



Professor Tadeusz Marek Krygowski

This special issue of *Polish Journal of Chemistry* appears on the occasion of the 70th birthday of Professor Tadeusz Marek Krygowski from the Department of Chemistry, of the University of Warsaw – one of the most outstanding Polish chemists and a distinguished scientist who has been working actively in various branches of physical organic chemistry such as electrochemistry, crystal chemistry or structural chemistry, as well as in specific problems, but still of the general importance, like aromaticity, inter- and intramolecular interactions in solid state and substituent effects, to mention just a few.

It is a great honor for me to be the editor of this special issue. As a one-time student of Professor T. M. Krygowski, I feel specially indebted to him who introduced me to the world of science, showed me how to be a researcher, outlined how to be a good scientist and, last but not least, touched me by his attitude to always behave ethically not only as concerns research but also in all kinds of human activities. It was at the beginning of the 1980s when I first met Professor T. M. Krygowski, first I attended his lectures and then in 1981, fascinated by his personality, I started to do my own research, as a PhD student under his guidance. Professor Krygowski taught me not only how to do the research, how to read and write scientific papers, how to struggle against scientific literature facts, how to find pearls inside them, but also, which was perhaps most important – he influenced me to try to be always creative and enthusiastic in science. Today, over twenty years later, I

have a position of full Professor at the University of Łódź and I am the leader of my own research group. All that I learnt from Professor Krygowski at that time, I try to convey to my students. What is important in this context, is that I still have a chance to enrich my experience, as I keep warm and direct contacts with the Professor. I highly appreciate His friendship, his readiness to offer generous help, his open-mindedness and kindness, but also his philosophy of life and sense of humor. During my visits to Warsaw I am truly grateful to Professor for uncountable discussions, fruitful cooperation, stimulating advice as well as critical and constructive comments, which concern not only scientific ideas and organizational matters but also some trivial problems of everyday life.

Tadeusz Marek Krygowski was born on April 27th 1937 in Poznań, Poland. His father Bogumił Krygowski was a Professor of Physical Geography at the University of Poznań. As a scientist he showed him how to do research and how to study science. Tadeusz Marek Krygowski was interested in chemistry very early, already in his teens he read for pleasure books on organic and inorganic chemistry. In 1955 he won the Polish Chemistry Olympics competition organized for students of high schools, that was the first chemistry Olympics organized in Poland in Katowice (at that time this city was called Stalinogród). He might have faced problems to start university studies because he refused to join the union of the communist youth (Związek Młodzieży Polskiej); however thanks to his great success in Chemistry Olympics competition he was admitted at the University of Poznań where he studied chemistry from 1956 to 1961 and graduated with the master's degree in chemistry. The title of his master thesis was "Synthesis of polymeric indicators of acidity co-condensed with formaldehyde". Then temporarily he came back to the interests of his school years and he worked for two years at the Academy of Mining and Metallurgy in Kraków doing research in geology and sedimentology. In 1964 Tadeusz Marek Krygowski decided to continue his research in chemistry and joined a research group led by Professor Wiktor Kemula at the Department of Chemistry, University of Warsaw. During that time Tadeusz Marek Krygowski worked on applications of quantum mechanics to chemistry problems, also on aromaticity, reactivity and stability of organic compounds as well as some other topics. His PhD thesis dealt with the influence of substituents on physicochemical properties of 9,10-anthraquinone derivatives.

After obtaining his PhD in 1969 Tadeusz Marek Krygowski started his own research connected with aromaticity, electroreduction, substituent and solvent effects as well as with aromatic compounds. He finished Habilitation on physical chemistry at the University of Warsaw in 1973 with a thesis entitled "Structural Aspects Observed in Physicochemical Properties of π -electron Compounds".

Since 1978 he has been the head of the laboratory of crystal chemistry at the University of Warsaw having the position of professor from 1983 and the position of full professor from 1991. He organized his own group of researchers working not only on crystal chemistry but also on other chemistry disciplines such as applied quantum chemistry, aromaticity, and many other areas, some of which were mentioned above. Such a broad range of topics considered by this group was connected with the broad interests of Professor T. M. Krygowski who as a scientist working with enthusiasm on chemistry in-

spired his young co-workers by his own example. As already mentioned, I had this good chance to be one of them. Already at that time Professor T. M. Krygowski was internationally recognized as an outstanding scientist and served as a visiting professor at the University of Guelph (Ontario, Canada), 1974/75. Then he was invited many times as a visiting professor, to mention Universite de Nantes, France, 1981, Johannes Kepler Universitaet, Linz/D, Austria, 1995, Ben Gurion University, BeerSheba, Israel, 1999, and recently Dong A University, Pusan, South Korea, 2003.

Professor Krygowski has also been very active in national and international scientific organizations. In 1977–1981 Professor T. M. Krygowski was a member of the Warsaw Division of the Polish Chemical Society. Then he worked as a Treasurer of the Society (1981–1984), the chairman of the Warsaw Division (1984–87) and the chairman of the Section of Crystallography (1988–1990). In 1992–1994, and 1994–1997 professor Tadeusz Marek Krygowski worked as a vice-president, and subsequently the president of the Polish Chemical Society, respectively. During his presidency and in cooperation with the German Chemical Society, Professor T. M. Krygowski together with Professor Z. Galus initiated the Maria Curie-Skłodowska – Wilhelm Klemm Lectures based on the exchange of Polish and German outstanding scientists for lectureships. A similar exchange program was organized by his inspiration with the French Chemical Society. Since 2004 Professor is a chairman of the section of Physical Organic Chemistry of the Polish Chemical Society and he was distinguished by this society as an Honorary Member. In the 1980s Professor T. M. Krygowski was among the founders of the International Group for Correlation Analysis in Chemistry, CAIC (since 2004 – Correlation and Modeling in Chemistry), an organization associated with the International Union of Pure and Applied Chemistry, while since 2004 he has been the President of the group. Since 2002 Professor T. M. Krygowski has been a Chairman of the Sub-committee of Structural and Mechanistic Organic Chemistry of IUPAC and Titular Member of the Division of Organic and Biomolecular Chemistry of IUPAC. In this field of activity he chaired three international conferences, which were organized in Poland: in 1988 CAIC-IV (Poznań), CAIC-IX in 2001 (Borówno) and in 2006 XVIII International IUPAC Conference on Physical Organic Chemistry in Warsaw. Professor T. M. Krygowski is also a member of the Editorial Board of *J. Phys. Org. Chem.*, *Arkivoc*, *Int. J. Mol. Sci.* and *Chemical Reactivity* (Tartu) and a member of the Advisory Board of *Chemical Papers*. He was also a guest editor of special issues of *J. Phys. Org. Chem.* and *Int. J. Mol. Sci.*, which were dedicated to outstanding scientists working in the field of physical organic chemistry and/or correlation analysis. As concerns his other activities in 1980–1982, Professor T. M. Krygowski was a Vice-Dean of the Department of Chemistry of the University of Warsaw whereas in 1991 he was a member of the advisory board of Lech Wałęsa during his presidential campaign – as a member of that board Professor T. M. Krygowski was responsible for matters concerning science and education.

There are also other activities of Professor T. M. Krygowski that are worth mentioning here: as a member of committee and of the presiding committee Poland 2000 of the Polish Academy of Sciences in 1989–1991 and 1991–1993, respectively; a member of Science Board of the Exams' Commission of the minister of education (1999–2001).

Since 1987 Professor T. M. Krygowski has been a real member of the Warsaw Scientific Society (by election).

Professor T. M. Krygowski is a leader of a small but very effective group of smart, talented and engaged researchers. Under his supervision 8 students graduated with PhD, three of them received degrees of habilitated doctors and are now professors: Professor Krzysztof Woźniak works in the Department of Chemistry of the University of Warsaw, Professor Ilona Turowska-Tyrk works in Wrocław University of Technology, the author of this preface (Sławomir J. Grabowski) is Professor in the University of Łódź, Michał Cyrański (PhD) is very close to habilitation (it is very probable that by the appearance of this issue he will have obtained the degree of habilitated doctor).

Professor T. M. Krygowski is the author of 238 papers and about 40 reviews (23 of them in English in peer-reviewed international journals), and among them 3 reviews appeared in *Chemical Reviews* journal. Most of his papers were produced in cooperation with other eminent researchers both in Poland and abroad. The joint projects were carried out (among others) with: K. Albert (Germany), C. W. Bird (UK), C. W. Bock (USA), R. Boese (Germany), G. J. Bodwell (Canada), S. Daehne (Germany), N. J. N. van Eikemma Hommes (Germany), O. Exner (Czech Republic), W. R. Fawcett (Canada, USA), L. Fisera (Slovakia), P. W. Fowler (UK), M. Fujio (Japan), P. George (USA), G. Häfelinger (Germany), T. Hanafusa (Japan), P. C. Hiberty (France), P. Hobza (Czech Republic), S. T. Howard (UK), L. W. Jenneskens (Netherlands), W. Jones (UK), K. Jug (Germany), A. R. Katritzky (USA), J. Klinowski (UK), E. Kolehmainen (Finland), A. Kotschy (Hungary), A. Krutosikova (Slovakia), J. Kuthan, (Czech Republic), C. Laurence (France), H.-H. Limbach (Germany), K. Nakata (Japan), Y. Ohashi (Japan), P.-L. Orioli (Italy), A. Perjessy (Slovakia), P. von Rague Schleyer (USA), W. H. E. Schwarz (Germany), M. Sawada (Japan), M. Sola (Spain), D. D. Sung (Korea), Ch. Reichardt (Germany), D. Topsom (Australia), Y. Tsuno (Japan), B. Wojtkowiak (France).

