



### **Professor Aleksander Koll**

Dr Aleksander Koll is professor of chemistry at the Faculty of Chemistry of Wrocław University. His basic research interests are connected with hydrogen bond studies, particularly intramolecular hydrogen bonds and the structure-property relationships of organic molecules.

Aleksander Koll was born on June 3, 1939, in Wilno. He spent the second world war in Orany (Varena) in Lithuania, where his father was an officer in the post office. After the war, the family moved to Głogów in Lower Silesia in 1945, where he finished primary and secondary school. In 1957 he started his studies at the Faculty of Mathematics, Physics, and Chemistry of Wrocław University, and graduated in 1962 with a Master of Science in chemistry. He began his research work under the supervision of Prof. Lucjan Sobczyk, studying the polarity of hydrogen bonds between phenols and amines.

In 1962 he started his Ph.D. studies at the Department of Physical Chemistry of Wrocław University. His dissertation was devoted to the correlation between the structures of bipyridineamines and their physicochemical properties. In 1968 he has

received his Ph.D. degree for the dissertation entitled "Structure and properties of (pyridil)<sub>2</sub>Y compounds". The supervisor of the dissertation was Prof. Lucjan Sobczyk. Simultaneously he studied the polarity of the hydrogen bonds in *ortho*-substituted phenols. He demonstrated that in compounds, which may form a chelate ring with  $\pi$ -electronic coupling, the vector of the "hydrogen bond polarity" is mainly determined by resonance effects.

The 1969/1970 academic year he spent as a postdoctoral researcher at Leningrad State University in the Department of Molecular Spectroscopy. He was involved together with Professors V.E. Borisenko, D.N. Shchepkin and G.S. Denisow in quantitative studies of the integrated intensity of HCl stretching vibrational bands in the complex with acetonitrile in CCl<sub>4</sub>.

After returning to Wrocław University he continued studies on the complexation of HCl as well as DCl, HBr, and DBr with oxygen bases in CCl<sub>4</sub> solutions by measuring IR spectra, dipole moments, and formation constants. The studies were carried out in cooperation with Prof. M. Rospenk and Prof. L. Sobczyk.

The second postgraduate studies, in 1975 and 1976 at Guelph University, Canada, under the supervision of Prof. C.A. Fyfe, were devoted to NMR kinetic studies of nucleophilic substitution of nitroaromatic compounds with the use of continuous flow method.

Since 1978 he has been intensively engaged in studies of the intramolecular hydrogen bond in *ortho*-hydroxy N-dialkyl benzyl amines (Mannich bases). On the basis of dipole moment measurements he suggested that in nonpolar solvents the molecules exist exclusively in nonplanar closed intramolecular forms. He constructed the Molecular Force Field (MM) with the Lippincott-Schroeder potential for a description of the hydrogen bonding interactions. He demonstrated that the conformation of the chelate ring formed by an intramolecular hydrogen bond is really nonplanar. With increasing strength of the hydrogen bond the molecules become more planar, but even for the strongest hydrogen bonds they approach some limit of nonplanar structures. Independent crystallographic determinations performed later positively verified this hypothesis. Calculated dipole moments gave the same dependence of the hydrogen bond polarity on  $\Delta pK_a$  as in intermolecular complexes, suggesting the same nature of the inter- and intramolecular hydrogen bond. UV-Vis spectroscopy was applied to determine the thermodynamic parameters of the intramolecular proton transfer reaction. It was shown that in all compounds the enthalpy of this process was negative and entropy changes were also negative and relatively high, suggesting a strong participation of solvent molecules in the proton transfer process. Such an effect was later demonstrated by using molecular dynamics in the dissertation of one of his Ph.D. students, Dr. Adam Fedorowicz. The change in the arrangement of solvent molecules resulting from intramolecular proton transfer was clearly demonstrated.

The polarity and structure of intramolecular hydrogen bonds were the topics of Prof. Koll's habilitation dissertation, completed in 1986. In 1988 he was promoted to

the position of docent, in 1992 he became associate professor, and in 1996 he received the title of professor.

