

Math/Chem/Comp 2017

29th MC² Conference

Inter University Centre Dubrovnik (IUC)

19 – 24 June 2017

BOOK OF ABSTRACTS

Editors: Hrvoj Vančik and Jerzy Cioslowski

THE ROLE OF GUAIACYL MOIETY IN RADICAL SCAVENGING BY 3,5-DIHYDROXY-4-METHOXYBENZYL ALCOHOL

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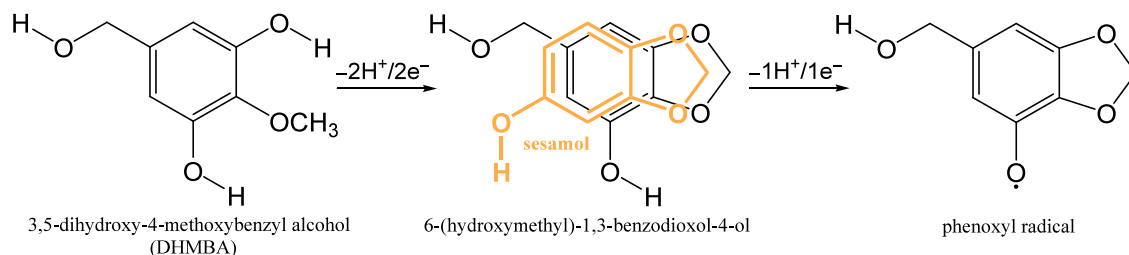
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The thermodynamic preference of different radical scavenging mechanisms of 3,5-dihydroxy-4-methoxybenzyl alcohol (DHMBA), a natural product identified in oysters, was studied using DFT. Geometry optimizations and frequency calculations were carried out using the M06-2X functional and the 6-311++G(d,p) basis set, in conjunction with the SMD continuum solvation model [1].

The involvement of guaiacyl moiety in multiple radical scavenging processes was investigated considering reaction energetics of triple hydrogen atom transfer (tHAT), triple electron transfer-proton transfer (tET-PT) and triple sequential proton loss electron transfer (tSPLET) mechanisms. All these mechanisms result in production of phenoxyl radical of 6-(hydroxymethyl)-1,3-benzodioxol-4-ol (sesamol like structure – sesamol: potent plant antioxidant with 1,3-benzodioxole core).



The Gibbs free energy change for reactions of inactivation of radicals of different chemical nature (HO^\bullet , HOO^\bullet , $\text{CH}_3\text{O}^\bullet$, $\text{CH}_3\text{OO}^\bullet$, $\text{CH}_2=\text{CH}-\text{O}-\text{O}^\bullet$, PhO^\bullet , $\text{Cl}_3\text{COO}^\bullet$ etc.) indicate tHAT and tSPLET mechanisms as thermodynamically feasible. Exceptional antioxidant activity of DHMBA can be explained by consideration of triple processes (based on involvement of guaiacyl moiety, i.e., vicinal phenolic $-\text{OH}$ and $-\text{OCH}_3$ group) in addition to single processes (dealing only with single phenolic $-\text{OH}$ group of DHMBA) recently studied by Villuendas-Rey et al [2].

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Acknowledgment

Financial support from The Foundation of the Croatian Academy of Sciences and Arts (project No. 10-102/244-1-2016.: Investigations of the antioxidant mechanisms of polyphenols and their metabolites) is gratefully acknowledged.

ON THE n -VERTEX BICYCLIC GRAPHS WITH MINIMUM REDUCED RECIPROCAL RANDIĆ INDEX

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Recent research indicates that the reduced reciprocal Randić (RRR) index possess the second-best correlating ability among several well-known molecular structure descriptors. Hence, it is meaningful to study the mathematical properties of the RRR index, especially bounds and characterization of the extremal elements for different graph families. In this presentation, the characterization of graph having minimum RRR index among the collection of all n -vertex bicyclic graphs will be dispensed.

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THE AROMATICITY IN LOW-LYING EXCITED STATES

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From the discovery of benzene in 1825 to the present day, the concept of aromaticity has experienced several revolutions that have fueled the interest of both theoretical and experimental chemists. Very recently, several works [1-3] have highlighted the importance of aromaticity in excited states. Aromaticity is essential to understand and predict many photochemical processes. This renaissance of excited state aromaticity represents an important revolution in the field of aromaticity. Although aromaticity is a property usually linked to the ground state of stable molecules, certain excited states are unquestionably aromatic. This is especially the case of annulenes in the lowest-lying triplet states whose aromaticity follows the 4N Baird rule [4]. In this work, we apply this rule to discuss the aromaticity of all-metal clusters, we discuss the existence of Hückel-Baird hybrid aromatic species [5], and we show how Clar's rule can be extended to the lowest-lying triplet excited states of certain polycyclic aromatic molecules.

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THE TOTAL π -ELECTRON ENERGY SAGA

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The total π -electron energy, as calculated within the Hückel tight-binding molecular orbital approximation, is a quantum-theoretical characteristic of conjugated molecules that has been conceived as early as in the 1930s. In 1978, a minor modification of the definition of total π -electron energy was put forward, that made this quantity interesting and attractive to mathematical investigations. The concept of *graph energy*, introduced in 1978, became an extensively studied graph-theoretical topic, with many hundreds of published papers. A great variety of graph energies is being considered in the current mathematical-chemistry and mathematical literature. Recently, some unexpected applications of these graph energies were discovered, in biology, medicine, and image processing.

We provide historic, bibliographic, and statistical data on the research on total π -electron energy and graph energies, and outline its present state of art.