In Poland Prof. Krygowski has established cooperation, among others, with the following researchers: R. Anulewicz., A. Ciesielski, M. K. Cyrański, Z. Czarnocki, T. Drapała, A. T. Dubis, T. Dziembowska, K. Ejsmont, S. Filipek, Z. Galus, R. Gawinecki, M. Gdaniec, M. Główska, S. J. Grabowski, A. Graja, E. Grech, J. Izdebski, T. Jagodziński, A. Jarmuła, M. Jaskólski, J. S. Jaworski, J. B. Kamiński, J. Karolak-Wojciechowska, M. K. Kalinowski, W. Kemula, Z. Kisiel, J. Konarski, W. Kołodziejwski, J. Kruszewski, M. Kryszewski, B. Krygowski, J. Maurin, I. D. Madura, P. Milart, J. Młochowski, R. Moszyński, J. Nowacki, B. Ośmiałowski, M. Palusiak, H. Piekarski, B. Pniewska, E. D. Raczyńska, D. Rasała, W. Rode, L. Sobczyk, B. T. Stępień, H. Szatyłowicz, S. Taniewska-Osińska, A. Temeriusz, P. Tomasiak, I. Turowska-Tyrk, I. Wawer, S. Witkowski, K. Woźniak, P. Wrona, J. E. Zachara-Horegląd, R. I. Zalewski and K. Zborowski.

The scientific interests of Professor Krygowski involve the following topics: sedimentology (1960s), solvent and substituent effects in electrochemistry (1960s and 70s), since the 1970s solvent and substituent effects on physicochemical properties of organic systems, modeling of physicochemical properties and structural consequences

of intra- and intermolecular interactions (oriented mostly towards the investigations of hydrogen bonds in model organic systems), the definition of aromaticity and application of statistics in chemistry.

In these fields we can point out the following achievements: the development of the concept of the Lewis acid-base amphoteric properties of solvents; estimation of the magnitude of the intramolecular and intermolecular charge transfer by analysis of deviations of the Bent-Walsh rule; the invention of the empirical model allowing one to establish the canonical structure weights and resonance energy from bond lengths of the π -electron systems or their fragments – the HOSE model; development of the definition of aromaticity based on geometric criteria – the HOMA model – this model has frequently been used for comparisons with the other definitions of aromaticity; HOMA is also a commonly known index applied to analyze the most important π -electronic systems such as fullerenes, benzenoid moieties, heterocyclic π -electron systems, porfirines, DNA and RNA bases *etc.*, demonstration of the factors influencing a decrease of the π -electron delocalization: the bond lengths alternation and the bond elongation; the discovery of a new kind of substituent effect (called AGIBA from Angular Group Induced Bond Alternation) observed in geometry of the substituted cyclic π -electron systems; the discovery of a new type of interrelations between the H-bond and the properties of moieties involved in this interaction, and long distance structural consequences of H-bonding.

This special issue of *Polish Journal of Chemistry* honoring the 70th birthday of Professor T. M. Krygowski includes 47 contributions written by his friends, co-workers and former students. The very number of papers reflects the major impact exerted by Professor T. M. Krygowski on modern physical organic chemistry and related fields of study, as well as the importance of his ideas and research work.

As the editor of this special issue I would like to thank all the authors who contributed in the project for accepting the invitations and for providing the issue with valuable papers.

On behalf of all of us let me express to Professor Tadeusz Marek Krygowski our most sincere wishes of further constant success, happiness and joy both in his private life and professional life, as well as of good health and always having many friendly people around.

Sławomir J. Grabowski

Stabilization of W^{VI} in Nitride Environment *via* Acid/Base Reactions, and General Route to Layered Transition Metal Nitrides

by W. Grochala^{1,2}

¹*Department of Chemistry, Warsaw University, Pasteur 1, 02-093 Warsaw, Poland*

²*Interdisciplinary Center for Mathematical and Computational Modeling, Warsaw University,
Pawińskiego 5a, 02-106, Warsaw, Poland, e-mail wg22@cornell.edu*

(Received July 18th, 2006)

DFT calculations for two hypothetical ternary nitrides of hexavalent tungsten: $LaWN_3$ and La_2WN_4 (in perovskite and K_2NiF_4 structures, respectively) show that these compounds should spontaneously form from WN_2 (acid) and LaN (base) reagents, or simply from $(WN + 1/2 N_2)$ or $(W + N_2)$ and LaN , at ambient or elevated temperature and high N_2 pressure to speed up the reactions. This concept may be utilized to stabilize other efemeric nitrides, like these of Re^{VII} , Os^{VIII} , and possibly even of unprecedented Ir^{IX} . La_2WN_4 is example of rare two-dimensional nitride materials. Band structure calculations confirm that $LaWN_3$, La_2WN_4 and several related compounds should exhibit metallic conductivity, and they show good prospect for 2D superconductivity *via* self-doping.

Key words: crystal structures, nitrides, polymorphism, transition metals, superconductivity

A Theoretical Study of Chiral Recognition in Bis[amino(phenyl)methanol]chromium(0) Complexes

by **K. Zborowski**¹, **I. Alkorta**² and **J. Elguero**²

¹*Faculty of Chemistry, Jagiellonian University, 3 Ingardena Street, 30-060 Krakow, Poland*

²*Instituto de Química Médica (C.S.I.C.), Juan de la Cierva, 3, 28006-Madrid, Spain
e-mail: ibon@iqm.csic.es*

(Received July 17th, 2006; revised manuscript September 3rd, 2006)

A theoretical study of the complexes formed by the chiral α -amino- α -phenylmethanol in the presence and absence of a chromium(0) atom has been carried out. The results indicate that in the presence of chromium, the most stable complex corresponds to that where the two amino(phenyl)-methanol molecules have the same chirality while in the absence of the mentioned atom the preferred one is that with the two molecules with different chirality.

Key words: bis(benzene)chromium, chiral recognition, hydrogen bonds, DFT

[2+3]-Cycloadditions of Diazoalkanes with Imines of Hexafluoroacetone and Chloral

by G. Mloston¹, A. Bodzioch¹, Z. Cebulska¹, A. Linden²
and H. Heimgartner^{2**}

¹*Section of Heteroorganic Compounds, University of Lodz, Narutowicza 68, PL-90-136 Lodz, Poland
e-mail: gmloston@uni.lodz.pl*

²*Institute of Organic Chemistry, University of Zurich, Winterthurerstrasse 190,
CH-8057 Zurich, Switzerland*

(Received September 13th, 2006)

The reactions of *N*-arylimines **1** and **2** of hexafluoroacetone and chloral, respectively, with diazoalkanes at -60°C to room temperature led to the corresponding 4,5-dihydro-1*H*-[1,2,3]triazoles **4** and **5**, in a regioselective [2+3]-cycloaddition. The structure of one example in each case has been established by X-ray crystallography. The thermal decomposition of these adducts yielded the corresponding aziridines, bearing two trifluoromethyl and one trichloromethyl group, respectively, at C(2).

Key words: 1,3-dipolar cycloaddition, imines, 4,5-dihydro-1*H*-[1,2,3]triazoles, aziridines, crystal structure

Structure and Vibrational Spectra of the 1:1 Squaric Acid (H₂SQ) – Tetramethylpyrazine (TMP) Adduct

by J. Nowicka-Scheibe¹, E. Grech¹, W. Sawka-Dobrowolska²,
G. Bator² and L. Sobczyk²

¹*Institute of Chemistry and Environmental Protection, Szczecin University of Technology,
Al. Piastów 12, 71-065 Szczecin, Poland*

²*Faculty of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383 Wrocław, Poland
e-mail: sobczyk@wchuwr.chem.uni.wroc.pl*

(Received July 11th, 2006; revised manuscript September 18th, 2006)

The crystal structure of the title complex was determined at 100 K by X-ray diffraction. It consists of double ionized dimeric (HSQ)₂⁻² species and protoned TMP-H⁺ cations. Strong charge assisted (OHO)⁻ and (NHO)⁺ hydrogen bonds are the main factor of crystal packing. A wealth of unconventional C–H...O and C–H...N relatively short bridges should be emphasized. Particularly important are the latter ones binding two adjacent TMPH⁺ cations. The structure is well manifested in the IR and Raman spectra, particularly in the region of $\nu(\text{OH})$ and $\nu(\text{NH})$ as well as of $\nu(\text{C}=\text{O})$ frequencies. The complexation of TMP leads to a marked change in the low and high frequency vibrations of the methyl groups. An anomaly on the DSC runs has been found at 163/175 K (cooling/heating) which can be assigned to the freezing of the methyl group rotations. No change of the crystal symmetry is observed at this temperature.

Key words: squaric acid, tetramethyl pyrazine, crystal structure, vibrational spectra

Patterns of Counter-Rotating Ring Currents in Two Valence Isomers of Corazulene

by M. Lillington¹, P.W. Fowler¹ and M.V. Diudea²

¹*Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, UK*

e-mail: P.W.Fowler@sheffield.ac.uk

²*Faculty of Chemistry and Chemical Engineering, "Babes-Bolyai" University, 400028 Cluj, Romania*

(Received June 12th, 2006; revised manuscript September 29th, 2006)

Current-density maps computed in the ipsocentric approach are presented for two isomeric polycyclic systems: corazulene (**1**) in which four azulene units are fused around a central square, and cornaphthalene (**2**) in which the azulene units of **1** are replaced by naphthalenes. Both show a strong central paratropic current on the square. Whereas **1** presents concentric counter-rotating rim-and-hub currents, **2** shows a 'Clar-like' structure of diatropic currents on the four outer hexagonal rings. Partition of the total current into orbital contributions, both canonical and localized, gives a clear rationale for the appearance of the maps.