As Mannich bases were used by Prof. Koll as model compounds in the study of the nature of hydrogen bonding, biphenyl-type molecules were applied as a model for the study of conformational equilibria. A subtle balance between steric and resonance effects in this type of molecules makes them especially sensitive to the surroundings and the influence of temperature. Derivatives substituted not on the rotational axis positions were applied in conformational studies with the use of dielectric methods. Prof. Koll performed experimental measurements in the laboratory of Dr. L. Hellemans at the Department of Biological Dynamics of Leuven Catholic University.

Prof. Koll spent two months there as a visiting professor and visited this laboratory many times for shorter periods. Prof. Koll proposed the molecular force field model for calculating the potential for internal rotation in such molecules. A particular achievement was introducing the resonance coupling effects to the force field.

In order to obtain better consistency between theoretical calculations and experiments done on nonpolar solvents, Molecular Dynamics calculations were performed in Prof. Koll's group by Dr. A. Szymoszek. It was demonstrated that, in agreement with the experiment, the nonpolar solvent  $\text{CCl}_4$  exerts influence on the solute molecules to make them more planar. A specific feature of these calculations was introducing the quantum mechanical potential for the solute molecules together with classical molecular mechanics for other movements in solution.

Semiempirical quantum mechanical methods were applied in calculation of the potential energy surface for molecules such as diphenylguanidine, dimesityl sulfone, and Mannich and Schiff bases. The results were verified by experimentally determined values of the dipole moments. Together with Dr. hab. A. Filarowski, he performed analysis of the structure and strength of intramolecular hydrogen bonds in Mannich bases and structurally related Schiff bases. It was found that Schiff bases form stronger intramolecular hydrogen bonds, but with lower intensity of the  $\nu(\text{OH})$  stretching band. The interpretation of such an effect was made on the basis of calculating derivatives of the dipole moments with respect to the OH bond distance. Anharmonic effects were discussed on the basis of the potential for the stretching of the O–H distance. In this study a sterically enhanced class of hydrogen bonds was discovered. It was demonstrated that such hydrogen bonds are shorter, but also reveal all features of stronger hydrogen bonds. Wide-ranging theoretical studies on the structural and energetic effects of the formation of intramolecular hydrogen bonds were performed in cooperation with Prof. P. Wolschann and Prof. A. Karpfen of the Institute of Theoretical Chemistry of Vienna University. Prof. Koll visited Vienna University many times and was the coordinator of joint bilateral programs under an agreement for scientific cooperation between Austria and Poland supported by the OAD. Ten original publications were prepared within the framework of this cooperation. Important topics of these studies are the resonance interactions within

intramolecular hydrogen bonds in Schiff bases as well as the thermodynamic cycle type scheme for establishing the energy of intramolecular hydrogen bond.

In cooperation with the Vienna University Center and with Prof. G. Koehler, studies on the properties of biologically important bilayers implemented by biologically active ligands were introduced in Prof. Koll's group. Theoretical and experimental studies were performed in which IR-ATR has become one of the most promising method.

The extensive cooperation between St. Petersburg and Wrocław Universities, particularly with Professors S.M. Melikova and K.S. Rutkowski, resulted in a set of publications on blue-shifting improper hydrogen bonds. An installation for IR measurements in liquefied noble gases was built in the Department of Chemistry of Wrocław University. These studies were supported by two grants of the Polish Committee for Scientific Research (KBN).

The following visitors have worked in his laboratory: Professors S.M. Melikova, S.F. Bureiko, and K. Rutkowski from St. Petersburg University, Prof. V.E. Borisenko from Tyumen University, and Prof. S. Mukherjee from the Indian Association for the Cultivation of Science of Calcutta.

Prof. Koll was promoted to ordinary professor position of Chemistry in Wrocław University in 1999. He served as a Vice-Dean of the Faculty of Chemistry of this University in 1996–2002. He has been head of the Structure and Molecular Interactions group in this Faculty since 1998 and head of the Department of Physical Chemistry since 2005. He is the author or co-author of 180 original research publications and one textbook on experimental physical chemistry together with L. Sobczyk, A. Kiswa, and K. Gatner.

He has been the supervisor of more than sixty master's theses and nine Ph.D. dissertations. Two more dissertations are being completed under his supervision. He has taught physical chemistry in the laboratory, seminars, calculations, and lectures as well as in more advanced monograph lectures and seminars on physical organic chemistry and molecular interactions. He also delivers the lectures on molecular modeling and physical organic chemistry for Ph.D. students. He is one of the organizers of the annual Schools of Physical Organic Chemistry.

