidative processes. Structures, electron ionization and excitation energies, and electron density distribution are studied for *N*-alkyl-3,6-bis(2-thiophene)carbazoles, and *N*-alkyl-*N,N*-bis(4-(2-thiophene)phenyl)amine derivatives. The calculated properties of the molecules directly or indirectly mimic molecular parameters that are important for the design of processes of polymerization or for modeling the final polymer. [J.Phys.Chem.A, **2006**, 110, 13989]

## 9. Theoretical Study and Potential Applications in Nanotechnology of New Symmetric Bis-pyridines Containing in Central Part Fluorene, Phenothiazine and Carbazole

Jacek Doskocz<sup>\*a</sup>, Joanna Cabaj<sup>a</sup>, Jadwiga Soloducho<sup>a</sup>, Anna Nowakowska<sup>a</sup>, Krystyna Palewska<sup>b</sup>, Szczepan Roszak<sup>b</sup>

<sup>a</sup>Department of Chemistry, Faculty of Medicinal Chemistry and Microbiology, Wrocław University of Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland

<sup>b</sup>Department of Chemistry, Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland

\*Corresponding author: jacek.doskocz@pwr.wroc.pl

Herein we report a theoretical study of symmetric bis-pyridine aryl derivatives, which are useful to design new type of materials. We also describe synthesis and physical properties (ability of aggregations, electronic absorption spectra, luminescence and redox properties) of novel compounds *N*-alkyl-3,6-bis(2-pyridyne)carbazole, 9,9'-dialkyl-2,7-bis(2-pyridine)fluorene, *N*-alkyl-3,7-bis(2-pyridine)phenothiazine, structures which may be used to build electroconducting LB layers based on hole flow, hydrogen bonding or metal-ligand coordination. The new synthesized structures have chromophore and luminescence character and could find potential applications in opto-devices and sensors. We made use of DFT methods (B3LYP/6-311(d,p), B3LYP/6-311+(d,p)) and ZINDO in this study.

## 10. Theoretical Study of the Long – Range Coupling Constant $^nJ_{PX}$ ( $n = 3 - 9$ , $X=C,H,P$ ) in Selected Phosphorus Compounds

Dawid Gaszowski<sup>\*</sup>, Marek Doskocz<sup>\*</sup>, Roman Gancarz

Department of Medicinal Chemistry and Microbiology, Faculty of Chemistry Wrocław University of Technology, Wyb. Wyspiańskiego 27; 50-370 Wrocław, Poland

\*Corresponding authors. Email: dgaszowski@gmail.com and doskocz@ccmis.us

Phosphorus Nuclear Magnetic Resonance ( $^{31}\text{P}$ NMR) is playing an ever-increasing role in structural characterization and qualitative identification of different phosphorus compounds. One of the most basic parameters, besides the chemical shift, are coupling constants, which supply information about the geometry and dynamics of individual moieties in the molecule, such like nuclei – nuclei motions data, leading in consequence to the knowledge about conformation of the molecule. Couplings through more than three bonds are called "long range". Sometimes couplings through up to nine bonds are observable. In some other cases, long range couplings through covalent bonds don't occur at all, but instead couplings across hydrogen bonds are being observed. The analysis of such data provide information about three dimensional features of the studied molecule as well as intermolecular interactions. We have been analysing long range couplings in model organic phosphorus compounds, such like hydrogen dialkylphosphonate (dimethyl, diethyl and diphenyl phosphonates), phosphoramidates and some phosphorus cations described by Griffin and co., and Gholivand and co. Our goal was to find out the theoretical method which can give us a possibility to appoint long range coupling constants with reasonable computational effort and satisfactory results. Several basis on DFT (B3LYP, B3PW91) and MP2 levels of theory was used in order to optimize and calculate NMR parameters. Calculation in the gas phase and using PCM model solvent has been applied. Obtained results have been verified with experimental data.

## 12. Quantum-chemical calculations of isomeric aza-styrylnaphthalenes in the ground and lowest singlet excited state

Mikhayl F. Budyka\* and Ilia V. Oshkin

Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Russia

\*Corresponding author. E-mail: budyka@icp.ac.ru

Structures of 1-styrylnaphthalene (1SN) and its aza-derivatives: 1-styrylisoquinoline (1SiQ), 4- and 8-styrylquinolines (4SQ and 8SQ) in neutral and protonated forms are calculated by semiempirical (PM3), and DFT (B3LYP/6-31G\*) methods. In the ground ( $S_0$ ) state, DFT predicts 1SN and neutral 4SQ to be non-planar, whereas in the protonated form all aza-styrylnaphthalenes become non-planar, with styryl group rotated out of the plane of aromatic nucleus by 14 - 38 degrees. The lowest singlet excited ( $S_1$ ) states are calculated by PM3-CI method (18 electrons, 13 orbitals, 1200 configurations). It is found that in the neutral form all the compounds have near similar adiabatic excitation energies ( $E_{ad}$ ) within 61 - 64 kcal/mol. However, in protonated form, the adiabatic excitation energies for aza-styrylnaphthalenes differ markedly:  $E_{ad}$  is equal to 48, 45 and 33 kcal/mol for 1SiQH<sup>+</sup>, 4SQH<sup>+</sup> and 8SQH<sup>+</sup>, respectively. In terms of the photoisomerization mechanism "through perpendicular conformer", the reduction of adiabatic excitation energy, i.e. the  $S_1$  level lowering, can result in an increase of the reaction barrier for trans  $\rightarrow$  perp twisting in the  $S_1$  state. Thus, the calculations can qualitatively explain "charge effect" observed in the reaction of trans  $\rightarrow$  cis photoisomerization of aza-styrylnaphthalenes: the quantum yield of the reaction remains nearly the same for 4SQ and reduces by about two orders of magnitude for 8SQ on going from the neutral form to the protonated one.