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ONE-ELECTRON DENSITIES OF FREELY ROTATING WIGNER MOLECULES

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A formalism enabling computation of the one-particle density of a freely rotating assembly of identical particles that vibrate about their equilibrium positions with amplitudes much smaller than their average distances is presented. It produces densities as finite sums of products of angular and radial functions, the length of the expansion being determined by the interplay between the point-group and permutational symmetries of the system in question. Obtaining from a convolution of the rotational and bosonic components of the parent wavefunction, the angular functions are state-dependent. On the other hand, the radial functions are Gaussians with maxima located at the equilibrium lengths of the position vectors of individual particles and exponents depending on the scalar products of these vectors and the eigenvectors of the corresponding Hessian as well as the respective eigenvalues. Although the new formalism is particularly useful for studies of the Wigner molecules formed by electrons subject to weak confining potentials, it is readily adaptable to species (such as "balliums" and Coulomb crystals) composed of identical particles with arbitrary spin statistics and permutational symmetry. Several examples of applications of the present approach to the harmonium atoms within the strong-correlation regime are given.

MOLECULAR DYNAMICS SIMULATION OF CARBON STRUCTURES INSIDE NANOCHAMBERS

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Based on recent experimental results of hydrocarbon formation in small diameter carbon nanotubes filled with ferrocene molecules [1,2], we have performed molecular dynamics calculations. We put 60, 80, 84, 85, 90 and 100 number of carbon atoms in a (14,0) nanotube of length 25.578 Å. In the initial position the carbon atoms were set in C5 rings and during the simulation the positions of the nanotube atoms were fixed. The carbon-carbon interactions inside the tube were calculated with a density functional adjusted tight binding method, whereas the carbon-carbon interaction with the nanotube was taken into account with a Girifalco-potential. The temperature inside the nanotube was controlled by a Nosé-Hoover thermostat and periodic boundary condition was applied in the model. We have found that the structures formed during the simulation depend on the temperature, the density of the carbon atoms and in some test calculations we have found dependency on the tube diameter as well. At lower temperatures we obtained graphene ribbons and at higher temperature nanotube or fullerene were obtained depending on the density of the carbon atoms. In order to test our results on larger systems, including also hydrogen atoms, molecular dynamics calculations are in progress using the open source code LAMMPS. Support from OTKA in Hungary (Grant No. K115608).

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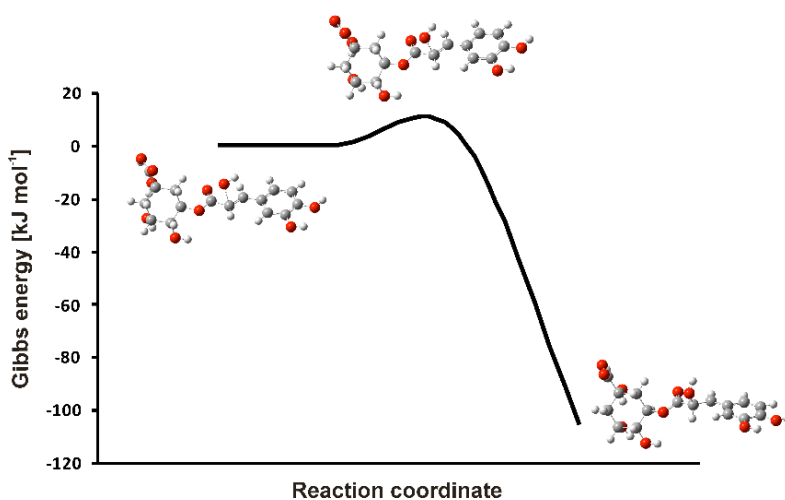
ANTIOXIDATIVE ACTIVITY OF CHLOROGENIC ACID: DFT STUDY

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Chlorogenic acid (5-*O*-caffeoylquinic acid) is a dietary phenolic acid, whose antioxidative activity has been proved in various experimental studies [1,2]. However, there are few results related to the mechanisms of antioxidative action of this compound [3]. The aim of the present study is to examine the four major antioxidative mechanisms through which chlorogenic acid can exert its activity: Hydrogen atom transfer (HAT), Radical adduct formation (RAF), Sequential proton lost - electron transfer (SPLET), and Single electron transfer – proton transfer (SET-PT). The investigation was performed by simulating the reactions of chlorogenic acid with hydroxyl radical. The



calculations were carried out using the M06-2X/6-311++G(d,p) theoretical model in combination with CPCM solvation model. It was found, on the basis of the reaction enthalpies and free energies, as well as of the

rate constants (activation energies), that chlorogenic acid and hydroxyl radical cannot undergo SET-PT mechanism under any conditions. In acidic and neutral media HAT and RAF are the most favorable and competitive mechanistic pathways. On the other side, in basic media (for example at physiological pH) SPLET mechanism is the most plausible and very fast antioxidative mechanism of chlorogenic acid.

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This work was supported by the Ministry of Science and Technological Development of the Republic of Serbia (project nos. 172016 and 172015) and bilateral project Serbia-Croatia 2016-2017.