*Editor*

## **2'-Hydroxybenzylideneanilines and 2-Hydroxyazobenzenes. The Role of Intramolecular O–H···N Resonance Assisted Hydrogen Bonds**

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A short review on the effect of the OH groups in the *ortho* position on the liquid crystalline properties of benzylideneanilines and azobenzenes is presented. Numerous examples show that there are no general rules governing the behaviour of these compounds. However one finds most frequently a broadening of the existence range of mesophases both due to a decrease of freezing temperature and an increase of the isotropisation temperature. In contrast, the presence of strongly polar groups such as –NO<sub>2</sub> and –CN leads to a reverse behaviour that can be explained by assuming a strong  $\pi$ -electron conjugation of these groups with the conjugate-chelate ring formed by intramolecular O–H···N hydrogen bond. These rings are analyzed by using data related to the structure of molecules and infra-red spectra in the region of the stretching  $\nu$ (OH) and bending  $\delta$ (OH) and  $\gamma$ (OH) modes.

**Key words:** liquid crystals, Schiff bases, azobenzenes, resonance-assisted OH···N H-bonds

## Hydrogen Bonds and Electrostatic Interactions in N-(Ethoxycarbonylmethyl)-quinuclidinium Chloride Dihydrate

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N-(Ethoxycarbonylmethyl)-quinuclidinium chloride crystallizes as dihydrate, QNBE·Cl·2H<sub>2</sub>O. The crystals are monoclinic, space group *C*2/*c*. Water molecules interact with the chloride anions and form a cyclic oligomer, through the O–H···Cl and O–H···O hydrogen bonds. The chloride anions and water molecules additionally interact electrostatically with the positively charged nitrogen atom of the quinuclidinium moiety. The optimized structure of QNBE·Cl·2H<sub>2</sub>O by the B3LYP/6-31G(d,p) level of theory reproduces well the molecular aggregation observed in the crystal. The FTIR spectrum of the solid compound is consistent with the X-ray structure.

**Key words:** 1-azabicyclo[2.2.2]octane; quinuclidinium salts, X-ray diffraction, FTIR, Raman, NMR spectra, DFT calculations, hydrogen bond, electrostatic interaction

## **Time-Resolved Infrared Spectroscopy of Water. Relation between the OH Stretching Frequency and the OO Distance**

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It is shown how infrared pump-probe spectroscopy can be used to measure sub picosecond variations of the oxygen-oxygen distribution function in liquid water. A diluted solution HDO/D<sub>2</sub>O rather than pure H<sub>2</sub>O is considered to switch off resonant vibrational interactions between water molecules; the local structure remains unchanged in this substitution. The present study is limited to times superior to 100–200 fs. This permits to avoid problems generated by hard sphere type collisions between water molecules, as well as the interference between ultrafast pump and probe pulses. It is then shown that the Novak-Mikenda type relations between the OH stretching frequency and the OO distance largely survive when going from standard to ultrafast infrared spectroscopy. Moreover, the infrared pump-probe profiles of OH stretching bands closely parallel the oxygen-oxygen distribution functions in this time domain. Infrared pump-probe spectroscopy is thus a useful substitute of time-resolved X-ray diffraction in this exceptional case.

**Key words:** time-resolved spectroscopy, water, hydrogen bonding, OO distance vs stretching frequency

## Structure of a New Schiff Base of Gossypol with Ethyl 4-Amino-1-piperidine Carboxylate in the Solid and in the Solution

by P. Przybylski, K. Pyta, M. Ratajczak-Sitarz, A. Katrusiak and B. Brzezinski\*\*

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Crystals of the Schiff base derivative of gossypol with ethyl 4-amino-1-piperidine carboxylate (GSPC) have been grown and subsequently examined by X-ray diffraction, FT-IR and NMR methods. The crystal space group is  $P2_1/n$  with  $a = 11.869(1)$  Å,  $b = 13.540(1)$  Å,  $c = 28.119(1)$  Å,  $\beta = 91.22(1)^\circ$  and  $Z = 4$ . In the crystal GSPC exists in the enamine-enamine tautomeric form. The intramolecular  $N(16)-H(16)\cdots O(2)$ ,  $N(16')-H(16')\cdots O(2')$  hydrogen bonds assisted by the resonance of the  $\pi$ -electrons in the aromatic system are the strongest. The FT-IR spectral features of the crystals are in agreement with the X-ray data indicating that both parts of the molecule are similarly intramolecular hydrogen-bonded but different intermolecular hydrogen-bonded, although the molecule is symmetrically substituted. The FT-IR as well as  $^1H$  and  $^{13}C$  NMR spectra have shown that in chloroform solution the enamine-enamine tautomeric form is preserved and the whole structure of GSPC becomes more symmetrical.