## 13. DFT Analysis and 3D QSAR Study of Anti-HIV HEPT Analogues

Farhan Ahmad Pasha\*, Muhammad Muddassar, Seung Joo Cho

Biochemical Research Center, Korea Institute of Science and Technology Seoul, South Korea.

\* Corresponding author. Email: fpasha@rediffmail.com

The series of HEPT analogues along with anti-HIV activities have been taken and QSAR models have been made on the basis of semi empirical AM1, DFT and 3D (CoMFA, CoMSIA) methods. The AM1 based two models has been made with MLR analyses. The value of  $r^2=0.66$ ,  $r^2_{cv}=0.60$  and  $r^2=0.69$ ,  $r^2_{cv}=0.61$  for first and second model respectively while the DFT based model was successful and have the values of  $r^2=0.70$ ,  $r^2_{cv}=0.62$ . The CoMFA and CoMSIA models of same series have also been made with PLS analyses. The CoMFA analyses significantly have the values of  $r^2=0.98$ ,  $q^2=0.87$  with both kind of fields while for CoMSIA analyses the values were  $r^2=0.87$  and  $q^2=0.76$  with steric field. The semiempirical and DFT analyses were carried out using Gaussian03, while CoMFA and CoMSIA studies were performed on Sybyl 7.3.

## 15. Anharmonic vibrational calculations on noble-gas-containing methyl halides

Jan Lundell<sup>1,\*</sup>, Arik Cohen<sup>2</sup>, R.Benny Gerber<sup>2,3</sup>

1 Department of Chemistry, University of Helsinki, P.O.Box 55 (A.I.Virtasen aukio 1), FIN-00014 University of Helsinki, Finland

2 Department of Physical Chemistry, Hebrew University, Jerusalem 91904, Israel

3 Department of Chemistry, University of California, Irvine, California 92697-2025, USA

\* Corresponding author; email: jan.lundell@helsinki.fi

In recent years a renaissance in noble gas chemistry has taken place. The chemistry of carbon-xenon compounds is one of the newest aspects of organoelement chemistry. The number of known Xe-C compounds is still limited but these molecules are considered as potentially efficient precursors in synthetic organic chemistry.

Here, quantum chemical calculations have been performed on novel compounds that may expand the scope of noble gas chemistry. These molecules are insertion compounds of various noble gas atoms into methyl halides. The xenon-compounds form the most stable group of these molecules but a few species containing krypton and argon are predicted to be stable as well. In order to facilitate the experimental detection of such species, also their infrared spectra have been computed. The harmonic vibrational calculations are supplemented with anharmonic vibrational calculations based on the CC-VSCF method. This allows us to predict the overtones and combination transitions in addition to the fundamental ones.

## **16. Computational chemistry emerging as a novel stronghold in research-based chemistry education**

Jan Lundell<sup>1,\*</sup> and Maija Aksela<sup>1</sup>

<sup>1</sup> Department of Chemistry, University of Helsinki, P.O.Box 55 (A.I.Virtasen aukio 1), FIN-00014 University of Helsinki, Finland

\* Corresponding author; email: jan.lundell@helsinki.fi

Computational chemistry is the fastest evolving discipline in chemistry. Traditionally chemistry has been considered as an experimental subject but due to the vast growth and development in computer technology, the computer-based approaches are becoming more widely adapted in research and education.

At the Department of Chemistry, University of Helsinki, a special modelling and visualisation course for chemistry educators has been developed. The course originates from the new educational programme introduced in Finnish secondary and high schools by the National Board of Education. The course introduces computational chemistry and computer-assisted visualisation as a modern research and educational tool to enlighten important topics and concepts within the scientific discipline. The topics considered during the course are, for example, energy, stereochemistry, chemical bonding and chemical reactions – all concepts and phenomena appearing in the new educational programme but being traditionally considered very difficult and complex subjects even at university-level chemistry education. The computational methods used are based on modern state-of-the-art computational chemistry research approaches but they are applied with strong educational bias. The course involves interactive lectures, hands-on sessions in the computer laboratory and practical exercises to demonstrate the power and applicability of the approaches acquainted with. Chemistry education research is adapted during the course in order to understand the "effectiveness" of modelling and visualisation in teaching.

Our goal is to give chemistry educators a first hand experience and training to use computational chemistry methods as well as ICT (information and communication technologies) in studying, teaching and understanding chemistry. The course and all its ideas originate from longstanding excellence in computer-assisted chemistry research. Now this knowledge is emerging in chemistry education as a standard educational tool with a strong emphasis of more efficient and more comprehensive understanding of chemistry. The "computational chemistry in chemistry education" course represents a synthesis of high-level scientific research and wide educational experience, which will modernise chemical education on every national and international educational frontier.