A MODEL FOR THE ESTIMATION OF THE FIRST OXIDATION POTENTIAL OF POLYPHENOLS

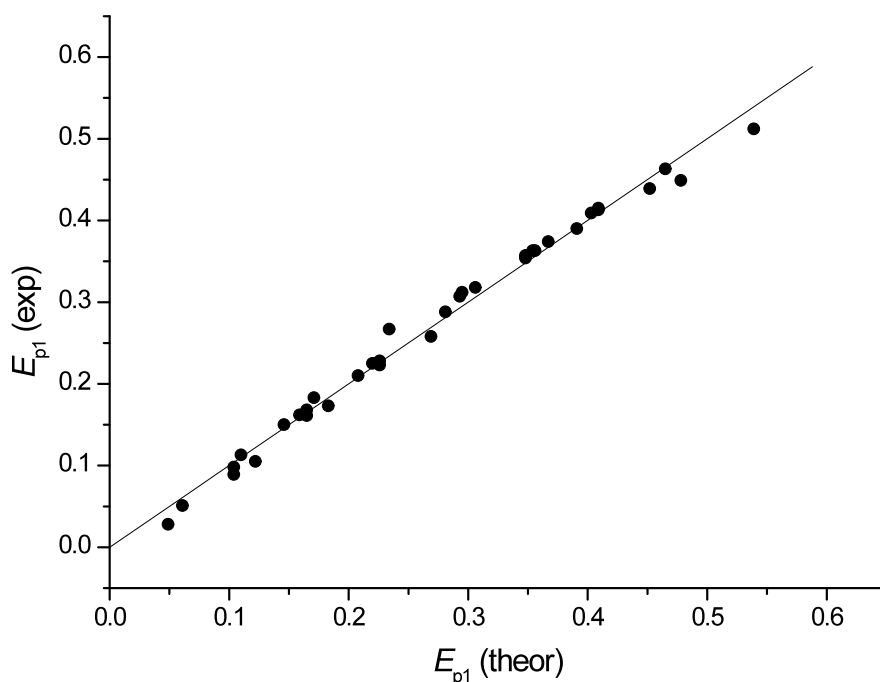
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This study developed linear model for the estimation of the first oxidation potential, E_{p1} , for seven polyphenolic compounds (myricetin (Myr), dihydromyricetin (DhMyr), epigallocatechin-3-gallate (EGCG), epigallocatechin (EGC), gallic acid (GA), epicatechin-3-gallate (ECG) and epicatechin (EC)) at different pH values. As descriptors, we used the number of vicinal (N_v) and non-vicinal (N_{nv}) OH groups, the number of OH neighbouring pairs (N_{ch}), the total number of OH groups (N_{OH}), and pH. The common model for pH = 2, 3, 5, 6, and 7:

$$E_{p1} = 0.06(1) N_v - 0.148(9) N_{nv} - 0.21(2) N_{ch} + 0.055(7) N_{OH} - 0.061(1) \text{pH} + 0.83(1)$$

yielded $r = 0.995$, S.E. = 0.013, S.E. = 0.016.



THERMODYNAMIC ANOMALIES AND NETWORK TOPOLOGY IN LIQUIDS

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Thermodynamic and kinetic anomalies are often encountered in tetrahedral liquids, most famously in water (for example, the density anomaly), but also in SiO₂ and Si. The origin of the anomalies is often linked to behaviour of quantities associated to phase transition phenomena which occur in the metastable supercooled regime that is largely inaccessible by conventional experiments leaving simulations as a convenient alternative. Several theories and scenarios have been proposed that link behaviour of anomalous properties to the existence of a liquid-liquid critical point [1] but none can predict or explain the appearance of anomalies. Stillinger-Weber (SW) potentials are often employed to model tetrahedral liquids. These potentials are composed of a standard pairwise term with exponential decay and a triplet term which penalizes deviations from ideal tetrahedral angles[2]. In recent years the critical point for SW silicon has been uncovered [3] and loci of anomalous properties calculated for constant pressure for different strengths of triplet term in SW potential[4]. However, no systematic study of the SW potential that links the emergence of anomalies to topology of network has yet been reported. In this study we take a systematic approach to explore the parameter space of the triplet term in the SW potential at various temperatures, pressures and densities. This enables us to more thoroughly understand the appearance of thermodynamic anomalies in tetrahedral liquids and their connection to the network topology of the system. A possible connection between the existence of anomalies and crystal phases underlying the liquid is also explored.

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SYMMETRY–BASED TOPOLOGICAL INDICES OF MOLECULAR GRAPHS

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Abstract

The first symmetry–based topological index was introduced by Graovac and Pisanski [1]. This symmetry–based graph invariant is an algebraic approach for generalizing the Wiener index by automorphism group of the molecular graph under consideration. To explain, we assume that G is a molecular graph with automorphism group $\Delta = \text{Aut}(G)$ and Γ is a subgroup of Δ . The Graovac–Pisanski index of G with respect to Γ can be defined as:

$$GP(G) = \frac{|V(G)|}{2|\Gamma|} \sum_{x \in V(G)} \sum_{\alpha \in \Gamma} d(x, \alpha(x)).$$

The aim of this talk is to present our recent results on this graph invariant [2,3]. Some open questions are also presented.

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MICROWAVE EFFECTS ON MODEL AQUEOUS SOLUTIONS

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Using the molecular dynamics simulations with separate thermostats for translational and rotational degrees of freedom, we investigate the effects of water's rotational motion on the interaction among Lennard–Jones solutes. The situation with rotational temperature higher than the translational one ($T_r > T_t$) is mimicking the effects of microwaves on model solutions. Molecular dynamics simulations suggest that solutions of Lennard–Jones solutes become increasingly more structured with the rise in T_r , while keeping the T_t constant. This is evidenced by an increase in the first and the second peak of the solute–solute radial distribution function. More evidence of strong effects of the rotationally excited water is provided by the simulations of short hydrophobic polymers, which upon an increase in T_r assume more compact conformations. Using identical methodology we also investigate the effects of water's rotational motion on the ion pairing of ionic solutes in aqueous solutions of alkali halide salts. The simulations reveal that an increase in the rotational temperature at constant translational temperature exerts significant changes in the structure of the solution. The latter are reflected in increased pairing of the oppositely charged ions, which can be explained by the weaker ability of rotationally excited water to screen and separate the opposite charges.