Key words: aromaticity, ring current, *ab initio*

Statistical Analysis of Consequences of *peri*-Interactions in 1-Si, 8-N- (and 1-X, 8-Y-) Substituted Naphthalenes

by P.M. Dominiak¹, G.P. Schiemenz² and K. Woźniak¹

¹Chemistry Department, Warsaw University, 02 093 Warsaw, Pasteura 1, Poland
e-mail: kwozniak@chem.uw.edu.pl

²Institute of Inorganic Chemistry, University of Kiel, D-24098 Kiel, Germany

(Received October 2nd, 2006)

A statistical analysis of geometrical parameters for 1-Si, 8-N-substituted naphthalenes retrieved from the CSD revealed three factors describing structural consequences of *peri* interactions in such derivatives. The most important of them is an *in-plane* deformation which may be estimated by a linear combination of several geometrical parameters of the naphthalene fragment. It is best approximated by values of splay angles. The second consequence is an *out-of-plane* deformation formally defined by all torsion angles. It is well approximated by the Si–C(1)...C(8)–N torsion angle. The third factor can be associated with substituent effects and it manifests itself mainly by changes of C_{ar}–N/Si bond lengths and their *ipso* angles. Similar analysis performed for a more general data set consisting of 1-X, 8-Y-disubstituted naphthalenes fully supports the above interpretation. The *peri* X...Y distance (PD) can be expressed as linear combinations of the factors obtained, which leads to a multiple regression line with the value of the free term very close to PD and coefficients being relative weights of particular factors. It appears that *in plane* deformation contributes to the d(X...Y) distance far more significantly than the other factors.

Key words: factor analysis, *peri*-naphthalenes, steric effects, multiple regression, substituent effects

The Properties of the Dihydrogen-Bonded Dimer $(\text{BH}_3\text{NH}_3)_2$

by H. Cybulski and J. Sadlej

Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland

***e-mail: sadlej@chem.uw.edu.pl*

(Received October 3rd, 2006)

The energetic and spectroscopic properties of the dihydrogen-bonded dimer $(\text{BH}_3\text{NH}_3)_2$ with the B–H bonds as proton acceptors and the N–H bonds as proton donors were calculated by means of the second-order Møller-Plesset perturbation theory and density functional theory methods. The C_{2h} head-to-tail structure with four equivalent dihydrogen bonds was found to be the most stable one. The symmetry-adapted perturbation theory calculations showed that $(\text{BH}_3\text{NH}_3)_2$ dimer is bonded by electrostatic-induction-dispersion interactions and the interaction energy decomposition is comparable with this calculated for water dimer. The protons acting as proton donors are deshielded while the protons acting as proton acceptors are shielded upon dimer formation. The one-bond dihydrogen-bond transmitted proton-proton coupling constant has a noticeable value of -1.9 Hz. Among the three-bond dihydrogen-bond transmitted reduced coupling constants the largest one is the coupling between nitrogen and boron nuclei with a value of $5.6 \cdot 10^{19} \cdot \text{T}^2 \cdot \text{J}^{-1}$.

Key words: dihydrogen bond, SAPT calculations, coupling constant, shielding constant, ammonia-borane

Magnetic Resonance Energies of Polycyclic Aromatic Hydrocarbon Molecular Ions

by T. Ishida¹, H. Kanno² and J. Aihara^{2**}

¹*Fukui Institute for Fundamental Chemistry, Kyoto University, Takano-Nishibirakicho,
Kyoto 606-8103, Japan*

²*Department of Chemistry, Faculty of Science, Shizuoka University, Oya, Shizuoka 422-8529, Japan,
**e-mail: scjaiha@ipc.shizuoka.ac.jp*

(Received October 9th, 2006)

Magnetic resonance energy (MRE), derived from the magnetic response of a cyclic π -system, is the first aromatic stabilization energy that does not rely on any hypothetical reference system. MREs for all possible molecular ions of typical polycyclic aromatic hydrocarbons (PAHs) were calculated and characterized. It was found that for all aromatic PAH molecular ions, MRE is highly correlative with topological resonance energy (TRE).

Key words: aromaticity, polycyclic aromatic hydrocarbon, magnetic resonance energy, circuit resonance energy

Charge Localization in Monothiophosphate Monoanions

by M. Rostkowski and P. Paneth

*Institute of Applied Radiation Chemistry, Technical University of Łódź,
Żeromskiego 116, 90-924 Łódź, Poland
e-mail: paneth@p.lodz.pl*

(Received October 10th, 2006)

We have examined charge distribution between exocyclic oxygen and sulfur atoms in 5,5-dimethyl-1,3,2-dioxaphosphorinan-2-oxy-2-thio monoanion. Our results indicate that while solvent polarity and substituents have minor effect, the presence of a counter-ion results in relative increase of the partial atomic charge on the oxygen atom. Thus it seems that change in the reactivity of this anion observed experimentally can be ascribed to ion pairing in low polarity solvent.

Key words: monothiophosphates, partial atomic charges, DFT

Five-Membered Heterocycles. Part V. Impact of Heteroatoms on Aromaticity of Five-Membered Heterocycles

by A. Mrozek and J. Karolak-Wojciechowska

*Institute of General and Ecological Chemistry, Technical University of Łódź,
Żeromskiego 116, 90-924 Łódź, Poland
e-mail: agnieszka.mrozek@p.lodz.pl*

(Received October 10th, 2006)

The aromaticity (in the form of HOMA index) of various five-membered heterorings systems and their bicyclic derivatives containing N, S, O, and P were studied on the basis of statistical data from Cambridge Structural Database (CSD). The calculations of HOMA were done for pyrroles, furans, thiophenes, phospholes, imidazoles, oxazoles, thiazoles, phosphazoles as well as for 6 + 5 fused systems: benzimidazoles, benzoxazoles, benzothiazoles, and benzophosphazoles. Detailed analysis showed that relationship between classical aromaticity and electronegativity of heteroatom is described by squared equation. An optimal value of electronegativity is about 2.9 (Pauling's scale) for which aromaticity of heterorings reaches the highest level. For fused systems, the presence of benzene ring causes the evident increasing of average value of HOMA indices.

Key words: heteroaromaticity, electronegativity, HOMA, CSD

Alternate Copolymer of 3,4-Dioctyloxythiophene and 2,2'-Bithiophene: Synthesis, Electronic and Spectroelectrochemical Properties

by R. Pokrop¹, I. Kasprzyk-Młynarczyk¹, M. Zagorska^{1**}, I. Wielgus¹, J. Mieczkowski^{2,3}, J.M. Verilhac⁴, J. Wery⁵, G. Louarn⁵ and A. Pron⁶

¹*Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland*

²*Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland*

³*Institute of Chemistry, Military University of Technology, 00-908, Warsaw, Poland*

⁴*CEA Liten-DTNM-LCH, 17 rue des Martyrs, 38054 Grenoble, Cedex 9, France*

⁵*Institut des Matériaux Jean Rouxel (IMN), 2 rue de la Houssinière, 44322 Nantes, France*

⁶*CEA DRFMC, UMR 5819-SPRAM (CEA-CNRS-Univ. J. Fourier-Grenoble I), 17 rue des Martyrs, 38054 Grenoble Cedex 9, France, E-mail: adam.pron@cea.fr*

(Received October 16th, 2006)

A new electroactive polymer has been prepared by oxidative (electrochemical or chemical) polymerization of 3',4'-dioctyloxy-2,2':5',2''-terthiophene. The polymer (**PDOIT**) is photoluminescent, emitting green light in solution and red light in the solid state. It can be used for the fabrication of organic field effect transistors, however the measured charge carriers mobilities in the transistor configuration ($\mu = 7 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) are lower than those found for the best polymers reported in the literature. **PDOIT** is much more promising for electrochemical and electrochromic applications since it shows perfectly reversible spectral response to potential switching. Moreover, in its doped state **PDOIT** is a strong near infrared absorber.

Key words: conjugated polymers, poly(3',4'-dioctyloxy-2,2':5',2''-terthiophene), UV-vis-NIR spectroelectrochemistry, Raman spectroelectrochemistry, organic field effect transistor

How the Bonding Mode in Cyclopentadienylaluminum Complexes Influences the Cp⁻ Ligand Aromaticity

by J. Zachara **, I.D. Madura and A.R. Kunicki

Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

***e-mail: janzac@ch.pw.edu.pl*

(Received October 16th, 2006)

The substantial influence of floating Cp–Al bond-modes from $\eta^5(\pi)$ to $\eta^1(\sigma)$ on the Cp⁻ ligand's aromaticity was discussed basing on the crystal data of organoaluminum complexes and DFT calculations (B3LYP/6-311G**) performed for model compounds. The aromaticity of cyclopentadienyl moiety was characterized by the HOMA index. The spread of HOMA values from 0.8 to –0.5 indicated the electronic structure of the cyclopentadienyl ligand bonded to aluminum center can be regarded as an intermediate between the highly aromatic, uncomplexed cyclopentadienyl anion Cp⁻ and the antiaromatic structure of cyclopentadiene CpH.

Key words: aromaticity, cyclopentadienyl, aluminum, DFT

Hydrogen Bonds in Boronic Acids and Their Complexes

by **A. Sporzyński**

*Faculty of Chemistry, Warsaw University of Technology,
Noakowskiego 3, 00-664 Warsaw, Poland
E-mail: spor@ch.pw.edu.pl*

(Received October 21st, 2006)

The structures of arylboronic acids, $\text{ArB}(\text{OH})_2$, are reviewed. These structures are different depending on the substituents in the aromatic ring. The main types of such forms are hydrogen-bonded dimers and chains in which the second B-OH group forms a hydrogen bond with donor atom. Diboronic acids form two-dimensional networks. The presence of an electron donor group in *ortho* position usually leads to the formation of intramolecular hydrogen bond, but in some cases intermolecular interactions are also observed. Heterodimers with anions of carboxylic acids and with amino acids are the stable complexes, in opposite to the complexes with monofunctional Lewis bases.