## 17. Quantum Chemical Calculations of HCOOH...Xe Complexes

Mia Melavuori<sup>\*,1</sup> and Jan Lundell<sup>1</sup>

<sup>1</sup> Department of Chemistry, University of Helsinki, P.O. Box 55, (A.I. Virtasen aukio 1), FIN-00014 University of Helsinki, Finland

\*Corresponding author. Email: mia.saarelainen@helsinki.fi

Quantum chemical calculations have been applied to study complexes between xenon and formic acid. The goal is to understand perturbations of the chemical properties of the complex subunits upon interaction. Equilibrium structures and vibrational spectra of the 1:1 van der Waals complex between formic acid and xenon have been computed on various computational levels. The binding properties of the complex are studied especially at the MP2 and CCSD(T) levels of theory, and the effect of BSSE on the intermolecular potential energy surface is assessed. The matrix effect of xenon on trapped formic acid molecule was mimicked by calculations with increased number of xenon atoms present. The present results of HCOOH...Xe and HCOOH@Xe clusters are compared with previous studies on lighter noble gases [1-3]. Finally, insights on the use of the computed data of the van der Waals complex for more extensive computational simulations of formic acid in solid xenon are considered.

## 18. Computational Analysis of Goodpasture Syndrome Associated Human alpha 3 type IV Collagen Proteins and Collagen Binding Proteins

K. Sivakumar<sup>\*1</sup>, S. Balaji<sup>1</sup> and Ganga Radhakrishnan<sup>2</sup>

<sup>1</sup>Department of Chemistry, Sri Chandrasekharendra Saraswathi Viswa MahaVidyalaya (Deemed University), Enathur, Kanchipuram – 631 561, Tamilnadu, INDIA

<sup>2</sup>EXCEL and Polymer Science Labs, Central Leather Research Institute, Adyar, Chennai – 600 020, Tamilnadu, INDIA

\*Corresponding author: shivamk25@yahoo.co.in

The aim of this study is to analyze, characterize and provide more detailed description of some selected Goodpasture syndrome (GP) associated human collagen proteins retrieved from RefSeq database. Primary structure analysis shows that GP syndrome associated human alpha 3 type IV collagen proteins consists of equal amount of polar and non-polar residues. The low hydrophobicity of GP syndrome associated human alpha 3 type IV collagen binding proteins [Accession No. NP\_112729.1 and NP\_005704.1] are due to the less content (42%) of non-polar residues. The aliphatic index computed by ExPasy's ProtParam infers that GP syndrome associated collagens may become unstable at high temperature. ExPasy's ProtParam classifies all collagen proteins as stable and collagen binding proteins as unstable on the basis of instability index. The computed pI value indicates that all the collagen proteins are basic and the collagen binding proteins are acidic in nature. The number of basic and acidic amino acids in each collagens correlates well with the corresponding pI computed. Secondary structure analysis shows that all GP syndrome associated proteins are found to be having predominant coil structure content. The SSCP server classifies the GP syndrome associated collagen binding proteins as mixed secondary structure class and the other collagens as irregular secondary structure class. The irregular structure of collagen proteins is due to the rich content of more flexible glycine and hydrophobic proline amino acids. SOSUI server predicts one transmembrane region in all the collagen proteins. The predicted transmembrane region (PRPQVLLLPLLLVLLAAAPAASK) is similar in all collagen proteins. The transmembrane region is visualized and analyzed using helical wheel plots generated by EMBOSS pepwheel tool. The transmembrane region is found to have more hydrophobic residues and it is well documented by the Kyte and Doolittle mean hydrophobicity profile.

## 19. A Density Functional Theory Study of CO Adsorption on Cu(I)-ZSM-5

Xiaobo Zheng

Department of Chemical Engineering, University of California, Berkeley, CA 94720-1462; phone: (510) 643-3535  
Email: xiaobo@berkeley.edu

The coordination and local geometry of  $\text{Cu}^+$  cations in Cu(I)-ZSM-5 and the adsorption of CO to such cations were explored using density functional theory. A thorough examination was made of the effects of placing  $\text{Cu}^+$  in each of the cation-exchange sites available in the MFI lattice, the location of the Al atom in the site, and the number of Al atoms in the site.  $\text{Cu}^+$  cations in I2 exchange sites, located at the edge of the main and sinusoidal channels, are coordinated to two framework O atoms before and after CO adsorption. The calculated adsorption energy for CO adsorbed on such cations lies between 30 and 33 kcal/mol and the C-O vibrational frequency lies between 2150 and 2158  $\text{cm}^{-1}$ .  $\text{Cu}^+$  associated with five- or six-membered rings, i.e., M5, M6, Z5, and Z6 exchange sites, located in the main and sinusoidal channels of the zeolite, are three-fold coordinated to framework O atoms but the coordination number can decrease to two upon CO adsorption. The calculated CO adsorption energy of  $\text{Cu}^+$  in such sites is in the range of 25 to 28 kcal/mol.  $\text{Cu}^+$  cations located in the basket structures formed by two fused five-membered rings, in M7 sites, bind CO with calculated adsorption energy of 21 kcal/mol. The results of this study indicate that the presence of  $\text{Cu}^+$  cation in different exchange sites cannot be identified based upon infrared spectra of adsorbed CO and would be difficult to identify by temperature-programmed desorption of adsorbed CO. Evidence for two types of  $\text{Cu}^+$  coordination can be obtained, though, from Cu K-edge EXAFS. It is also shown that changes in  $\text{Cu}^+$  coordination occurring upon CO adsorption can be observed by Cu K-edge XANES.