EXACT SOLUTION OF SCHRODINGER EQUATION FOR TETRAQUARK SYSTEMS

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A hadronic system is composed of interacting non-relativistic constituent quarks. To determine the wave function in this model, many-body Schrodinger equation should be solved. This is difficult to perform since quark-quark interaction depends on flavor, color, and spin. Several approximate methods are used to solve this equation.

Multiquark exotic hadrons such as tetraquarks and pentaquarks have been studied for many years. They are different from ordinary mesons and baryons. The tetraquark was first introduced by Jaffe[1] as a bound state formed by two quarks and two antiquarks[2].

In this paper, an exact analytical solution is suggested for four interacting quarks. we solved Schrodinger equation for tetraquarks in the framework of two-body problem[3,4]. For this purpose, we utilized Yukawa potential in Jacobian coordinates, also finding a relation between the coupling constant and reduced masses of these systems we obtained the coupling constant of Yukawa potential for tetraquark systems. Finally, We calculated the energy of these systems in their ground state. The results were well consistent with the theoretical results. Our procedure to obtain these results is appropriate for other potentials and n-body systems.

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Structural, optical and photocatalytic studies of $\text{Nd}_2\text{Zr}_2\text{O}_7\text{-Nd}_2\text{O}_3$ nanocomposites: New facile synthesis and characterization

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$\text{Re}_2\text{Zr}_2\text{O}_7$ are widely employed in high-temperature fuel cell, oxide conductor, gas turbines, nuclear waste form, fluorescence centers, actinide transmutation and photocatalyst due to their interesting properties. So far, various routes including sol-gel, complex precipitation, hydrothermal and Pechini polymeric route have been reported to prepare rare-earth zirconates. Among of these routes, Pechini polymeric approach is facile, cost effective, reliable and friendly to the environment procedure, potential for large-scale fabrication and effective control the grain size and shape for synthesizing of $\text{Re}_2\text{Zr}_2\text{O}_7$ and its nanocomposites. $\text{Nd}_2\text{Zr}_2\text{O}_7\text{-Nd}_2\text{O}_3$ nanocomposites have been synthesized through a simple modified Pechini approach using salicylic acid as novel complexing agent and propylene glycol as new cross-linking agent. The effect of various basic agents and space-filling templates on the morphology and size of the $\text{Nd}_2\text{Zr}_2\text{O}_7\text{-Nd}_2\text{O}_3$ nanocomposites were studied. The results revealed that altering these preparation factors could be effective in grain size and shape control. The results indicated that altering these synthesis factors could be effective in grain size and shape control. The as-produced nanocrystalline $\text{Nd}_2\text{Zr}_2\text{O}_7\text{-Nd}_2\text{O}_3$ as novel type of photocatalyst under UV light demonstrated better photocatalytic behaviour than the nanocrystalline Nd_2O_3 . It seems that the better photocatalytic performance of the as-produced nanocrystalline $\text{Nd}_2\text{Zr}_2\text{O}_7\text{-Nd}_2\text{O}_3$ than the nanocrystalline Nd_2O_3 may be ascribed to its lower energy gap compared with nanocrystalline Nd_2O_3 . In the case of nanocrystalline $\text{Nd}_2\text{Zr}_2\text{O}_7\text{-Nd}_2\text{O}_3$ with lower E_g , the recombination of charges (electron and hole) is reduced and therefore the photocatalytic efficiency increases.

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Quantum Chemical Calculation of Amino-substituted But-2-yne Dications

Distonic and Gitonic character?

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Konstantin Drandarov², Ioannis Tiritiris², and Willi Kantlehner²**

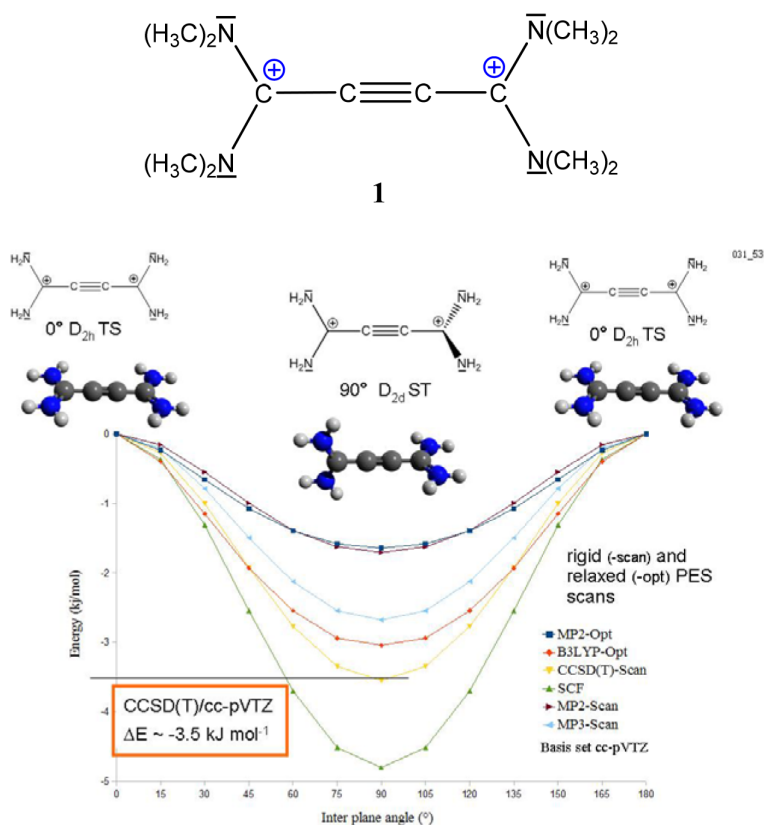
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The tetrakis-dimethylamino substituted but-2-yne dication **1** and related model cations are investigated by DFT, MP2, CCSD and CCSD(T)) quantum chemical calculations to elucidate structural and electronic details, energy barriers and conformational preferences in order to rationalize experimental NMR-spectra and crystallographic structural data of tetrafluoroborate and tetraphenylborate salts of **1**. Very small energy differences between different conformations are caused by electronic and steric effects in the cation. In addition, solid-state effects such as anion cation interactions may lead to conformational differences in the salts. In dication **1** and analogous model cations, the distonic arrangement of the charges is preferred over a gitonic configuration.