Key words: boronic acids, hydrogen bond, substituent effect, complexes with Lewis bases

Infrared and Raman Intensities in Proper and Improper Hydrogen-Bonded Systems

by M. Jabłoński and A.J. Sadlej**

*Department of Quantum Chemistry, Institute of Chemistry,
Nicolaus Copernicus University, Gagarina 7, PL-87 100 Toruń, Poland,*

** e-mail: teoajs@chem.uni.torun.pl

(Received October 27th, 2006)

The IR intensities and Raman activities of the C–H stretching mode as well as some other spectroscopic and structural features of NCH...NCH and F₃CH...NCH are calculated in the MP2 approximation with a variety of correlation consistent basis sets. In agreement with earlier studies the traditional hydrogen bond in NCH...NCH results in the elongation of the C–H bond distance in the proton donor and the red shift of the corresponding vibration frequency. The opposite changes are found in F₃CH...NCH. The IR intensity of the C–H stretching band in the NCH...NCH dimer markedly increases whereas for the blue-shifting F₃CH...NCH complex the IR intensity of the corresponding band is significantly reduced. The Raman activity of the C–H stretching band in both investigated complexes increases upon the hydrogen bond formation. These results are analysed in terms of the interaction induced dipole moments and polarizabilities, and their derivatives with respect to the C–H bond distance. The difference between IR intensities of the C–H stretching band calculated for NCH...NCH and F₃CH...NCH is, however, a particular feature of the F₃CH...NCH complex and cannot be used to distinguish between traditional and improper hydrogen bonds. Neither the Raman activities offer such a possibility. The present study of interaction induced properties shows that the blue shift of the X–H frequency in systems with improper hydrogen bonds is primarily due to particular features of the electronic structure of the proton donor.

Key words: hydrogen bonding, improper hydrogen bonds, IR intensities, Raman activities

Is the Aromaticity of the Benzene Ring in the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ Complex Larger than that of the Isolated Benzene Molecule?

by F. Feixas¹, J.O.C. Jiménez-Halla¹, E. Matito^{1,2}, J. Poater³ and M. Solà¹

¹*Institut de Química Computacional and Departament de Química, Universitat de Girona, 17071 Girona, Catalonia, Spain*
e-mail: miquel.sola@udg.es

²*Institute of Physics, Szczecin University, 70-451 Szczecin, Poland*

³*Afdeling Theoretische Chemie, Scheikundig Laboratorium der Vrije Universiteit, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands*

(Received October 27th, 2006)

The aromaticity of the benzene ring in the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ complex is analyzed using several indicators of aromaticity based on different physical manifestations of this property. All indices used except NICS show that there is a clear reduction of the aromaticity of benzene upon coordination to the $\text{Cr}(\text{CO})_3$ complex. The particular behavior of the NICS index has been analyzed in detail and we have concluded that the reduction of the NICS value in the benzene ring of the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ complex is not a manifestation of an increased aromaticity but is due to the ring currents generated by the electron pairs that take part in the benzene– $\text{Cr}(\text{CO})_3$ bonding.

Key words: aromaticity, benzene, $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ complex, Nucleus-Independent Chemical Shift (NICS), *Para*-Delocalization Index (PDI), Harmonic Oscillator Model of Aromaticity (HOMA), Aromatic Fluctuation Index (FLU), Six Center Index (SCI), Atoms in Molecules (AIM) Theory

Intramolecular O–H...O Hydrogen Bonds – the Influence of External Agents on Their Properties

by S.J. Grabowski**

Department of Physics and Chemistry, University of Łódź,

Pomorska 149/153, 90 236 Łódź, Poland

***e-mail: slagra@uni.lodz.pl*

(Received October 31st, 2006)

Intramolecular O–H...O hydrogen bond in malonaldehyde is analyzed. *Ab initio* MP2/6-311++G(d,p) calculations were carried out for this isolated moiety as well as for malonaldehyde assisted by external systems: Li⁺, Na⁺ ions and HF molecule. The latter moieties act as Lewis acids interacting with the oxygen carbonyl atom or with the oxygen hydroxyl atom. The influence of these external agents on the characteristics of H-bond, the π -electron delocalization within six-member pseudo-ring and on the proton transfer process is also analyzed. The Bader theory is also applied to characterize intramolecular O–H...O hydrogen bond.

Key words: malonaldehyde, intramolecular OH...O hydrogen bond, bond critical point, ring critical point, the Bader theory, proton transfer process, MP2 calculations, π -electron delocalization

**Monitoring Structural Transformations in Crystals.
Part 10. Monitoring Molecular and Crystal Structures
During a Yang Photocyclization Reaction
– Comparative Studies**

by **I. Turowska-Tyrk¹**, **I. Łabęcka¹**, **J.R. Scheffer²** and **W. Xia^{2,3}**

¹*Department of Chemistry, Wrocław University of Technology,
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
e-mail: ilona.turowska-tyrk@pwr.wroc.pl*

²*Department of Chemistry, University of British Columbia, 6174 University Blvd.,
Vancouver, British Columbia, Canada V6T 1Z3*

³*Research Academy of Science & Technology, Harbin Institute of Technology,
Harbin, 150080, People's Republic of China*

(Received November 2nd, 2006)

Structural changes in a crystal, brought about by the Yang photocyclization of the 2-(4-carboxybenzoyl)-2-methyl-*endo*-bicyclo[2.1.1]hexyl salt with (*S*)-(-)-1-phenylethylamine, were monitored by means of X-ray structure analysis. The changes taking place in the reaction centre, as well as changes in molecular orientation and cell constants are discussed. Analysis of the geometrical parameters describing the reaction centre enabled an evaluation of the possibility of formation of the opposite enantiomer in a crystal. The results are compared with data for other intramolecular photochemical reactions.

Key words: crystals, photochemical reactions, X-ray structure analysis

**Conformation, Hydrogen Bonds and
Their Effects on the Packing of
Phenol, 2,2'-bis-[1,3-phenylenebis(methylidynenitrilo)] and
Phenol, 2,2'-bis-[2,5-thiophenediylbis(methylidynenitrilo)]**

by **N. Fridman and M. Kaftory**^{**}

Department of Chemistry, Technion – Israel Institute of Technology, Haifa 32000, Israel

***e-mail: kaftory@tx.technion.ac.il*

(Received September 25th, 2006; revised manuscript November 5th, 2006)

The crystal structure of phenol, 2,2'-bis-[1,3-phenylenebis(methylidynenitrilo)] (**1**), and phenol, 2,2'-bis-[2,5-thiophenediylbis(methylidynenitrilo)] (**2**) are described with connection to the effect of hydrogen bonding on the molecular conformation and on the packing of molecules in the unit cell. The conformation is compared to the conformation observed in similar compounds. The geometric parameters of hydrogen bonding between hydroxyl groups are analyzed from crystallographic data provided by the Cambridge Crystallographic Data Center.

Key words: conformation, hydrogen bonds, molecular packing

On Barrier Formation of Long-Lived Doubly Charged Benzene Dimer

by E.S. Kryachko**

Department of Chemistry, Bat. B6c, University of Liege, Sart-Tilman, B-4000 Liege 1, Belgium and Bogoliubov Institute for Theoretical Physics, Kiev, 03143 Ukraine

***e-mail: eugene.kryachko@ulg.ac.be*

(Received November 6th, 2006)

It has recently been demonstrated [*J. Am. Chem. Soc.*, **127**, 16824 (2005) Ref. [30]] that a fused carbon–carbon bond appears in the long-lived dicationic states of the benzene dimer to defy the law of Coulomb repulsion between like charges. The present work sheds a light on the formation of a high Coulomb barrier that separates the usual fission reaction pathway on the potential energy surface of the doubly-charged benzene dimer from the fusion one and renders the dicationic benzene dimer with a fused interring bond a substantial lifetime. For this purpose, a high computational levels is invoked in the present work to demonstrate that a variety of the lower-energy structures of the benzene dimer cation are mainly determined by their origin, either by the compressed-obtuse or elongated-acute ground-state conformers of the benzene cation radical and also includes two novel saddle homodimers. The latter, being ionized, form the striking patterns on the dicationic potential energy surface yielding thus the Coulomb barrier which is the rate-limiting step in formation of the fused C–C interring bond.

Key words: benzene, benzene dimer, benzene dimer cation, doubly charged benzene dimer, Coulomb repulsion, Coulomb barrier, lifetime

Cyclic Voltammetric, Chronoamperometric and Quartz Crystal Microbalance Study on Hydrogen Absorption into and Dissolution of Pd and Pd-noble Metal Alloys

by **M. Łukaszewski**¹ and **A. Czerwiński**^{1,2}

¹*Warsaw University, Department of Chemistry, Pasteura 1, 02-093 Warsaw, Poland*

***e-mail: aczerw@chem.uw.edu.pl*

²*Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland*

(Received September 13th, 2006; revised manuscript November 7th, 2006)

Hydrogen absorption into and electrochemical dissolution of thin Pd and Pd alloy (Pd–Au, Pd–Rh) layers have been studied in acidic solutions (0.5 M H₂SO₄) with the use of cyclic voltammetry (CV) and chronoamperometry (CA) coupled with the electrochemical quartz crystal microbalance (EQCM). Currents due to hydrogen adsorption and absorption in α - and β -phase are distinguished on CV curves. The amount of absorbed hydrogen depends on electrode potential and increases with the potential decrease. Hydrogen absorbed in Pd–Au and Pd–Rh alloys is oxidized at a lower potential than in the case of pure Pd. In the case of the Pd–Au system the potential region of phase transition is shifted positively in comparison with Pd indicating higher stability of the β -phase, while for the Pd–Rh system the potential region of phase transition is shifted negatively indicating lower stability of the β -phase. Hydrogen absorption is accompanied by stresses inside Pd crystal lattice, both phenomena affecting the EQCM response. EQCM experiments indicate that the magnitude and distribution of stresses are different for absorption and desorption processes, which seems to confirm the important role of the stress effect in the phenomenon of absorption/desorption hysteresis. Pd dissolves electrochemically during polarization to sufficiently high potentials in a CV experiment. The amount of dissolved metal increases with an increase in electrode potential and a decrease in scan rate. Due to Pd preferential dissolution during potential cycling of Pd–Au alloys both cyclic voltammogram and frequency-potential response transform towards curves typical of Au electrode.