**Key words:** gossypol, Schiff base, X-ray, FT-IR,  $^1H$ ,  $^{13}C$  NMR

## **DFT Studies of H<sub>3</sub>N–X (X = Li, Na, K, Rb, Cs and Fr) Systems**

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Complexes of alkali atoms with ammonia have been studied using the Density Functional Theory with nonlocal and quasi-relativistic corrections. The stable complexes were found for all alkali atom–ammonia complexes. The calculated interaction energies decrease as one progresses down the periodic table and are in range from –18.9 kcal/mol for lithium system up to –6.5 kcal/mol for the francium complex. Similar tendency is noted for the calculated values of charge transfer. The influence of calculated quasi-relativistic (QR) corrections on values of interaction energies is determined. The QR corrections have no effect on lithium complexes whereas reduce the binding energy from 0.1 kcal/mol for Na system up to 0.9 kcal/mol for Fr complex. The DFT calculated IR harmonic frequencies are compared with experimental values and discussed. The calculated vibrational frequencies of ammonia in complexes exhibit trends that for all systems they are parallel to the strength of the binding energies. For the H<sub>3</sub>N–Li complex the vibrational analysis was supported by anharmonic calculations at the MP2 level. It has been shown that there is a discrepancy between the experimental assignment and MP2 harmonic and anharmonic low frequency intermolecular modes.

**Key words:** density functional methods, MP2 method, molecular complexes, alkali atoms, ammonia, relativistic effects, vibrational frequencies, anharmonic vibrational spectra

## **Molecular Interactions and Structure of H-Bonded Complexes of Bifunctional Nitrogen-Containing Molecules**

by **S.F. Bureiko\*\***, **S.Yu. Kucherov** and **V.M. Schreiber**

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The results of experimental studies and quantum chemical calculations of vibrational spectra and structure of H-bonded complexes formed by N-containing bases 3,5-dimethylpyrazole, diphenyltriazene and diphenylformamidine with carboxylic acids and HHal are discussed. The IR spectra of solutions in CH<sub>2</sub>Cl<sub>2</sub> and CCl<sub>4</sub> and low temperature NMR spectra show the existence of equilibrium between monomers and cyclic selfassociates of the molecules studied. Under the interaction with weak carboxylic acids the complexes have molecular structure with two H-bonds NH...O=C and OH...N, and the interaction with strong acids results in formation of cyclic H-bonded ionic pairs with proton transfer to the N atom of the base. The proton transfer in solution was observed also for open complexes with HHal. The quantum chemical DFT calculations in harmonic and anharmonic approximations confirm the formation of cyclic complexes, while the proton transfer along the OH...N bridge was supported for the complexes with strongest acids. It was shown that the use of variational multidimensional anharmonic approach is the most preferable for calculations of the high-frequency XH stretch in systems where the corresponding normal mode is less characteristic and involves motions of many atoms.

**Key words:** hydrogen bonding, solutions, proton transfer, ionic pairs, IR absorption spectra, quantum chemical calculations

## How Does the Bent–Walsh Rule Work in Molecules of *para*-Disubstituted Benzene Derivatives? The Case of *para*-Nitrophenol and *para*-Nitrophenolate