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Computational study of dipeptidyl peptidase III from thermophile *Caldithrix abyssi*

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Dipeptidyl peptidase III isolated from the thermophilic bacteria *Caldithrix abyssi* (*CaDPP* III) is a two-domain zinc exopeptidase, a member of the M49 family according to the MEROPS database. Like the other DPPs III it cleaves dipeptides from the N-terminus of its substrates but differently from human, yeast and *Bacteroides thetaiotaomicron* (mesophile) ortholog, it has the pentapeptide, HEISH, instead of the hexapeptide motif HEXXGH in the active site.

The aim of our study was to investigate structure and dynamics of *CaDPP* III and to find possible differences with already characterised DPPs III from mesophiles, especially DPP III from the mesophilic bacteria *B. thetaiotaomicron*, which might rationalize its higher stability and its higher temperature optimum determined experimentally.¹ Further on in order to understand the structural and catalytic significance of the HEISH motif unique to *C. abyssi*, we also performed long MD simulations of the mutant with the HEISGH motive, as well as its complex with RRNA.

The enzyme stability and the possible conformational changes were investigated using 200 ns long classical and accelerated MD simulations. We have identified distinct "open" and "closed" conformations in line with those previously reported for human DPP III² and *BtDPP* III. During the simulations the zinc ion was mostly hexacoordinated with amino acid residues (His379, His383 and Glu412) and two to three water molecules. The simulations of *CaDPP* III complexes with synthetic substrates Arg₂-2-naphtylamide (RRNA) and Gly-Arg-2-naphtylamide (GRNA) revealed their binding modes and helped us to rationalize the experimental data on their *CaDPP* III catalysed hydrolysis.

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EXAMINATION OF ANTIOXIDANT ACTIVITY OF PHENOLIC FUNCTIONALIZED PIPERIDINE

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The multicomponent reactions (MCRs) are considered to be an efficient tool which provide effective, atom economic, energy-saving and environmentally benevolent processes [1,2]. These reactions often find applications in the organocatalysis and synthesis of structurally more or less complex biologically active compounds. The functionalized piperidines represent an important class of heterocycles, and can be found in many naturally occurring alkaloids, biologically active synthetic molecules, and fine organic chemicals [3]. These compounds are useful drugs against several metabolic disorders and human ailments. Over the last ten years, a lot of them have been included into preclinical and clinical trials. Owing to their importance in medicinal chemistry, scientists have developed a lot of methods for their preparation, but still searching for new with less limitations and disadvantages. The piperidine derivative methyl-2,6-bis(4-hydroxy-3-methoxyphenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate was synthesized in the green and efficient one-pot five-component organocatalyzed reaction and its antioxidant activity was tested using DPPH test. The Gaussian 09 program package was used to perform all electronic calculations [4]. Density functional theory (DFT) is a powerful tool which was used for examining the free radical scavenging mechanisms. The equilibrium geometries of the examined compound, its radical cation, radicals and anions, as well as all other species that participate in the reactions of all studied mechanisms were calculated using the B3LYP functional in conjunction with the 6-311+G(d,p) basis set. The influence of methanol as a polar solvent ($\epsilon = 32.6$) was estimated using CPCM solvation model.

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Interface theory of benzenoid structures

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A novel formulation of the theory of Kekulé structures, Clar covers [1] and Zhang-Zhang polynomials [2-5] of benzenoid structures, [6-10] based on the concepts of interfaces and connectivity graphs, is presented. An interface \mathbb{I} is the sequence of Clar covering characters for a certain set of bonds in a given benzenoid \mathbf{B} , which determines the local Clar covering topology of \mathbf{B} . As a result, every Clar cover of \mathbf{B} can be conveniently expressed as a unique sequence $\mathbb{I}=\mathbb{I}_1, \mathbb{I}_2, \dots, \mathbb{I}_n$ of interfaces. The set of conceivable interfaces can be used for constructing the interface connectivity graph of \mathbf{B} , on which every Clar cover of \mathbf{B} is encoded as some walk. The interface connectivity graph allows a direct and robust computation of the Zhang-Zhang polynomial of \mathbf{B} . Further analysis of the connectivity graphs reveals direct conditions for verifying whether some benzenoid has Kekuléan character, as well as an easy method for computing its Clar number.

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Zhang-Zhang polynomials of benzenoid structures and their application to geometry optimization of molecular crystals

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We present a survey of available results on the theory of Zhang-Zhang (ZZ) polynomials [1-4] for benzenoid structures. Various techniques for determination of the ZZ polynomials are presented and discussed [1-10]. We present also a computer environment called ZZDecomposer [7] (which we make available to the participants of the conference in form of free-of-charge DVD installation package), which helps one to derive and compute ZZ polynomial formulas for arbitrary benzenoid structures. Applications of the presented software will be presented together with the accompanying techniques for solving the resulting recurrence relations [11-16]. At the end of the talk, we discuss a list of open problems in the theory of ZZ polynomials.