## 20. Density Functional Theory Study of Furfuraldehyde, Thiofurfuraldehyde and Selenofurfuraldehyde

Ashish Hatchootah and Ponnadurai Ramasami\*

Department of Chemistry, University of Mauritius, Réduit, Republic of Mauritius. Fax: 00 230 465 6928; Tel: 00 230 454 1041

\*Corresponding author. Email: p.ramasami@uom.ac.mu

Furfuraldehyde is known to exist in the gas phase as the cis and trans forms with the trans form being more stable. The experimental energy difference between these two forms has converged to 3.40 kJ/mol. The energy difference has also been obtained by theoretical method and it is reported to be 3.89 kJ/mol [B3LYP/6-31+G(d)]. However the sulphur and selenium analogues of furfuraldehyde have not been comparably studied neither at experimental nor theoretical levels although there are increasing possibilities for the synthesis of these analogues. In order to address this deficiency, this work explores the cis and trans forms of furfuraldehyde, thiofurfuraldehyde and selenofurfuraldehyde using density functional theory calculations. Their transition states have also been explored. All calculations have been done at the B3LYP/6-311++G(d,p) level using Gaussian 03W. The optimised structures of cis, trans and transition state are reported. The frequencies of these structures are also reported with appropriate assignments. The energy difference between the cis and trans forms, associated barriers and thermodynamical parameters have been derived from the calculations. It is found that the trans form is more stable and energy differences between the two forms are furfuraldehyde (3.10 kJ/mol), thiofurfuraldehyde (2.96 kJ/mol), and selenofurfuraldehyde (2.76 kJ/mol). The rotational barriers between the cis or trans form and transition state are larger than the energy difference. Since the literature of these compounds is limited



particularly for the sulphur and selenium analogues, data from this work will be useful for reference.

## 24. Tautomerism and Aromaticity of Selected Ligands From Kojic Acid Family

Krzysztof Zborowski<sup>1</sup>, Anna Korenova<sup>2</sup>, Michal Uher<sup>2</sup> and Leonard M. Proniewicz<sup>1,3</sup>

<sup>1</sup> Faculty of Chemistry, Jagiellonian University, 3 Ingardena Str., 30-060 Krakow, Poland

<sup>2</sup> Department of Organic Chemistry, Faculty of Chemical Technology, Slovak Technical University, 9 Radlinského Str. 812-37 Bratislava, Slovakia

<sup>3</sup> Regional Laboratory of Physicochemical Analysis and Structural Research, Jagiellonian University, 3 Ingardena Str., 30-060 Krakow, Poland

\*Corresponding author. Email: zborowsk@chemia.uj.edu.pl

Three important members of the kojic acid family have been theoretically studied, namely: kojic acid, chlorokojic acid and azidokojic acid. These compounds are important thanks to their antibacterial, fungicidal, herbicidal and growth regulatory properties. They are also widely used in coordination chemistry. Researches have been focused on tautomeric equilibria (that are present in neutral but also in protonated species of studied compounds) and aromatic properties (heteroaromaticity and quasiaromaticity of kojic acids seems to be important for stability of their metalcomplexes). Determination of the most stable tautomers has been based on calculated tautomers energies and tautomeric equilibrium constants. Computations were performed for all possible structures of compounds under investigation using the B3LYP/6-311++G(d,p) method. Tautomeric equilibrium constants among the most stable tautomers were then calculated using estimated free energy values. Our calculations clearly show, that for neutral molecules enolic form is strongly preferred. On the other hand, the cationic species are formed by protonation of the keto oxygen atom. The most stable tautomeric structures of kojic acids are the same as previously observed for other hydroxypyrones like pyromeconic acid, maltol and ethylmaltol. Equilibrium geometries of kojic acid, chlorokojic acid and azidokojic acid anions were also determined. Heteroaromaticity (in the pyran ring) and quasiaromaticity/electron delocalisation (in the OCCO group involved in metal binding) was investigated in neutral, anionic and cationic forms of studied compounds at the same level of theory. Aromatic properties have been studied by several aromaticity indices, like: HOMA, EN, GEO, NICS(0), NICS(1) and NICS(1)zz. Differences in the aromaticity level (both neutral and charged forms) between studied kojic acids and other hydroxypyrones are negligible. Relative aromaticity/ $\delta$ -electron delocalisation order determined previously for pyromeconic acid, maltol and ethylmaltol (anions < neutral molecules < cations) is valid also in the kojic acid family. It is the same for pyran rings and the OCCO group. Electron delocalization in the pyran ring of studied ligands seems to be slightly higher than in the OCCO group.

## 25. Theoretical Study on Sulphur Derivatives of Maltol.

Krzysztof Bolechala<sup>1</sup>, Krzysztof Zborowski<sup>1</sup>, Grzegorz Zuchowski<sup>2</sup> and Leonard M. Proniewicz<sup>1,2</sup>.

<sup>1</sup> Faculty of Chemistry, Jagiellonian University, 3 Ingardena Str., 30-060 Krakow, Poland

<sup>2</sup> Department of Organic Chemistry, Medical College, Jagiellonian University, 9 Medyczna Str., 30-688 Krakow, Poland.

<sup>3</sup> Regional Laboratory of Physicochemical Analysis and Structural Research, Jagiellonian University, 3 Ingardena Str., 30-060 Krakow, Poland.

\* Corresponding author. Email: zborowsk@chemia.uj.edu.pl

Replacement of oxygen by sulphur in maltol generates a family of new very interesting ligands - thiohydroxypyrones. In this work theoretical calculations have been performed for all seven maltol derivatives created by consecutive substitution

of oxygen atoms by sulphur. The research are focused on molecular properties of thioligands that are important for their destination – formation of new metal complexes useful in medicinal and environmental chemistry. Geometrical, energetic, tautomeric, aromatic and charge distribution data are reported and the results are compared with maltol properties. It is shown, that the most stable tautomer (like in maltol) for all thio derivatives is that which has the keto-enol group. The protonation in cations occurs always on the oxygen from the keto group. The research has been carried out with the aid of some aromaticity indices, like: HOMA, NICS and ASE. Aromaticity is studied in the heterocyclic pyran ring and in the XCCX part (where X – oxygen or sulphur). All calculations were executed on the B1LYP/6-311++G(d,p) level of theory. It is concluded that the aromaticity order determined previously for maltol (cation > neutral molecule > anion) is also true for thiohydroxypyrones. Among all studied compounds, the most interesting one is the monosubstituted thiohydroxypyrene with sulphur in the heterocyclic ring. This compound is probably able to form more stable metal complexes than maltol. The final aim of this study was encourage the experimental chemist to synthetizing all presented compounds and studying their properties.