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DFT (B3LYP/6-311+G\*\*) optimization of nitrobenzene, 4-nitrophenol and 4-nitrophenolate with the constraints for the rotating nitro group, with an interval of 15°, allowed us to show how the Bent–Walsh rule works in a whole range of variation of geometry in the vicinity of both substituted carbon atoms, C1 and C4. For scatter plots of geometry parameters in the vicinity of the C1 carbon atom the general view is in line with the Bent–Walsh rule. The relationship between the mean value of C1C2 and C1C6 bond lengths and the CO bond length has a negative slope, as expected. Two other dependences, this is the above mentioned bond lengths on C6–C1–C2 angle, have also rational slopes but present a relationship between two clusters, for 4-nitrophenol and 4-nitrophenolate, and within these clusters the slopes are opposite, due to the dominant resonance effect over the electronegativity one. In the case of scatter plots of geometry parameters in the vicinity of the C4 carbon atom the general view is again in line with the Bent–Walsh rule, but irregularities are of different shape: they result from strong interactions between oxygen atoms of the nitro group and both CH in *ortho* positions. These interactions become the strongest for planar conformation of the nitro group and decrease in strength with an increase of the rotation angle. This results in a perturbation in the resonance/electronegativity blend leading to substantial deviations from linear dependences of the CN bond length vs. the mean value of C4C3 and C4C5 bond lengths, and the CN bond length vs. C3–C4–C5 angle.

**Key words:** nitro group, substituent effect, electronegativity, Bent–Walsh rule, hydrogen bond

## The Nature of Hydrogen Bonding in Selected Hydrazide Derivatives Investigated *via* Static Models and Car-Parrinello Molecular Dynamics

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The geometric and spectroscopic properties of 2-hydroxy-thiobenzhydrazide and 2-hydroxy-benzhydrazide were investigated within the framework of Density Functional Theory (DFT). Special attention was devoted to the description and analysis of intra- and intermolecular hydrogen bonds. The choice of the compounds was dictated by their structural similarity and the presence of two types of hydrogen bridges: O–H...S (in 2-hydroxy-thiobenzhydrazide, less common) and O–H...O (in 2-hydroxy-benzhydrazide). The latter could be classified as a low-barrier hydrogen bond (LBHB). First the DFT method was used to obtain the geometric parameters for the monomeric and dimeric forms of the compounds at various levels of theory. Then the binding energy was calculated for the dimeric forms to estimate the strength of the intermolecular hydrogen bonds. Atoms in Molecules (AIM) theory was applied to show quantitatively how the formation of the intermolecular hydrogen bonds affects the strength of the intramolecular hydrogen bonds. The electron density and its Laplacian were calculated for the bond critical points defining the H-bridges. Car-Parrinello molecular dynamics (CPMD) was then used to investigate the changes in the geometric parameters as a function of simulation time. This part of the computational study was performed *in vacuo* and in the solid state. The vibrational properties of the investigated hydrazides were obtained *via* Fourier transform of the autocorrelation functions of the dipole moment and atomic velocity. It was found that the formation of the intermolecular H-bonds does not significantly affect the strength of the intramolecular H-bonds. Therefore inductive and steric effects outside the immediate vicinity of the intramolecular bridge have minor influence on its investigated properties. The application of CPMD gave a more detailed picture of the bridged protons' dynamics. The computational results agree with available experimental data. The influence of the intermolecular hydrogen bonding network and non-bonded crystal field interactions on the vibrational features of the investigated molecules is demonstrated and discussed.

**Key words:** hydrogen bond, BSSE, AIM, CPMD, gas phase, solid state

## Change of Prototropic Equilibria for Uracil when Going from Neutral Molecule to Charged Radicals. Quantum-Chemical Studies in the Gas Phase

by E.D. Raczynska<sup>\*\*1</sup>, K. Zientara<sup>2</sup>, K. Kolczyńska<sup>2</sup> and T.M. Stępniewski<sup>2</sup>

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To understand various substitution, oxidation or degradation reactions for uracil, quantum-chemical calculations were performed for two classes of charged radicals (cations and anions) of uracil ( $U^+$  and  $U^-$ ) and model compounds: phenol ( $P^+$  and  $P^-$ ) and hydroxyazines ( $HP1-4^+$  and  $HP1-4^-$ ). In calculations, all possible eighteen prototropic tautomers-rotamers of  $U$  and all possible five prototropic tautomers-rotamers of  $P$  and  $HP1-4$  were considered. Stabilities, internal effects and aromatic character, estimated for charged radicals, were compared with those observed previously for neutral molecules. The greatest changes of the tautomeric preferences take place for radical anions. One-electron reduction stabilizes the keto and amide functions in studied compounds, whereas one-electron oxidation favors the enol function for phenol and the amide function for uracil and hydroxyazines.