An important application of the ZZ polynomials is their use for computations of local aromaticity in a given benzenoid structure [17-19]. Computations based on these ideas will be presented together with perspectives of using such a concept for determination of stable structures of molecular crystals built of aromatic hydrocarbons.

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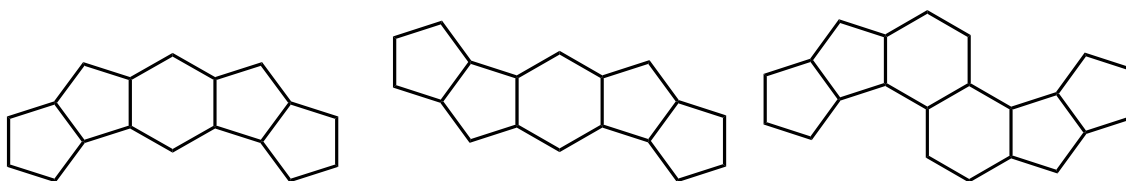
RING-CURRENT PROPERTIES OF BISPENTALENES — COMPARISON OF *AB INITIO* AND HÜCKEL–LONDON–POPLE–MCWEENY (HLPM) ‘TOPOLOGICAL’ CALCULATIONS

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Cao *et al.*^[1] recently reported experimental and theoretical work on the magnetic properties of some derivatives of $[4n+2]$ - π -electron conjugated systems (called ‘bispentalenes’), formed by annelating two pentalene groups with a benzene, or a naphthalene, moiety; their molecular graphs are illustrated below.



This motivated Sundholm *et al.*^[2] to study the same systems by means of their GIMIC *ab initio* formalism.^[3,4] This therefore gives the opportunity to consider further what Coulson^[5] once famously called ‘primitive patterns of understanding’, by subjecting the above structures (and others) to calculations based on the simple, essentially graph-theoretical, ‘topological’ ring current approach.^[6–8] It is shown that there is frequently qualitative, or even semi-quantitative, agreement between a complex (but, presumably, numerically accurate) *ab initio* calculation and a conceptually simple, quasi graph-theoretical one, whose predictions depend only on the carbon-carbon connectivity of the structure being investigated, and on the (geometrical) areas of its individual rings.

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Finding Largest small polygons via symbolic computations

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A small polygon is a convex polygon (in the euclidean plane) of unit diameter. The problem of determining the largest area of small n -gons was already studied by Reinhardt in 1922. He showed that for n odd the regular n -gon is optimal .For even n this is not the case.For $n=6$ the largest area F_6 ,a plane hexagon of unit area can have, satisfies a 10th degree irreducible equation wit integer coefficients.This is the famous Graham's largest little hexagon (1975). R.L.Graham (with S.C.Johnson) needed factoring a 40-degree polynomial with up to 25- digit coefficients. Graham introduced the diameter graphs by joining the vertices at maximal distance. For $n=6$ (resp.8) there are 10 (resp. 31) possible diameter graphs .The case $n=8$ was attacked by C.Audet ,P.Hanson,F. Messine via global optimization (10 variables and 20 constraints) which produced (an approximate) famous Hansen's little octagon.

In this talk we report on reduction for F_6 of the auxiliary polynomial to degree 14 (instead of 40) by rational substitutions (a „missed opportunity“ in Graham and Johnson's approach). Also for the first time ,under axial symmetry conjecture, we obtained an explicit equations for F_8 (resp F_{10}) of degree 42(resp 152) via intriguing symbolic iterated discriminants computations (sometimes involving almost 3000 digit numbers).

WHY IS SOFT INDEPENDENT MODELING OF CLASS ANALOGY NO STANDARD FOR CLASSIFICATION?

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Supervised and unsupervised pattern recognition techniques are two of the largest and most frequently-used branches of chemometric methods. Soft independent modeling of class analogies (SIMCA) is a supervised classification method that has been extensively used in the field of chemometrics in the past decades. Although SIMCA is a supervised method, it is based on disjoint principal component analyses: applying one PCA for each class of the whole dataset separately.

This study answers the question in the title. A thorough survey of classification data sets and a rigorous comparison of classification methods clearly show the unambiguous superiority of other techniques over soft independent modeling of class analogy (SIMCA).

Two non-parametric methods: sum of ranking differences (SRD) [1,2] and the generalized pairwise correlation method (GPCM) [2] have been used to rank and group the classifiers. Both techniques need a supervisor (a reference) and their results support and validate each other, despite being based on entirely different principles and calculation procedures. To eliminate the effect of the chosen reference, comparisons with one variable (classifier) at a time were calculated and presented as heatmaps. Six case studies show unambiguously that SIMCA is inferior to other classification techniques such as linear and quadratic discriminant analysis, multivariate range modelling, etc.

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LARGE-SCALE COMPARISON OF SIMILARITY METRICS FOR MOLECULAR FINGERPRINTS

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Molecular fingerprints are ubiquitously applied to represent molecular structure in a wide range of applications in cheminformatics, computational drug discovery and related fields [1]. Their greatest advantages are their compactness and machine-readability: the latter enables the fast comparison of molecular structure and the quantification of their similarity. However, there are a great number of methods for calculating the similarity of two binary data structures and – despite the general preference of the Tanimoto coefficient – the choice of similarity metric is not trivial.