Key words: palladium, palladium alloys, hydrogen absorption, hysteresis, stress, electrochemical dissolution, electrochemical quartz crystal microbalance

Gas-phase Enthalpies of Formation of Tri-, Tetra- and Pentachloroanilines: Combined DFT and Experimental Study

by M.A.V. Ribeiro da Silva, L.M.P.F. Amaral and J.R.B. Gomes

*Centro de Investigação em Química, Departamento de Química, Faculdade de Ciências,
Universidade do Porto, Rua do Campo Alegre, 687, P-4169-007, Porto, Portugal
**e-mail: risilva@fc.up.pt*

(Received September 28th, 2006; revised manuscript November 7th, 2006)

The gas-phase standard molar enthalpy of formation, at $T = 298.15$ K, of the 2,3,5,6-tetrachloroaniline was derived as $-(10.6 \pm 3.2)$ kJ·mol⁻¹ from the enthalpies of combustion of the crystalline solid, measured by rotating-bomb combustion calorimetry, and its enthalpy of sublimation obtained by Calvet microcalorimetry. The standard molar enthalpies of formation of all the isomers of the trichloro-, tetrachloro- and pentachloroaniline were calculated by computational thermochemistry based on a Density Functional Theory approach. The calculated values show a good agreement with the experimental results available for some of those isomers.

Key words: chloroanilines, thermochemistry, enthalpies of formation, enthalpies of sublimation, combustion calorimetry, Calvet microcalorimetry, computational thermochemistry

Centrohexaindanes Bearing Methyl Groups in Their Molecular Propellane Cavities

by **D. Kuck, T. Hackfort, B. Neumann and H.-G. Stammler**

Department of Chemistry, Bielefeld University, Universitätsstraße 25, D-33615 Bielefeld, Germany
e-mail: dietmar.kuck@uni-bielefeld.de

(Received September 29th, 2006; revised manuscript November 7th, 2006)

The syntheses of two new centrohexaindane derivatives bearing methyl groups in their molecular propellane-type cavities are described. These new topologically non-planar hydrocarbons, 1,8-dimethylcentrohexaindane **6** and 1,4,8,28-tetramethylcentrohexaindane **7** were obtained from suitable 1,3-indanediones following the shortest *aufbau* strategy, the propellane route, representing a six-step access to these unusually highly condensed polycyclic hydrocarbons. X-ray single crystal structure analysis of **6** revealed that the presence of the two methyl groups in the cavities of the centrohexaindane framework does not give rise to significant distortion of the T_d -symmetrical molecular skeleton; however, their efficient hiding within two of the four equivalent cavities allows for strong intermolecular disorder in the crystal.

Key words: topology, three-dimensional frameworks, concave molecules, cyclization reactions, indane derivatives, propellanes, triquinacenes, fenestranes

Synthesis and $^1\text{H-NMR}$ Characterization of the Self-Assembly Based on Melamine – 5,5'-Diethylbarbituric Acid

by A. Pokrop¹, P. Lipkowski² and J. Jurczak^{1,2}

¹*Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*

²*Institute of Organic Chemistry, Polish Academy of Science, Kasprzaka 44/52, 01-224 Warsaw, Poland*
e-mail: jurczak@icho.edu.pl

(Received October 9th, 2006; revised manuscript November 8th, 2006)

This paper describes the results of systematic studies of various parameters which are responsible for the hydrogen-bond stabilization of self-assemblies based on melamine and 5,5'-diethylbarbituric acid. The 1:1 self-assembly is exemplified by eight supramolecular aggregates. In these aggregates, two molecules of the starting materials are joined by six hydrogen bonds. A correlation between the size of the substituents and the preorganization of the precursors and the stability of the derived aggregates is discussed. The $^1\text{H-NMR}$ spectroscopy observations indicate that the aggregate comprising a short, flexible spacer with oxygen present in the carbon chain has the most stable structure in the solution.

Key words: self-assembly, melamine, barbituric acid, hydrogen bonds

π -Electron Communication Through the Metal Valence Shell – W, Mo and Fe Complexes Containing Maleimidato Moiety

by M. Palusiak

Department of Crystallography and Crystal Chemistry,
University of Łódź, Pomorska 149/153, 90-236 Łódź, Poland
e-mail: marcinp@uni.lodz.pl

(Received September 24th, 2006; revised manuscript November 13th, 2006)

The characterization of carbonyl–metal and maleimidato–metal bonding has been performed using the topological analysis of electron distribution function estimated for molecules of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3(\eta^1\text{-N-maleimidato})$ ($\text{M} = \text{W}, \text{Mo}$) and $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-N-maleimidato})$. The Atoms in Molecules (AIM) approach has been applied for characterization of σ and π -components of the metal–ligand bonds. The π -electron communication between *trans*-placed ligands is present in W and Mo derivatives. The *ellipticity* parameter is suggested to be a useful and highly sensitive parameter in the analysis of the metal–ligand bonding

Key words: *trans*-effect, organometallic complexes, DFT, AIM

Analysis of Electron Density in *trans*-N,N'-Bis-(R-salicylidene)-1,2-cyclohexanediamines

by T. Dziembowska¹ and I. Majerz²

¹*Institute of Chemistry and Environmental Protection, Szczecin University of Technology,
Al. Piastów 42, PL-71065, Poland
e-mail: terd@ps.pl*

²*Institute of Chemistry, University of Wrocław, Joliot-Curie 14, PL-50383 Wrocław, Poland*

(Received October 9th, 2006; revised manuscript November 13th, 2006)

The hydrogen bonds in three tautomeric forms of *trans*-N,N'-bis-(R-salicylidene)-1,2-cyclohexanediamine (R = H, 5-NO₂, 4,6-di-OCH₃ and 3,5-di-Cl) have been studied by DFT calculations and topology of density charge function according to Bader's AIM theory. Comparison of the ρ_{BCP} values at the H...N and H...O bond critical points (BCP) for the compounds studied has revealed the effect of substituents on the hydrogen bonds strengths in the two chelate rings of *trans*-N,N'-bis-(R-salicylidene)-1,2-cyclohexanediamines.

Key words: Schiff bases, tautomerism, electron density, AIM calculations

The Role of Alkali and Alkaline Earth Metal Ions on the Hydrolysis of 2-Ferrocenyl-1,3-dioxane in Acetonitrile Solutions

by E. Navarro, F.J. González **, P.D. Astudillo, M. Vázquez-Hernández, M. Hernández-Rodríguez and E. Juaristi

Departamento de Química, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Apartado Postal 14-740, 07000-México D. F., Mexico
e-mail: fgonzale@cinvestav.mx

(Received October 14th, 2006; revised manuscript November 13th, 2006)

The hydrolysis of 2-ferrocenyl-1,3-dioxane in the presence of different alkali (Li^+ , Na^+ , K^+), alkaline earth (Mg^{2+} , Ca^{2+}), and transition metal ions (Zn^{2+}) was studied in acetonitrile solutions. The evolution of the hydrolysis of the dioxane ketal moiety and the formation of the reaction products was monitored by analysis of the electrochemical oxidation potential of the ferrocenyl redox centre, which maintains its integrity in the reaction and facilitates the determination of the concentrations of both the starting material and products. It was found that only Ca^{2+} promotes the hydrolysis of 2-ferrocenyl-1,3-dioxane to produce ferrocenecarboxaldehyde and 1,3-propanediol in up to quantitative yield when an excess of the Ca^{2+} metal ion is present. Theoretical calculations (B3LYP/3-21G*) led to a proposal for the hydrolysis mechanism, in which coordination of solvated calcium to the O–C–O dioxane segment is determinant for the process to begin.

Key words: ferrocenyldioxane, hydrolysis, salt effects, stereoelectronic interactions, metal ions, DFT calculations

Crystal and Molecular Structure of 1:1 Complex Between Piperidine-3-carboxylic Acid and *p*-Hydroxybenzoic Acid Studied by X-ray Diffraction, FTIR, ^1H and ^{13}C NMR Spectroscopy, and B3LYP Method

by Z. Dega-Szafran¹, M. Jaskólski^{1,2} and M. Szafran¹

¹Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

**e-mail: degasz@amu.edu.pl

²Center for Biocrystallographic Research, Institute of Bioorganic Chemistry, Polish Academy of Sciences, Poznań, Poland

(Received October 12th, 2006; revised manuscript November 16th, 2006)

A 1:1 complex between the zwitterionic piperidinium-3-carboxylate (P3C) and *p*-hydroxybenzoic acid (HBA), P3C·HBA, has been characterized by single crystal X-ray analysis. The crystals are orthorhombic, space group *Pbca*, with $a = 11.913(1)$, $b = 9.407(1)$, $c = 22.124(2)$ Å. There is a short O–H \cdots O bridge (2.507(2) Å) connecting P3C with HBA. The proton is located at the benzoic acid carboxylate but the O–H bond is elongated (1.08 Å) and the geometry of the COO groups suggests a nearly equivalent participation in this strong hydrogen bond. The piperidine ring adopts a chair conformation. The bulky carboxylate substituent takes an axial orientation in which it is stabilized by an intramolecular N⁺–H \cdots O bond (2.880(2) Å). In the crystal packing, the P3C·HBA units are connected with crystallographic neighbors by hydrogen bonds that involve only molecules of the same type. In this system of interactions, a zwitterionic molecule attracts two zwitterionic neighbors *via* its two N⁺–H₂ donors (accepted by the alternate O atoms of the carboxylate group; 2.823(2) and 2.841(2) Å), while an aromatic molecule is connected to another aromatic molecule *via* a hydrogen bond of length 2.655(2) Å, involving the *para*-hydroxyl donor and the carbonyl acceptor of the carboxylic group. In a model optimized by the B3LYP/6-31G(d,p) method, P3C in its neutral form interacts *via* a C=O \cdots HOOC hydrogen bond with HBA. The FTIR spectrum shows a broad absorption in the 3100–2400 cm⁻¹ region attributed to νNH and νOH vibrations. The broad absorption in the 1495–910 cm⁻¹ region is attributed to the short O(3)–H \cdots O(1) hydrogen bond (νOH and γOH). The ^1H and ^{13}C NMR spectra have been analyzed to elucidate the complex structure in solution.