**Key words:** uracil, hydroxyazines, charged radicals, prototropic equilibria, gas phase, AM1, DFT

## Structural and Vibrational Investigation of 2-Amino-5-nitropyridine. A Combined Experimental and Theoretical Studies

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The crystal structure of 2-amino-5-nitropyridine at low temperature was previously determined by other authors [1]. In this paper, the complementary X-ray study at ambient temperature is reported. The small differences in lattice parameters measurement in both experiments were found. The differential scanning calorimetric (DSC) measurements were performed. No phase transition was found in the temperature range 100–300 K. Additionally, the detailed vibrational spectroscopic analysis of 2-amino-5-nitropyridine are reported. Powder infrared and Raman spectra of the title compound were measured at room temperature. The molecular structure of 2-amino-5-nitropyridine has been calculated with the aid of density functional (B3LYP) method with the extended 6-311++G(d,p) basis set. The calculated geometrical parameters of investigated molecule in gas phase were compared with experimental X-ray data. The harmonic frequencies, potential energy distribution (PED) and IR intensities of 2-amino-5-nitropyridine were calculated with B3LYP method. The assignment of the experimental spectra has been made assuming the calculated PED.

**Key words:** 2-amino-5-nitropyridine, vibrational spectra, DFT, hydrogen bonds, PED

## **Adenine and Some of Its Analogues in DMSO-d<sub>6</sub> Solution: an NMR and GIAO-DFT Study**

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The results of GIAO-DFT calculations [at B3LYP/6-311++G(2d,p) PCM and PBE1PBE/6-311+G(2fd,p) PCM levels] of <sup>13</sup>C NMR and <sup>15</sup>N NMR parameters have been employed to reinvestigate tautomerism of adenine in DMSO solution. The separate <sup>13</sup>C NMR signals of N7-H and N9-H adenine tautomers have been observed for the first time. The experimental <sup>13</sup>C chemical shifts, <sup>3</sup>J(C,H) coupling constants and <sup>15</sup>N chemical shifts of adenine and three of its methyl derivatives (9MeA, 7MeA and 3MeA) have been quantitatively analyzed using the calculated parameter values. This procedure has provided the solution populations of the predominant adenine tautomers being in agreement with the available literature data. The apparent dependence between the amino group geometry and the chemical shift of the adjacent carbon in 2-aminopyridine system has also been discussed.

**Key words:** adenine, methyladenines, tautomerism, GIAO-DFT study, NMR

## Effects of Strong Inter-hydrogen Bond Dynamical Couplings in the Polarized IR Spectra of *trans*- $\beta$ -Hydromuconic Acid Crystals

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This paper presents the results of investigations of polarized IR spectra of *trans*- $\beta$ -hydromuconic acid (HMA) crystals. The spectra were measured by a transmission method using polarized light at room temperature and at 77 K for three different crystal-line faces. Theoretical analysis of the results concerned linear dichroic effects, H/D isotopic and temperature effects observed in the spectra of the hydrogen and deuterium bonds in HMA crystals at the frequency ranges of the  $\nu_{\text{O-H}}$  and the  $\nu_{\text{O-D}}$  bands. The basic crystal spectral properties could be satisfactorily interpreted in a quantitative way for a centrosymmetric cyclic hydrogen bond dimer model. Model calculations, performed within the limits of the “*strong-coupling*” model, allowed for quantitative interpretation and for the understanding of the basic properties of the hydrogen bond IR spectra of HMA crystals including H/D isotopic, temperature and dichroic effects. Such a model explains not only the two-branch structure of the  $\nu_{\text{O-H}}$  and  $\nu_{\text{O-D}}$  bands in crystalline spectra, but also some essential linear dichroic effects in the band frequency ranges measured for isotopically diluted HMA crystals. In the scope of our studies the mechanism of H/D isotopic “*self-organization*” processes, taking place in the crystal hydrogen bond lattices, was also studied. It was proved that for isotopically diluted crystalline samples of HMA, a non-random distribution of protons and deuterons occurs exclusively in the hydrogen bond dimers. Nevertheless, these dynamical co-operative interactions between the hydrogen bonds do not involve of the adjacent hydrogen bond dimers in each unit cell. The two-branch fine structure pattern of the  $\nu_{\text{O-H}}$  and  $\nu_{\text{O-D}}$  bands was ascribed to the vibronic mechanism of vibrational dipole selection rule breaking for IR transitions in centrosymmetric hydrogen bond dimers. The linear dichroic effect, differentiating properties of the two opposite spectral branches of the  $\nu_{\text{O-H}}$  and  $\nu_{\text{O-D}}$  bands, was also discussed.