We have shown with robust statistical methods on a large dataset that the Tanimoto coefficient is a justified choice from a small pool of commonly known and easily available similarity metrics – although other, equally consistent metrics could be identified as well [2]. Following a different methodology, Todeschini and coworkers have compared a greater number of similarity metrics on simulated and real virtual screening datasets [3].

We are extending our methodology to a larger pool of similarity metrics [1,3] and molecular fingerprints, implemented in various cheminformatics packages. General conclusions for various fingerprint types will be drawn and similarity metrics will be compared and ranked based on their consistency with a suitable reference method (data fusion). We also plan on releasing an open-source Python module implementing the studied similarity metrics, which will be readily applicable with the Cinfony toolkit, the open-source aggregator of cheminformatics software [4].

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BOOTSTRAP-LIKE VALIDATION FOR SUM OF RANKING DIFFERENCES

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Sum of (absolute) Ranking Differences (SRD) readily became a popular technique for method and model comparison. Earlier papers [1-3] have shown its usefulness, applicability. Two types of validation have been elaborated: i) Comparison of Ranks with Random Numbers (CRRN) *i.e.* a randomization test and ii) sevenfold cross-validation [2]. Later the ordering procedure has been extended for cases, when equal numbers (ties) are present in the input matrix [3]. Scaling (standardization, normalization, *etc.*) of the data is necessary if the variables are measured on various scales.

Computer codes are freely available from our homepage:

<http://aki.ttk.mta.hu/srd>

We have observed, however, that some of the SRD distributions are polluted with outliers; extreme skewness and kurtosis can be observed. Therefore, a large scale bootstrap-like validation has been elaborated to evaluate the role of anomalies in the ranking, grouping and decision process: i) the algorithm contains a leave-one-out procedure for small numbers of objects (rows), ii) SRD values are also calculated with many-fold cross-validation (5-10) and using random selections of objects until about 50 SRD values. Then, the different variable distributions can be compared and a nonparametric test (*e.g.* Wilcoxon matched pair test) orders and groups the methods and models (variables) extracting as much information as possible.

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The role of topochemical effects on energetics of solid-state reactions

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After the pioneering work of Cohen and Schmit [1] on the photochemically induced chemical processes, reactions in crystals start to be studied in the frame of the concepts of topochemistry. An intriguing discovery that nitroso dimers undergo photodissociation in crystals has at least two perspectives [2]. First includes a study of topochemical effects in the solid-state chemical reactivity and energetics, while the second includes a possibility of application of such effects in the molecular ON-OFF switches in the field of molecular electronics. Since topochemical postulate will be fulfilled only in case when the monomer molecule affords close contacts between the reactive centers of neighboring molecules, dimerization of 4-bromnitrosobenzene was studied by measuring of kinetics at different temperatures and by analyzing corresponding activation parameters under different phase conditions.

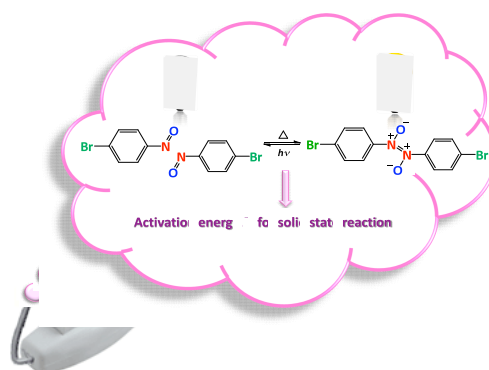


Figure 1 Photothermal formation and bond breaking: the molecular ON-OFF switch.

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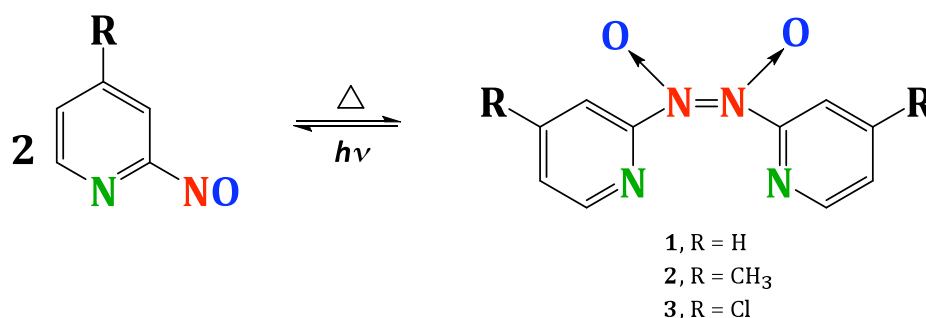
The work was supported by the Croatian Science Foundation, Grant No. 7444, ORGMOL.

BEHAVIOUR OF 2-NITROSPYRIDINES IN SOLUTION AND IN SOLID STATE

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It is already well known that nitrosobenzenes in solution at room temperature appear exclusively as monomers [1], but 2-nitrosopyridines prefer to exist in a form of *Z*-dimers. In addition, whereas nitrosobenzenes are mostly present as *E*-dimers in solid state, 2-nitrosopyridines are present like *Z*-stereomers as well. In the present work we were investigating monomer-dimer equilibrium of 2-nitrosopyridine (**1**) and its 4-methyl- (**2**) and 4-chloro- (**3**) derivatives (Scheme 1) both in solution and in solid state.



Scheme 1. Photo-thermal formation and bond breaking of 2-nitrosopyridine derivatives.