## **26. A Conceptual DFT Study of N-amino and Hydrazino Peptides : Assesment of the Nucleophilicity of the Nitrogen Atoms By Means of the Dual Descriptor $\Delta f(r)$ .**

Alexandre Hocquet<sup>1\*</sup>, Christophe Morell<sup>2</sup>

<sup>1</sup> LCPM, ENSIC, BP451, 54000 Nancy, France

<sup>2</sup> CEA/DRFMC/LCIB/ (FRE2600), 38054 Grenoble, France.

\* corresponding author : alexandre.hocquet@ensic.inpl-nancy.fr

N-amino and hydrazino peptides are pseudopeptides molecules containing a N-N bond. To understand the compared reactivity as a nucleophile of the two nitrogen atoms included in this moiety with respect to the surrounding rest of the molecule, a conceptual DFT study is carried on with the analysis of the dual descriptor  $\Delta f(r)$  in a series of molecules, at the B3LYP/6-31G(d,p) level. The dual descriptor is a tool based on the principle of maximal hardness within the framework of conceptual DFT which characterizes the nucleophilic and electrophilic areas within a molecule.

## **28. The Triple Catalytic Power of the Active Site of the CcrA Metallo- $\beta$ - Lactamase**

Anastassia N. Alexandrova

Department of Chemistry, Yale University, 225Prospect Street, New Haven, CT 06520,USA

Hydrolysis of  $\beta$ -lactam, as a model of  $\beta$ -lactam antibiotics, at the active site of the CcrA metallo- $\beta$ -lactamase from *Bacteroides fragilis* has been studied via QM/MM Monte Carlo simulations in the context of Free Energy Perturbation method in explicit solvent. The two Zn-centers of the active site, their immediate residues, and the substrate were treated using the semiempirical PM3 QM method, whereas the OPLS-AA force field was employed for the rest of the system. The binding mode of antibiotics to the active site has been elucidated. Various reaction mechanisms have been considered, activation barriers have been computed, and the preferred reaction pathway has been found. The chemical bonding analysis of the bound CcrA- $\beta$ -lactam complex shed light on the mechanistic preference, and revealed the triple catalytic power of the CcrA active site.

### 29. Data Mining on Structure-Activity/Property Relationships Models

Sorana Daniela BOLBOACA (\*) & Lorentz JÄNTSCHI

"Iuliu Hatieganu" University of Medicine and Pharmacy, 13 Emil Isac, Cluj-Napoca, 400023, Romania, <http://sorana.academicdirect.ro>; and Technical University of Cluj-Napoca, 15 Constantin Daicoviciu, Cluj-Napoca, 400020, Romania, <http://lori.academicdirect.org>

\* Corresponding author: [sbolboaca@umfcluj.ro](mailto:sbolboaca@umfcluj.ro)

Molecular descriptors family on structure-activity/property relationships studies were carried out in order to identify the link between compounds structure and their activity/property. A number of fifty-five classes of properties or activities of different compounds sets were investigated. Single and multi-varied linear regression models using molecular descriptors as variables were identified. The models with estimation and prediction abilities and associated characteristics were stored into a database. A data mining analysis using classification and clustering were applied on the obtained database for searching and extracting useful information. The methodology applied in searching and extracting for information and the obtained results are presented.

### 30. Proton Affinities of Dehydroporphyrin and Subporphyrin in Ground and Excited States Obtained by High Level Computations

Zoran Glasovac, Mario Vazdar, Mirjana Eckert-Maksic and Davor Margetic\*

Laboratory for Physical Organic Chemistry, Department of Organic Chemistry and Biochemistry, Rudjer Boskovic Institute, Bijenicka cesta 54, 10000 Zagreb, Croatia

**Keywords:** DFT, NICS, TDDFT, proton affinity, basicity

High level computations have been employed for design of novel 'super-bases' containing dehydropyrrole moiety, which was incorporated in the large polycyclic structures such as porphyrin and subporphyrin. The basicity of porphyrin derivatives such as dedihydroporphyrin (P), dehydroporphyrin (HP) and dehydrosbporphyrin (P2) was studied in ground and excited states. Ground state total energies and proton affinities were obtained at HF/6-31G\* and MP2 levels, while vertical excitation energies and excited state gas phase proton affinities were obtained by TDDFT/B3LYP/6-31G\*\*//HF/6-31G\* method. Furthermore, aromaticity of these species was estimated by means of NICS values at the GIAO/B3LYP/6-311+G\*\*//HF/6-31G\* level. Basicities of porphyrin H2P and its subporphyrin analogue P2 indicate the importance of multiple nitrogen lone-pair coordination on acid/base properties of the molecules. There is a significant lp-lp interaction in P and stabilization of its protonated form. Planarization of the protonated structure leads to the complete reversal of the pi-electron ring currents indicating aromaticity of the protonated form. P2 does not show significantly higher basicity than H2P what is due to smaller ring size that forces non-planar geometry.