Key words: piperidine-3-carboxylic acid, nipecotic acid, *p*-hydroxybenzoic acid, X-ray diffraction, FTIR and NMR spectroscopy, hydrogen bonds, DFT calculations

Paracyclophanes. Part 58 [1]. On the Use of the Stilbene-Phenanthrene Photocyclization in [2.2]Paracyclophane Chemistry

by H. Hopf¹, J. Hucker¹ and L. Ernst^{2*}

¹*Institut für Organische Chemie, Technische Universität Braunschweig,
Hagenring 30, D-38106 Braunschweig, Germany
e-mail: H.Hopf@tu-bs.de*

²*NMR-Laboratorium der Chemischen Institute der Technischen Universität Braunschweig,
Hagenring 30, D-38106 Braunschweig, Germany*

(Received September 9th, 2006; revised manuscript November 20th, 2006)

The application of the stilbene→phenanthrene photocyclization to [2.2]paracyclophane chemistry has been investigated. For the model system 4-styryl[2.2]paracyclophane (**2**) to [2.2]phenanthrenoparacyclophane (**3**) the reaction allows the introduction of alkyl substituents in the 6-, 7-, 8- and 9-position of the phenanthrene moiety. However, when the substituent in the 9-position (bay area of phenanthrene nucleus) becomes too large, *viz. tert*-butyl, no ring closure is observed anymore. The side products of the process (ring cleavage products of the cyclophane core such as **9** and **10**) have been characterized for the first time. Extension of the condensed deck is possible leading to PAH-phanes as demonstrated by the preparation of the chrysenophanes **45** and **60**; the cyclization to novel helicenophanes such as **50** also takes place without difficulties. In the case of 1,2-di-(4-[2.2]paracyclophanyl)ethene (**63**) the triply-layered hydrocarbon **65** is produced on irradiation in small amounts.

Key words: photocyclization, condensed aromatic systems, reactions mechanisms, cyclophanes/layered molecules/stilbenes

Complete Assignment of All ^{13}C NMR Signals of C_5 Symmetric Monoazafullerene Derivatives by Comparison of Experimental and Calculated Spectra

by F. Hauke¹, Z.-F. Chen² and A. Hirsch¹

¹*Institut für Organische Chemie, Henkestrasse 42, 91054 Erlangen, Germany*

E-mail: hirsch@chemie.uni-erlangen.de

²*Current address: Center for Computational Chemistry, Department of Chemistry, University of Georgia, Athens, GA 30602, USA*

(Received September 12th, 2006; revised manuscript November 24th, 2006)

The complete assignment of all 31 ^{13}C NMR signals which are due to the fullerene carbon atoms of monoazafullerene derivatives has been carried out for the first time by the systematic comparison of experimental and theoretical spectra calculated by high level DFT methods (GIAO-B3LYP/6-31G*/B3LYP/6-31G*). The assignment is facilitated by the striking similarities of the signal patterns of the sp^2 -fullerene carbon atoms of two different families of such heterofullerene derivatives with both aryl and alkyl addends.

Key words: fullerene, heterofullerene, NMR spectroscopy, DFT calculation, chemical shift

“Atoms in Molecules” Analyses on Topological Properties of Bonds in Hydrazo-, Azo-, Azoxy- and Azodioxybenzene

by K. Ejsmont

*Institute of Chemistry, University of Opole, Oleska 48, 45-052 Opole, Poland
e-mail: ejsmont@uni.opole.pl*

(Received October 3rd, 2006; revised manuscript November 24th, 2006)

The Bader’s theory, Atoms in Molecules (AIM), has been applied for the topological analysis of the C–N, N–N and N–O bonds in hydrazo, *cis/trans*-azo, *cis/trans*-azoxy and *cis/trans*-azodioxybenzene. This investigation has been extended for the following reference compounds: nitrosobenzene, nitrobenzene, aniline, hydrazine and pyridine *N*-oxide. The intramolecular C–H...O hydrogen bonds present in *trans*-azoxy and *trans*-azodioxybenzene have also been analysed. The calculations were performed at the DFT B3LYP/6-311++G** level of theory.

Key words: theoretical charge density, hydrazo, azo, azoxy, azodioxy compounds

Substituent Effects in the *ortho* Position: Model Compounds with a Removed Reaction Centre

by S. Böhm¹ and O. Exner²

¹Department of Organic Chemistry, Institute of Chemical Technology, 16628 Praha 6, Czech Republic

²Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic,
16610 Praha 6, Czech Republic
e-mail: exner@uochb.cas.cz

(Received August 25th, 2006; revised manuscript November 28th, 2006)

2'-Substituted phenylpropynoic acids **1** and - in less details - 2'-substituted (*E*)-phenyl-iminoacetic acids **3** were investigated theoretically as model for the *ortho* substitution, in which direct steric interaction is prevented by the extended side chain bearing the reaction centre. Energies of the acid molecules and of their deprotonated forms were calculated within the framework of the density functional theory at the level B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p). The substituent effects were evaluated in terms of isodesmic reactions, on the one hand for the acidity, on the other separately for the acid molecules or for the anions. Contrary to the expectation, the steric interaction of the substituent with the side chain is rather strong. The substituent effects represent a blend of polar and steric effects, and cannot serve for deriving any set of standard *ortho* substituent constants free of proximity effects as it was originally believed.

Key words: substituent effect, density functional theory, *ortho* effect, steric effect

**New Polymorphic Form of
1,4-Bis(3-pyridyl)-2,3-diaza-1,3-butadiene**

by **Z. Ciunik**** and **K. Drabent**

Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie Str., 50-383 Wrocław, Poland

***e-mail: ciunik@wchuwr.pl*

(Received September 29th, 2006; revised manuscript November 29th, 2006)

Comparison of the Proton (H^+) and Alkali Metal Ion (Li^+ , Na^+ and K^+) Binding Affinities of Pyruvate and Oxamate Anions in the Gas Phase. Quantum-Chemical Studies

by K. Duczmal¹, M. Hallmann¹, E.D. Raczynska¹, J.-F. Gal² and P.-C. Maria²

¹Department of Chemistry, Agricultural University (SGGW),
ul. Nowoursynowska 159c, 02-776 Warszawa, Poland
e-mail: ewa_raczynska@sggw.pl

²Laboratoire de Radiochimie, Sciences Analytiques et Environnement, Institute of Chemistry of Nice,
Universit de Nice - Sophia Antipolis, Parc Valrose, 06108 Nice Cedex 2, France

(Received September 20th, 2006; revised manuscript November 30th, 2006)

Proton affinity (PA), lithium, sodium and potassium cation affinities (CA) in the gas phase were estimated by Gaussian-2 (G2), Möller-Plesset (MP2) methods and/or hybrid density functional theory calculations (B3LYP) for pyruvate and oxamate anions. Comparison of these affinities shows that the COO^- groups of both anions have similar basicities. Differences between their calculated PAs as well as between their calculated CAs are not larger than 3 kcal mol^{-1} . Somewhat larger differences are evidenced for the formations of the alkali metal complexes with the cation located between the oxygen atoms of the $^{\alpha}C=O$ and COO^- groups for which the lithium, sodium and potassium cation affinities are larger for oxamate than for pyruvate (by $4 \pm 0.5 \text{ kcal mol}^{-1}$ at the G2 level and by $6 \pm 0.5 \text{ kcal mol}^{-1}$ at the DFT(B3LYP)/6-31++G** level). This is a consequence of the chelate effect on the cation binding seen on the calculated most stable structures of the adducts.

Key words: pyruvate, oxamate, proton affinity, gas-phase alkali metal complexes, Li^+ , Na^+ and K^+ cation affinities, quantum-chemical study

Molecular Clusters to Nanomaterials

by N.J. Singh¹, H.M. Lee¹, S.B. Suh¹, M. Kołaski^{1,2} and K.S. Kim¹

¹*Center for Superfunctional Materials, Department of Chemistry,
Pohang University of Science and Technology, San 31, Hyojadong, Namgu, Pohang 790-784, Korea
e-mail: kim@postech.ac.kr*

²*Permanent address: Department of Theoretical Chemistry, Institute of Chemistry,
University of Silesia, 9 Szkolna Street, 40-006 Katowice, Poland*

(Received October 12th, 2006; revised manuscript December 11th, 2006)

Theoretical investigations of gas phase clusters enable the evaluation of intrinsic molecular properties and intermolecular interactions. Based on the microscopic determination of the properties of individual atoms, molecules, or clusters, one can predict the macroscopic properties of bulk matter. With the aid of theoretical insights into the interaction forces holding these clusters and subsequent properties of a large number of cluster systems (ranging from simple water clusters to large π -systems), we have investigated the properties of various novel molecular systems including endo/exohedral fullerenes, nanotori, nonlinear optical materials, ionophores/receptors, polypeptides, enzymes, organic nanotubes, nanowires, and electronic and nano-mechanical molecular devices. This mini-review highlights some of the interesting results obtained in the course of our extensive theoretical investigations of clusters toward the molecular design approach of nanomaterials.

Key words: computer-aided molecular design, molecular clusters, ionophores, nanotubes, nanomaterials, nanodevices

Structural Studies of 1-Aryl-2-aminoimidazolinium Bromides: Focus on Tautomer Preference of the 2-Aminoimidazoline Moiety in the Solid State

by M.A. Dobrowolski¹, M.K. Cyrański¹, M. Pisklak²,
I. Wawer^{2**} and D. Matosiuk³

¹Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland
e-mail: chamis@chem.uw.edu.pl

²Department of Physical Chemistry, Faculty of Pharmacy, Medical University,
Banacha 1, 02-097 Warsaw, Poland

³Department of Synthesis and Chemical Technology of Pharmaceutical Substances,
Faculty of Pharmacy, Medical University, Staszica 6, 20-081 Lublin, Poland

(Received October 20 th, 2006; revised manuscript December 11th, 2006)

The crystal structures of five 1-(4-X-phenyl)-2-aminoimidazolinium bromides (where X = -OCH₃, -CH₃, -H, -Cl and -NO₂) were determined by X-ray crystallography with the aim to investigate the tautomer preference of the aminoimidazoline moiety in the solid state. The molecular structures clearly indicate that only the ring nitrogen is protonated. The crystals are stabilized by interactions between the hydrogens of the amino group (also NH fragment of the imidazoline ring) and bromide anion. In the case of the nitro derivative additional strong hydrogen bonds are a consequence of the presence of water molecule in the crystal lattice. The methoxy and nitro derivatives were studied by ¹⁵N CP/MAS NMR and the analysis of the tautomer preference was completed by *ab initio* calculations at the B3LYP/6-311+G** level.