The equilibrium constants and thermodynamic parameters of three 2-nitrosopyridine derivatives were determined by UV-Vis spectroscopy. By using variable temperature ¹H NMR spectroscopy it was found that compound **1** is able to form the heterodimers with 4-nitronitrosobenzene. Solid-state photo-thermal studies of 2-nitrosopyridine derivatives were studied by IR spectroscopy at cryogenic conditions indicating that both, the *Z*- and *E*-dimers can be photolysed to corresponding monomers which re-dimerize by warming to room temperature. For the first time, monomers of 2-nitrosopyridine derivatives were detected in solid state enabling analysis of their IR spectra. Furthermore, the kinetics of the re-dimerization of monomers of 2-nitrosopyridines prepared by photolysis of corresponding dimers at 13 K and by cryogenic deposition were investigated as well. Estimated activation parameters were enabled from obtained reaction rates at different temperatures. The results of this study demonstrate that different topochemical conditions affect the kinetics of solid-state dimerization of 2-nitrosopyridine derivatives.

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Acknowledgment

The work was supported by the Croatian Science Foundation, Grant No. 7444, ORGMOL.

STRUCTURAL DEPENDENCE OF EXTENDED ENERGY

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An entry of the extended adjacency matrix is defined as

$$a_{rs}^{ex} = \begin{cases} 0 & \text{if } r = s \text{ or vertices } r \text{ and } s \text{ are not adjacent} \\ \frac{1}{2} \left(\frac{d_r}{d_s} + \frac{d_s}{d_r} \right) & \text{if vertices } r \text{ and } s \text{ are adjacent.} \end{cases}$$

where d_r and d_s are the degrees of the vertices r and s .

Thence, the extended energy of a graph $E_{ex}(G)$ is defined as the sum of the absolute values of eigenvalues of the extended adjacency matrix. Some lower and upper bounds of $E_{ex}(G)$ in terms of common graph parameters will be presented, as well as the relation between ordinary and extended energies.

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THE OUTCOME OF REASONING BASED ON MODELS GREATLY DEPENDS ON THE PROCEDURE USED FOR THEIR VALIDATION

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In modeling process, three main validation procedures can be used: fitting (the obligatory one), cross-validation, and prediction. The first two are internal validations, and are based on the training data set used also for estimation and optimization of model coefficients. The last one is called external validation, and is performed on external data set containing additional samples (compounds) never used in training. According to literature, severity of these validation methods increases in this order: fitting, cross-validation, and prediction. For each validation procedure corresponding statistical parameters are calculated and reported, like standard errors or correlation coefficients. Conclusions on quality of models or on quality of novel molecular descriptors involved in the models can be different or even opposite if one draws conclusions based on statistical parameters calculated in fitting or in prediction. It will be illustrated on data sets from literature related to structure-property modeling of organic compounds. Also, the lack of pure external validation in modeling of secondary structure of proteins will be addressed. It comes out that more rigorous validation of models should be completed if one wants to draw more definite conclusions based on models.

COMPARATIVE MODELING OF ANESTHETIC ACTIVITIES OF ORGANIC COMPOUNDS BY SEMI-EMPIRICAL STRUCTURAL PARAMETERS AND TOPOLOGICAL DESCRIPTORS

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Anesthetics can reversibly block electrical activity, and it appears that they span a large space of variety of chemical structures. The mechanism of action of local anesthetics was investigated in attempts to relate minimum blocking concentrations (MBC) of compounds to their polarizabilities and ionization potentials [1]. It was found that the logarithm of MBC, defined as the minimum anesthetic's concentration in the external solution necessary for complete block of membrane's excitability, is significantly correlated with a descriptor calculated as the product of polarizability and ionization potential of compounds. Later, Kier *et al.* [2] developed a very significant linear correlation of product-connectivity index [3] with polarizability and anesthetic activity expressed as log (MBC).

In this work we developed models of anesthetic activities starting from polarizability, ionization potentials and other enthalpy parameters that are indicators of reactivity a molecule, and compared them with the structure-activity models based on connectivity. These models were also compared with other models based on topological descriptors and we found that anesthetic activity of 39 compounds are strongly related to size-dependent descriptors. Based on these results, suggestion for selection of data set of compounds and their properties/activities that will be used in testing the validation of usefulness of novel descriptors are proposed.

- [1] D. Agin, L. Hersh, D. Holtzman, The action of anesthetics on excitable membranes: A quantum-chemical analysis. *Proc. Nat. Acad. Sci. (USA)*, **53** (1965) 952-958
- [2] L. B. Kier and L. H. Hall, Molecular connectivity I: Relationship to nonspecific local anesthesia. *J. Pharm. Sci.* **64** (1975) 1971-1974.
- [3] M. Randić, *J. Am. Chem. Soc.* **97** (1975) 6606-6615.

Workshop: Advanced statistical analysis of molecular dynamics data

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A molecular dynamics simulation provides a wealth of sampling information. These data can be used for identification of stationary points and determination of reaction pathways between *e.g.* conformers. The main problem in this type of analysis is the high dimensionality of the data, which is of order number-of-steps $\times 3N$ (N is the number of atoms in the system). 2nd order tensor decomposition methods can be used for reduction of dimensionality along one dimension (*way*). A series of molecular dynamics simulation started from different initial conditions will produce the 3rd order data tensor and much more information can be gained from it, but it requires higher order tensor decomposition tools. *Multi-way analysis* will be presented from theoretical background to application for molecular dynamics simulation data.

Please bring your laptop.

Workshop: Basic ideas in philosophy of chemistry

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Philosophy of chemistry appeared within the last thirty years as a subfield of philosophy of science. The basic general ideas which appeared during the development of chemical concepts will be presented: the problem of structure, the methods of analogy and systematizations, the origins of periodic system of chemical elements, the problem of chemical identity, as well as the modelling of electronic structure of molecules. The discussion will be extended to the concepts of complexity, reductionism-holism, emergence, and the position of chemistry between physics and biology.