### 31. Computational Study of Pyrrolo-Guanidines

Davor Margetic\* and Pavle Troselj

Laboratory for Physical-Organic Chemistry, Division of Organic Chemistry and Biochemistry, Rudjer Boskovic Institute, 10001 Zagreb, Croatia, e-mail: [margetid@emma.irb.hr](mailto:margetid@emma.irb.hr)

\*Corresponding author. Email: [margetid@emma.irb.hr](mailto:margetid@emma.irb.hr)

A series of novel pyrrolo-guanidinobenzenes possessing guanidine moiety was investigated computationally employing HF and DFT methods. These results were compared to variously substituted pyrroles. The influence of guanidine substituents on the cycloaddition reactivity of pyrroles was investigated in ground and transition state at the B3LYP/6-31G\* level. Model Diels-Alder reaction of pyrrologuanidines with ethylene was studied and activation barriers estimated. Furthermore, the basicities of novel compounds were also evaluated and correlations with cycloaddition reactivity established.

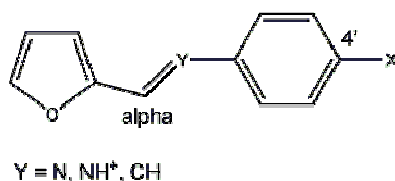
### 32. Conformational and NMR study of some furfural derivatives by DFT methods

David Santos, Reynier Suardiaz, Rachel Crespo, Leandro Gonzalez, Carlos Pérez\*

Dpto. de Química Física, Facultad de Química, Universidad de la Habana, La Habana 10400, Cuba.

\*Corresponding author. Email: cp@fq.uh.cu

Rotational barriers of benzene ring were calculated for 4'-substituted neutral/protonated furfurylidenanilines (FA, Y = N, NH<sup>+</sup>) and cis/trans styrylfuranes (SF, Y = CH) by DFT methods (B3LYP/6-31G(d,p)) and the corresponding equilibrium geometries were identified. 4'-substituted neutral FA have equilibrium dihedral angle values sensitive to the substituent. An NBO and AIM analysis related to these barriers were performed.



<sup>1</sup>H and <sup>13</sup>C substituent induced shifts were calculated (B3LYP/6-311G(d,p)) from shielding tensors and compared with experimental ones. The experimental trends in the induced shifts of these compounds are well reproduced by the calculations. Differences in Mulliken charges were correlated with <sup>1</sup>H and <sup>13</sup>C experimental chemical shifts differences. The experimental trends in the chemical shifts are well reproduced by charge differences. Only the alpha hydrogen in neutral FA shifts does not correlate with charge, reflecting the variable effect of the anisotropy term due to the benzene ring. Protonation of FA removes this variability.

### 38. Density Functional Study of Acrylamide and Glycidamide Adducts of DNA

Kaliappan Muthukumar<sup>1\*</sup>, Perumal Gurusamy<sup>2</sup>, Chandran Karunakaran<sup>3</sup>,

<sup>1</sup> University College Cork, Ireland

<sup>2</sup> Sri. Ramasamy Naidu Memorial College, Sattur, India

<sup>3</sup> VHNSN College, Virudhunagar, India. Present address: Department of Biophysics, Medical College of Wisconsin, Milwaukee, WI

\* Corresponding author Email: muthukumar2k3@yahoo.com

Carcinogenesis is a complex pathological process where normal cells become neoplastic and is largely associated with chemical modification of DNA. This can also occur due to viruses causing mutations, photochemical reactions, and reactions induced by chemicals. Acrylamide (AA) is a carcinogenic material formed in heat processed foods like potato chips and classified as "Probably Carcinogenic" in animals and in human beings. They found to form adduct with guanine at N7- position through its epoxide metabolite Glycidamide (GA) in the C:G pair. The two strands of DNA are held together by hydrogen bonds between base pairs and are most important in maintaining the conformation, geometry and specificity of DNA. In this study, we have investigated the changes in the hydrogen bonds between the guanine and cytosine and associated structural changes in the pair upon attack of AA and GA through quantum-mechanical calculations. The DFT studies carried out on the G:C pair shows that AA and GA rotate the pair due to their steric and electronic properties. These lead to the changes in the structural features of DNA viz., major and minor grooves affecting DNA-protein molecular recognition. The implications of the results on carcinogenesis will be presented.

#### 40. 2D Substructure Analysis of Tautomers of Anionic Guanine

Maciej Haranczyk,<sup>a</sup> John Holliday,<sup>b</sup> Maciej Gutowski<sup>a,c</sup>

<sup>a</sup> Department of Chemistry, University of Gdansk, 80-952 Gdansk, Poland

<sup>b</sup> Department of Information Studies, University of Sheffield, Sheffield S1 4DP, UK

<sup>c</sup> Chemistry-School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, UK

Recently, we have described a procedure of finding low energy tautomers of a molecule [1]. The procedure consists of (i) combinatorial generation of a library of tautomers, (ii) screening based on the results of geometry optimization of initial structures performed at the density functional level of theory, and (iii) final refinement of geometry for the top hits at the second order Möller-Plesset level of theory followed by single-point energy calculations at the coupled cluster level of theory with single, double, and perturbative triple excitations. The library of initial structures of various tautomers is generated with TauTGen, a tautomer generator program. The procedure proved to be successful for these molecular systems for which common chemical knowledge had not been sufficient to predict the most stable structures. For example, we were able to identify the most stable tautomers of anionic guanine among not-studied so far enamino-imino tautomers. Moreover, we demonstrated that thirteen of these tautomers are adiabatically bound with respect to the neutral canonical tautomer. In the present contribution we investigate structural similarity of the studied library of tautomers. 2D substructure features of a set of 165 tautomers were coded into Boolean arrays using the BCI Fingerprint toolkit available from Digital Chemistry [2]. They were later compared using various similarity coefficients and clustered using a hierarchical aggregate group-average algorithm. We were able to find a cluster containing 24 elements including all the most stable tautomers (3% of total tautomers). When compared with the canonical tautomer, the distinct substructural features of tautomers from this cluster are additional hydrogen atoms at C8 and/or C2 atoms.