Key words: 2-aminoimidazolines, tautomer preference, X-ray diffraction, ¹⁵N solid state NMR, *ab initio* calculations

The Mediatory Activity of Ce(IV)/Ce(III) Redox System Immobilized in Nafion[®] Film on Glassy Carbon

by S. Domagała¹, J. Dziegieć¹, M. Cichomski² and J. Grobelny²

¹*Department of General and Inorganic Chemistry, University of Łódź,*

90-136 Łódź, ul. Narutowicza 68, Poland

e-mail: domagala@chemul.uni.lodz.pl

²*Department of Chemical Technology and Environmental Protection, University of Łódź,*

90-236 Łódź, ul. Pomorska 163, Poland

(Received October 11th, 2006; revised manuscript December 21st, 2006)

Properties of the glassy carbon modified with Ce(III) ions immobilized in Nafion film and the catalytic activity of these ions or the catalytic activity of the modified conducting phase in electrochemical oxidation of some hydroquinone, phenylenediamine and 4-hydroxybenzoic acid derivatives were investigated. The redox activity was characterized in aqueous solutions of perchloric acid by cyclic voltammetry. The redox process was diffusion-limited which can suggest that the cerium(III) ions immobilized in the Nafion multilayer was rate-controlling. The increase of anodic peaks of investigated compounds during oxidation on the modified electrode (GC/Nafion/Ce(III)), and drastic decrease of cathodic peak related to Ce(IV) ions reduction, points to the mediatory activity of these ions. The increase of oxidation currents observed during preparative electrolyses indicates the catalytic properties of the modified conducting phase. The preparative electro-oxidation of investigated compounds showed that the 100% conversion of the substrate occurs in the shortest time on glassy carbon modified with Ce(III) ions immobilized in Nafion film. AFM tapping mode phase imaging was used to identify the hydrophobic and hydrophilic regions of Nafion perfluorosulfonate cation exchange membranes. The clusters agglomerates have a range of sizes from 5 to 30 nm.

Key words: Nafion, chemically modified electrodes, cerium(III), redox mediator

A New Chiral 4-[(*E*)-2-Ferrocenylvinyl]-1-methylpyridinium Iodide Exhibiting Bulk Second-Order Nonlinear Optical Properties

by **I. Janowska**¹, **J. Zakrzewski**^{1**}, **M. Palusiak**² and **K. Nakatani**³

¹*Department of Organic Chemistry, University of Łódź, 90-136 Łódź, Narutowicza 68, Poland*

***e-mail: janzak@uni.lodz.pl*

²*Department of Crystallography and Crystal Chemistry, University of Łódź, 90-236 Łódź, Pomorska 149/153, Poland*

³*Laboratoire de Photophysique et Photochimie Supramoléculaires et Macromoléculaires (PPSM, CNRS UMR 8531), Ecole Normale Supérieure de Cachan, 61, Avenue du Président Wilson, 94235 Cachan Cedex, France*

(Received November 2nd, 2006; revised manuscript December 28th, 2006)

Two new chiral 4-[(*E*)-2-ferrocenylvinyl]-1-methylpyridinium iodides, having in the 2-position of the ferrocenyl group (*R*)-1-*N,N*-dimethylaminoethyl and (*S*)-2-methoxy-methylpyrrolidin-1-yl substituents were synthesized. The latter compound showed weak second harmonic generation efficiency (0.5 x urea) at 1907 μm . The molecular structure and crystal packing of this compound were determined by single-crystal X-ray diffraction and are discussed in relation to its nonlinear optical properties.

Key words: ferrocene, planar chirality, nonlinear optics, second harmonic generation

Synthesis of O-Arylxanthates Esters and Derivatives

by **E. Humeres, N.A. Debacher and E.P. de Souza**

*Departamento de Química, Universidade Federal de Santa Catarina,
88040-900 Florianópolis, SC, Brazil
**e-mail: humeres@mbox1.ufsc.br*

(Received November 8th, 2006; revised manuscript December 28th, 2006)

No successful attempts have been made to synthesize O-arylxanthate esters from metal salts with alkylating agents because the metal derivatives are too unstable for the effective synthesis of the esters. In this work, substituted R-phenylxanthates (R = H, *p*-MeO, *o*-Me, *p*-F) were obtained as barium salts that upon reaction with alkyl halides produced O-arylxanthate esters. The ethylaminolysis of methyl O-phenylxanthate formed diethyl thiourea as the final product because of the similar nucleofugality of phenoxy and ethylthioxy moieties. A new method was used to obtain N-ethyl O-*p*-methoxyphenylthioncarbamate from the reaction of *p*-methoxyphenol and N-ethylisothiocyanate in a heterogeneous mixture of dichloromethane and aqueous phosphate buffer, pH 7.

Key words: O-arylxanthate esters, O-arylthioncarbamate esters, O-arylxanthate, barium salts, N-ethyl O-*p*-methoxyphenylthioncarbamate

Characterization of the Structure of PDP-DPPC Bilayers by DFT and PM3 Calculations

by K. Cieřlik-Boczula and A. Koll**

Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland

***e-mail: akoll@chem.uni.wroc.pl*

(Received November 7th, 2006; revised manuscript January 3rd, 2007)

The character of 3-pentadecylphenol (PDP)-dipalmitoylphosphatidylcholine (DPPC) interactions in a bilayer system was investigated using DFT and semi-empirical calculations. The obtained results were supported by ATR-IR spectra. The strongest intermolecular hydrogen bond was found between the phenolic OH and the PO₂⁻ groups of the DPPC molecule. The presence of water and hydrocarbon chains slightly weakens the strength of this PDP-DPPC interaction. In contrast to a pure DPPC bilayer, the water molecules do not destroy the H-bonds formed by PO₂⁻ moieties and even enhance the total energy of the interaction. Both the van der Waals' interactions in the hydrophobic core of the PDP-DPPC aggregate and the intermolecular H-bond in the hydrophilic part make this complex more rigid, which influences its physical and chemical properties.

Key words: phenolic lipid, doped DPPC bilayer structure, ATR-IR spectra, molecular interaction

Co-crystals of 2,4,6-Trihydroxybenzoic Acid with Aromatic Diazaheterocycles – Crystallographic Studies

by W. Jankowski, A. Kadzewski and M. Gdaniec

Faculty of Chemistry, Adam Mickiewicz University, 60-780 Poznań, Grunwaldzka 6, Poland
e-mail: magdan@amu.edu.pl

(Received November 8th, 2006; revised manuscript January 3rd, 2007)

Binary co-crystals of 2,4,6-trihydroxybenzoic acid with pyrazine (1:1), quinoxaline (1:1) and phenazine (1:2) were prepared and their structure determined by X-ray crystallography. In the complex with pyrazine the carboxylic group of the acid is in the *syn* configuration and is connected *via* strong hydrogen bond to the N atom of the heterocyclic base. In the complex with phenazine the carboxylic group adopts the *anti* form and the acid molecule binds, *via* the phenolic groups, to two molecules of the base, in a manner typical for interaction of resorcinol with azaheterocycles. In the complex with quinoxaline the asymmetric part of the unit cell consists of two pairs of acid-base hydrogen-bonded units. In the first pair, 2,4,6-trihydroxybenzoic acid binds to quinoxaline *via* the carboxylic group, which is in the *syn* form. In the second pair, proton is transferred from the carboxylic group to the heterocyclic base, and the ions join *via* N-H⁺...O⁻(carboxylate) interaction. In both units acidic hydrogen atom is significantly shifted towards the center of hydrogen bond. Hydrogen bonds between the carboxyl group and the pyrazine and quinoxaline N-atoms are linear and short [O...N distances in the range 2.570(2)–2.630(2) Å].

Key words: co-crystals, carboxylic acids, diazaheterocycles, hydrogen bonding, crystal structure, crystal engineering

Computational Study of Deprotonation of Cyclopropa-Fused Quinones

by M. Eckert-Maksić and Z. Glasovac

*Division of Organic Chemistry and Biochemistry, Rudjer Boskovic Institute,
P.O.B. 180, HR-10002, Zagreb, Croatia
e-mail: mmaksic@emma.irb.hr*

(Received October 27th, 2006; revised manuscript January 9th, 2007)

The acidities of cyclopropa-fused quinones **1H**–**3H** were calculated by employing MP2 and B3LYP methods utilizing the 6-31+G(d) basis set. Analysis of the results shows that all three isomers are considerably more acidic than the previously studied cyclopropabenzene. It is also shown that acidity of **1H** is significantly higher than acidity of **2H** and **3H**. The acidity ordering of the studied species is rationalized by a triadic formula, which is capable of delineating the initial, intermediate and the final state effects in the deprotonation process. It is found that the ordering of the calculated proton affinities is mainly determined by an interplay of two terms: Koopmans' ionization energy and the relaxation energy.