**Key words:** hydrogen bond, molecular crystals, polarized IR spectra, H/D isotopic effects, linear dichroic effects, temperature effects, isotopic dilution, H/D isotopic “*self-organization*” effects

## **Studies on the Deamination of the Ethyl Ester of 5-Amino-3-methylisoxazole-4-carboxylic Acid**

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The unusual behavior of the ethyl ester of 5-amino-3-methylisoxazole-4-carboxylic acid (**1**) during deamination is described. Possible explanations for the anomalies of the diazotization reaction are proposed. Deamination methods leading to ethyl ester of 3-methylisoxazole-4-carboxylic acid (**5**) are presented. **5** will serve as a lead compound for a new series of immunomodulatory agents.

**Key words:** isoxazoles, diazotization, deamination, hydrogen bonding, immunological activity

## Theoretical and Spectroscopic Study of Infrared Spectra of Hydrogen-Bonded 2,4-Dithiouracil Crystal and Its Deuterated Derivative

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Theoretical simulation of the bandshape and fine structure of the N–H(D) stretching bands is presented for 2,4-dithiouracil and its deuterated derivative taking into account anharmonic coupling between the high-frequency N–H(D) stretching and the low-frequency N···S stretching vibrations, resonance interaction between two equivalent hydrogen bonds in the dimer, anharmonicity of the potentials for the low-frequency vibrations in the ground and excited state of the N–H(D) stretching mode, Fermi resonance between the N–H(D) stretching and the first overtone of the N–H(D) bending vibrations, and electrical anharmonicity. The effect of deuteration has been successfully reproduced by our model calculations. Infrared, far-infrared, Raman and low-frequency Raman spectra of the polycrystalline 2,4-dithiouracil have been recorded. The geometry and experimental frequencies are compared with the results of harmonic and anharmonic DFT calculations.

**Key words:** 2,4-dithiouracil, hydrogen bond, vibrational spectra, quantum-mechanical calculations

## **Nonconventional Hydrogen Bonding and Vertical Electron Detachment in Anionic Complexes of Gold with DNA Bases: Few Essayistic Fragments**

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The present work performs the computational Gedanken experiments on anion photoelectron spectroscopy for the complexes  $[\text{Au-DNA base}]^-$  established between the auride anion  $\text{Au}^-$  and the DNA bases thanks to the nonconventional hydrogen bond where  $\text{Au}^-$  casts as the nonconventional proton acceptor. The fascinating phenomenon of the proton acceptor character of  $\text{Au}^-$  to form a variety of nonconventional hydrogen bonds with the DNA bases is computationally unveiled in the present work which also shed a light on the mechanism of the vertical electron detachments of  $[\text{Au-DNA base}]^-$  and their further access of the ground electronic states of the neutral parenthood complexes  $[\text{Au-DNA base}]$ .

**Key words:** hydrogen bond, gold, DNA bases, nonconventional hydrogen bond, vertical electron detachment

## **Diazene, a Potential New Hydrogen Bond Donor and Acceptor with Blue-Shifted N–H Stretching Modes: A Theoretical Study**

by **A. Karpfen**<sup>\*\*</sup>, **E. Liedl** and **P. Wolschann**<sup>\*\*</sup>

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The structure and vibrational spectra of hydrogen-bonded complexes formed between *trans*-HNNH (diazene or diimide) and the fluoromethanes CH<sub>3</sub>F, CH<sub>2</sub>F<sub>2</sub>, and CHF<sub>3</sub> are studied at the MP2/6-311++G(2d,2p) level. For each fluoromethane, complex structures were detected in which diazene plays either the role of a hydrogen bond donor or a hydrogen bond acceptor. In addition to the well-known blue shifts of the fluoromethane C–H stretching frequencies, blue-shifted N–H stretching frequencies are predicted for the diazene molecule, irrespective of whether HNNH acts as donor or acceptor. It is shown that this finding can be interpreted as a consequence of the negative intramolecular coupling (NIC) between N–N and N–H stretching degrees of freedom in the isolated HNNH molecule which, upon complex formation, leads to a negative intramolecular response (NIR).