#### 41. Parameter Estimation on Geeves Three-State Rigid Chain Model via a Damped Least Squares (DLS) Method

Xiaochuan Li<sup>1,\*</sup>, Juan Del Almo De Pedro<sup>1,3</sup>, R. Hugh Griffiths<sup>2</sup>, Michael A. Geeves<sup>2</sup>, Srboljub M. Mijailovich<sup>1</sup>

<sup>1</sup> Dept. of Environmental Health, Harvard School of Public Health, Boston MA 02115,

<sup>2</sup> Dept. of Biosciences, University of Kent, Canterbury, Kent CT2 7NJ, U.K.,

<sup>3</sup> Dept. of Mech. and Aerospace Eng. and Dept. of Bioengineering, UCSD, La Jolla, CA.

\* Corresponding author. Email: xiaochuan.li@gmail.com

In order to estimate chemical kinetic rate parameters  $K_B$  and  $K_T$  of Geeves three-state model and evaluate their behavior within their physical meaning range of bounds, the sensitivity matrix and Damped Least Squares (DLS) inversion method is developed. Geeves et al proposed a three-state rigid chain model to explain the isotherm binding of myosin S1 with regulated actin filament. The computer probabilistic and stochastic methods are implemented to provide basis for parameter estimation. Quasi-Newton and Simulated Annealing (SIMANN) methods, two common optimization methods, are implemented with DLS for comparison. Three methods are applied to a family of time course data in the excessive actin. All of three methods give out the excellent estimation on the fractional effective rate constant,  $K_{obs}^f$ , which is the effective kinetic binding parameter. The SIMANN gives out the best estimation on parameters  $K_B$  and  $K_T$  in addition of the fractional  $K_{obs}^f$ . But it converges very slow and infeasible to be implemented in stochastic methods. The quasi-Newton method converges rapidly, but is frequently influenced by initial guess values and it requires medium amount of function evaluations. This limits its application on stochastic methods as well. The DLS method not only gives out excellent estimation of the fractional  $K_{obs}^f$  and kinetic parameters  $K_B$  and  $K_T$ , but also

it provides the model resolution matrix with a few iterations. It can be used in stochastic simulations. The main advantage of DLS is its fast convergence even with a large complex reaction system and its model resolution matrix providing information about uniqueness of parameters. In addition,  $K_{\text{obs}}^f$  obtained by three methods reveals that  $\text{Ca}^{2+}$  concentration has a positive cooperativity and Hill coefficient is 2.67 meaning with 5-fold increasing in  $\text{Ca}^{2+}$  concentration,  $K_{\text{obs}}^f$  will increase from 0.1 to 0.9. From our results, we believe the DLS method is suitable for any complex chemical reaction system, big or small.

#### **44. Density Functional Theory Studies of Sulfur Trioxide-Water Cluster Interactions**

Jean M. Standard\* and Mary T. Van der Hoven

Department of Chemistry, Illinois State University, Normal, IL 61790-4160

\*Corresponding author. Email: standard@ilstu.edu

Intermolecular complexes of sulfur trioxide and water are important species in atmospheric chemistry, for example in the formation of acid rain. Heterogeneous chemistry, including reactions taking place on ice surfaces, plays a key role in reactions of sulfur oxides in the atmosphere since it is estimated that 50 percent of atmospheric sulfur dioxide reactions occur heterogeneously. In this work, we report on the results of density functional theory studies of sulfur trioxide interacting with large water clusters of up to 39 water molecules in order to model the interaction with an ice surface. Results have been obtained at the B3LYP/6-31G(d) level of theory. Optimized geometries and vibrational frequencies have been computed for all structures, and minima on the potential energy surface as well as transition states for conversion to sulfuric acid have been located. The calculated binding energy of sulfur trioxide to the water clusters ranges from 13-20 kcal/mol and the activation barrier for conversion to sulfuric acid ranges from 3-6 kcal/mol. The results will be correlated with previous studies of the interaction of sulfur trioxide with small water clusters.

#### **45. Conformational space and molecular properties of complexes between drugs and transdermal delivery penetration enhancers.**

B. Drakulic<sup>1</sup>, I. Juranic<sup>2</sup>, M. Zloh<sup>3\*</sup>

<sup>1</sup> Institute of Chemistry, Technology and Metallurgy, Department of Chemistry, Njegoseva 12, 11000 Belgrade, Serbia

<sup>2</sup> Faculty of chemistry, University of Belgrade, P.O.Box 158, Serbia

<sup>3</sup> The School of Pharmacy, University of London, Department of Pharmaceutical and Biological Chemistry, 29/39 Brunswick Square, London, WC1N 1AX, UK

\*Corresponding author: Email: mire.zloh@pharmacy.ac.uk

The use of chemical penetration enhancers (CPE) is growing due to their ability to alter the drug delivery through the skin. A possible mechanism of penetration enhancement could involve the complex formation between drug and components in the drug formulation, thus altering the molecular properties of the active. Previous modelling studies have shown that hydrocarbon and oxygen containing terpenes (penetration enhancers) could form complexes with drugs. Here, we correlate the predicted molecular properties of enhancers with their enhancement effects. Also, structural features of drug-enhancer complexes modelled using conformational search implemented in MacroModel are used to explain enhancers potencies.