Key words: acidities, cyclopropaquinones, quantum chemical calculations

On the Way to Physical Interpretation of Hammett Constants: How Substituent Active Space Impacts on Acidity and Electron Distribution in *p*-Substituted Benzoic Acid Molecules

by **N. Sadlej-Sosnowska**

*National Medicines Institute, 30/34 Chełmska Street, 00-725 Warsaw, Poland
e-mail: sadlej@il.waw.pl*

(Received August 24th, 2006; revised manuscript January 10th, 2007)

Electron distribution was investigated in molecules of *p*-substituted benzoic acids by means of Natural Population Analysis. The analysis offers a valuable insight into the impact of a given substituent on the individual atoms' charges in the molecules, on the excess of π electrons in the ring and on the uniformity of their distribution. The more uniform the distribution, measured by means of standard deviation of π electrons amounts localized on individual atoms in the ring, the more acidic is the molecule. On the other hand, an increase of the π electron number in the ring brings about an opposite effect. No correlation was found between the total substituent charges and the Hammett constants. However, a new variable, composed of charges of substituents, added to charges of the ring C_{ipso} atoms, was highly correlated with charges of acidic hydrogens, with the π -electron populations on the individual ring atoms, and eventually, with the Hammett constants. On that basis a notion of the active substituent space was introduced, which comprises the substituent itself and the ring ipso carbon atom. It has been found that it is the charge of the active space, but not the charge of the substituent itself, which is well correlated with the acidity and other properties of *p*-substituted benzoic acids.

Key words: acidity, *p*-substituted benzoic acids, Hammett constants, resonance constants, π -electron distribution, charge distribution, Natural Population Analysis

Thermo-Solvatochromism of Zwitterionic Probes in Binary Mixtures of Tetramethylurea and Water: Relevance to Gelation of Lysozyme Solutions

by **M.A. da Silva, C.T. Martins, E.P.G. Arêas and O.A. El Seoud****

Instituto de Química, Universidade de São Paulo, C. P. 26077, 05513-970, São Paulo, S.P., Brazil,

***e-mail: elseoud@iq.usp.br*

(Received November 8th, 2006; revised manuscript January 30th, 2007)

Solutions of lysozyme in mixtures of tetramethylurea, TMU, and water, W, undergo “gelation” above a certain critical composition, at room temperature; the threshold composition for gelation shows some dependence on temperature. Lysozyme gelation in TMU/W has been explained by solvent-induced protein unfolding, due to the protein exposure to a more hydrophobic microenvironment. This preferential solvation can be readily quantified from the study of polarity indicators, serving as simple models for the protein domains. Thermo-solvatochromism of two indicators, 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl) phenolate, and 4-[(E)2-(1-methylpyridinium-4-yl) ethenyl] phenolate, has been studied in mixtures of TMU-W, from 10 to 60°C. Both probes are preferentially solvated by TMU and, more efficiently, by the hydrogen-bonded species, TMU-W. The maximum concentration of the latter is close to the “critical” threshold mole fraction of water (*ca.* 0.8.) at which lysozyme gelation occurs. As TMU is added to water the protein, by analogy to polarity indicators, undergoes progressive solvation by less polar, hydrophobic microenvironment leading, at a critical composition, to its unfolding with concomitant gelation of the solution.

Key words: thermo-solvatochromism, polarity indicators, tetramethylurea, lysozyme, protein gelation

Identification of Adducts Formed in the Reaction of the Bacterial Mutagen 3-Chloro-4-(chloromethyl)-5-hydroxy-2(5*H*)-furanone with Cytidine

by D. Pluskota-Karwatka², T. Munter¹, F. Le Curieux^{3,4}, R. Sjöholm¹, H. Koroniak² and L. Kronberg¹

¹Laboratory of Organic Chemistry, Abo Akademi University,
Biskopsgatan 8, FIN-20500 Turku/Abo, Finland

**e-mail: leif.kronberg@abo.fi

²Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

³Département Toxicologie-Santé Publique-Environnement,
Faculté des Sciences Pharmaceutiques et Biologiques, B.P. 83, 59006 Lille Cedex, France

⁴Laboratoire de Toxicologie, Institut Pasteur de Lille,
1 rue du Professeur Calmette BP 245, 59019 Lille Cedex, France

(Received October 27th, 2006; revised manuscript February 5th, 2007)

3-Chloro-4-(chloromethyl)-5-hydroxy-2(5*H*)-furanone (CMCF), a strong bacterial mutagen reacts with cytidine in buffered aqueous solutions. The reaction products were separated by preparative HPLC C18 column chromatography and were structurally characterized by UV absorbance, ¹H NMR and ¹³C NMR spectroscopy, and mass spectrometry. The main products were identified as 7-(β-D-ribofuranosyl)-4-carboxy-6-oxo-6,7-dihydro-4*H*-pyrimido[1,6-*a*]pyrimidine-3-carbaldehyde (cM₁FA-Cyd), and 7-(β-D-ribofuranosyl)-6-oxo-6,7-dihydro-4*H*-pyrimido[1,6-*a*]pyrimidine-3-carbaldehyde (M₁FA-Cyd). The highest yields of cM₁FA-Cyd and M₁FA-Cyd, being 12 and 1 mol % respectively, were obtained in the reaction performed at pH 4.6 and 37°C for 7 days. M₁FA-Cyd and cM₁FA-Cyd are structurally related to pfA-dR, the adduct previously identified in the reaction of 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5*H*)-furanone (MX) or 3-chloro-4-(chloromethyl)-5-hydroxy-2(5*H*)-furanone (CMCF) with 2'-deoxyadenosine.

Key words: DNA adducts, chlorohydroxyfuranones, structural characterization

***Ab initio* Optimizations of Molecular Structures and GIAO NMR Calculations of Chemical Shieldings of [8]- and [10]Paracyclophane and of [8](1,4)Naphthalenophane. Basis Set Dependence in Relation to Experimental 2D-NMR-Spectra and to Our APUDI Ring Current Model**

by F.-P. Dietrich, T. Zuschneid, G. Ritter, C.U. Regelman,
D. Kaiser and G. Häfelinger

*Institute of Organic Chemistry at the University of Tübingen,
Auf der Morgenstelle 18, D-72076 Tübingen, Germany
e-mail: guenter.haefelinger@uni-tuebingen.de*

(Received November 3rd, 2006; revised manuscript February 8th, 2007)

The molecular structures of the minimum energy conformations of [8]- and [10]paracyclophanes (**1**) and (**2**) have been calculated by full gradient optimizations using the *ab initio* HF method with four Pople basis sets and by the DFT/B3LYP method with two split-valence basis sets under the constraint of assumed C_2 symmetry. The calculation for [8](1,4)naphthalenophane (**3**) was performed in the HF/6-31G* method in comparison to a force-field PIMM calculation. For each final geometry, ^1H and ^{13}C chemical shieldings have been calculated by the GIAO MO method and converted to chemical shifts by calculated TMS values for geometries optimized in the corresponding method/basis set combination. Compounds **1** to **3** have been synthesized by known procedures and their experimental NMR chemical shifts were measured at 400 MHz. 2D homo- and heteronuclear chemical shift correlations allow non arbitrary signal assignments. The calculated shift values have been correlated with experimental shifts by linear least squares regressions for proton and carbon NMR data. Best statistical parameters are obtained for ^1H NMR values by HF/6-31G* calculations but for ^{13}C NMR shifts from HF/6-311G* data. Surprisingly, regressions with our APUDI geometric factors lead to similar accuracy if the point dipoles are located at the carbon atom positions ($p = 0.0 \text{ \AA}$) for both ^1H and even ^{13}C NMR values. These regressions show clearly that not only the ^1H NMR data but also ^{13}C NMR values in the vicinity of a benzene ring are determined by a long range ring current anisotropy effect reproduced by the GIAO and the APUDI calculations.

Key words: paracyclophanes, *ab initio* optimizations, GIAO NMR calculations, out-of-plane ring current effects, APUDI model

Synthesis, Characterization and Crystal Structure Studies of 1-(4-Chloro-benzenesulfonyl)-piperidin-4-yl-diphenyl-methanol

by S.B. Benakprasad¹, S. Naveen², C.S. Anandakumar¹, Y.C. Sunilkumar¹,
M.A. Sridhar², J. Shashidhara Prasad² and K.S. Rangappa¹

¹Department of Studies in Chemistry, University of Mysore,
Manasagangotri, Mysore 570 006, India
**e-mail: rangappaks@gmail.com

²Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore 570 006, India

(Received October 28th, 2006; revised manuscript February 15th, 2007)

1-(4-Chloro-benzenesulfonyl)-piperidin-4-yl-diphenyl-methanol was synthesized by the condensation of [piperidin-4-yl]-diphenyl-methanol with *p*-chlorobenzene sulfonylchloride in methylene dichloride as solvent and triethylamine as the base. The compound obtained was characterized by spectroscopic techniques and confirmed by X-ray crystallographic studies. The crystallographic data analysis reveals that the title compound crystallizes in the monoclinic space group $P2_1/c$ with cell parameters $a = 10.214(9) \text{ \AA}$, $b = 11.371(5) \text{ \AA}$, $c = 20.939(16) \text{ \AA}$, $\beta = 115.399(2)^\circ$, $V = 2197(3) \text{ \AA}^3$ for $Z = 4$. The structure has been solved by direct methods and refined to $R_1 = 0.0560$ for 3658 observed reflections with $I > 2\sigma(I)$. The piperidine ring is in a chair conformation. The geometry around the S atom is distorted from regular tetrahedron.

Key words: sulfonyl chloride, condensation, crystal structure, chair conformation

Intermolecular Interactions in Three Crystalline Acid Salts of Monocarboxylic Acids

by **A. Madej**, **B.J. Oleksyn**^{**} and **J. Śliwiński**

Faculty of Chemistry, Jagiellonian University, ul. R. Ingardena 3, 30-060 Kraków, Poland

^{**}*e-mail: oleksyn@chemia.uj.edu.pl*

(Received November 8th, 2006; revised manuscript March 2nd, 2007)

Three new acid salts of two monocarboxylic acids were obtained and their crystal structure analysis performed using experimental data collected with KM-4 diffractometer. The crystal structures of hydrogen bis(sulfosalicylates) of sodium and potassium contain hydrogen-bonded acid-anion dimers of very similar geometry and are classified to type A and pseudo A of hydrogen bis(monocarboxylates). Crystalline sodium hydrogen bis(3,5-dinitrobenzoate) contains a trimer acid-anion-acid. Its structure, which differs from that of potassium salt determined earlier, is classified as type B. The role of cations and anions in the investigated structures is discussed.

Key words: acid salts, crystal structure, hydrogen bonds