#### 46. Proton hydration in water clusters: insights from a combined quantum chemical and experimental study

Kono H. Lemke,<sup>1,\*</sup> Alexander Likholyot,<sup>1</sup> Jamey K. Hovey,<sup>1</sup> Terry M. Seward<sup>1</sup>

<sup>1</sup> Geochemistry Group, Institute of Mineralogy and Petrology, ETH Zürich, Universitätsstrasse 16, CH-8092 Zürich, Switzerland

\* Corresponding author: kono@erdw.ethz.ch

We report here on the thermochemistry of proton hydration by water in the gas phase both theoretically using multilevel G3, G3B3, CBS-Q, CBS-QB3, CBS/QCI-APNO calculations and experimentally using high-pressure mass spectrometry (HPMS). Gas phase hydration enthalpies and entropies for protonated water cluster equilibria with up to 7 waters (i.e.  $n < 7$   $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$ ) were observed and exhibited non-monotonic behavior for successive hydration steps as well as enthalpy and entropy anomalies at higher cluster rank numbers. In particular, there is a significant jump in the stepwise enthalpies and entropies of cluster formation for  $n$  varying from 6 to 8. This behavior can be successfully interpreted using cluster geometries obtained from quantum chemical calculations by considering the number of additional hydrogen bonds formed at each hydration step and simultaneous weakening of ion-solvent interaction with increasing cluster size. The measured and calculated total hydration energy for the attachment of the first seven water molecules around the  $\text{H}_3\text{O}^+$  ion was found to account for more than 60% of total bulk hydration free energy.

#### 47. Differences in Electrostatic Potential Around DNA Fragments Containing Thymine and Thymine Glycol

Maciej Haranczyk,<sup>a,b</sup> Iwona Dabkowska,<sup>a,b</sup> Maciej Gutowski<sup>a,b,c</sup>

<sup>a</sup> Department of Chemistry, University of Gdansk, Sobieskiego 18, 80-952 Gdansk, Poland

<sup>b</sup> Chemical Sciences Division, Fundamental Sciences Directorate, Pacific Northwest National Laboratory, Richland, Washington 99352, USA

<sup>c</sup> Chemistry-School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, UK

Changes of electrostatic potential (EP) around the DNA molecule resulting from chemical modifications of nucleotides may play a role in enzymatic recognition of damaged sites. Effects of chemical modifications of nucleotides on the structure of DNA have been characterized through large scale computations. Quantum mechanical structural optimizations of fragments of five pairs of nucleotides with thymine or thymine glycol were performed at the density functional level of theory with a B3LYP exchange-correlation functional and 6-31G\*\* basis sets. The electrostatic potential around the DNA fragments was analyzed with the newest implementation of our cylinder projection technique. The electrostatic potential was projected on a surface around the double helix. The 2D maps of EP of intact and damaged DNA fragments were analyzed to identify modifications of the EP that result from the occurrence of thymine glycol. It was found that distortions of phosphate groups and displacements of the accompanying counterions are clearly reflected in the EP maps.

#### 48. Design of Low Band Gap Conjugated Polymers Through Ladders With Acetylenic Crosspieces

Shujiang Yang\* and Miklos Kertesz

Department of Chemistry, Georgetown University, Washington, DC 20057-1227

\* Corresponding author. Email: sy37@georgetown.edu

Building ladder polymers provides an alternative way to design intrinsically low band gap conjugated polymers. Using conventional conjugated polymers, polyacetylene, polydiacetylene and polytriacetylene as sidepieces, we propose a series of novel

types of ladder polymers with conjugated acetylenic blocks  $(-C\equiv C-)_m$  serving as crosspieces. Periodic boundary conditions density functional calculations are performed to investigate the effect of the acetylenic cross-couplings between two sidepieces. Results show that the so-constructed ladder polymers exhibit a band gap of about half an electron volt at the B3LYP level, significantly reduced comparing with the parent sidepiece polymers at the same theoretical level. The reduction mechanism is investigated and discussed. The effect of varying the length and spacing of the crosspieces along the sidepieces is investigated in order to maximize the effect of the gap reduction. Unusual electronic and optical properties are expected from these series of ladder conjugated polymers.

## **50. Structure, Thermodynamics, and Stability of Clustered DNA Damages from Molecular Simulations**

L. Douali<sup>1\*</sup>, J. Miller<sup>2</sup>, M. Ernst<sup>2</sup>, M. Dupuis<sup>1</sup>

<sup>1</sup>Pacific Northwest National Laboratory, P.O.Box 999, k1-83 Richland, WA 99352 USA

<sup>2</sup>School of Electrical Engineering and Computer Science, Washington State University Tri-Cities, Richland, WA 99354 USA

\* Corresponding author. E-mail: latifa.douali@pnl.gov

Endogenous oxidative processes create mainly singly damaged DNA sites (SDS). In contrast ionizing radiation creates also clusters of DNA damages within one or two turns of the DNA called multiply damaged sites (MDS). To gain a better understanding of the chemistry of the MDS, the perturbation of duplex DNA stability due to single and multiple 8-oxoguanine (8-oxoG) lesions and abasic sites was estimated by thermodynamic integration based on molecular dynamics (MD) simulations. The interaction between two lesions in the opposite strands is also discussed. In this presentation we show how modern computational approaches offer detailed characterization of damages in DNA, including structures and thermodynamic stability via free energies extracted from molecular dynamics simulations.