**Key words:** blue-shift, hydrogen bond, diazene, MP2, N–H stretch

## **Infrared Matrix Isolation and Theoretical Study of Methylglyoxal**

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Methylglyoxal (MG) was studied by matrix-isolation IR spectroscopy supported by MP2/6-311++G(2d,2p) calculations. The experimental results show that the molecule exists in the *trans* conformation ( $C_s$  symmetry). The *trans*-MG isomer is estimated to lie 4.96 kcal/mol below the *cis*-MG isomer and the rotational barrier is 5.48 kcal/mol on the ground-state pathway from *trans*- to *cis*-MG. The spectra evidence formation of weak molecular  $MG \cdots N_2$  complexes when the argon matrix is doped both with MG and  $N_2$ .

**Key words:** methylglyoxal, infrared spectra, matrix isolation, *ab initio* calculations

## **Assembly of Protonated Tetramethylpyrazine (TMP) in Triiodide. Vibrational Spectra and DFT Simulations**

by L. Sobczyk<sup>1</sup>, G. Bator<sup>1\*\*</sup>, W. Sawka-Dobrowolska<sup>1</sup>, J. Nowicka-Scheibe<sup>2</sup>,  
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In the complex of tetramethylpyrazine (TMP) with HI<sub>3</sub> two protonated molecules of TMP form the assembly of composition (TMP H<sup>+</sup>)<sub>2</sub>TMP(I<sub>3</sub>)<sub>2</sub>. The X-ray structure, determined at 100 K, shows the <sup>+</sup>N-H...N hydrogen bonds markedly shorter than those found previously [13] at room temperature (2.828 vs. 2.894 Å). The DFT calculations for isolated cation yield the value of 3.038 Å that reflects the softness of the hydrogen bond potential. The calculations of vibrational frequencies for crystalline state reflect very well the IR spectra. This relates particularly to the (NH<sup>+</sup>) mode. A remarkable discrepancy is observed when calculations are performed for isolated assemblies.

**Key words:** protonated tetramethylpyrazine, complexation, vibrational spectra, DFT calculations

## Blue and Red Frequency Shift Effects Related with $\text{XA-H}\cdots\text{B-Y}$ Complex Formation

by K.S. Rutkowski<sup>1\*\*</sup>, A. Karpfen<sup>2</sup>, S.M. Melikova<sup>1</sup> and P. Rodziewicz<sup>3</sup>

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Results of FTIR spectroscopic measurements in cryosolutions and *ab initio* calculations performed for a set of complexes stabilized by conventional and “improper” H-bonds have been presented and analyzed. The main attention is paid to the blue and red frequency shift effects on the stretching vibrations which were observed/or predicted for complexes of a weak to medium strength, formed between so called CH acids and various electron donor counterparts. It has been shown that the features of the dipole moment function and the type of intramolecular coupling between the vicinal bonds of the interacting counterparts predefine in the most extent the sign of the frequency shift of respective stretching vibrations.

**Key words:** hydrogen bond,  $\text{CH}\cdots\text{B}$  interactions, blue and red shifts, liquid phase

**Synthesis, Pharmacological Properties,  
and Computational Study  
of 1-[3-(4-Aryl-1-piperazinyl)]propyl Derivatives  
of Amides of 7-Methyl-3-phenyl-2,4-dioxo-1,2,3,4-  
tetrahydropyrido[2,3-*d*]pyrimidine-5-carboxylic Acid**

by A. Sabiniarz<sup>1\*\*</sup>, H. Śladowska<sup>1</sup>, J. Sapa<sup>2</sup>, B. Filipek<sup>2</sup>, M. Dudek<sup>2</sup>,  
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Two series of novel 1-[3-(4-aryl-1-piperazinyl)]- and 1-[2-hydroxy-3-(4-aryl-1-piperazinyl)]propyl derivatives of amides of 7-methyl-3-phenyl-2,4-dioxo-1,2,3,4-tetrahydropyrido[2,3-*d*]pyrimidine-5-carboxylic acid (**32–46**) were synthesized. In the "writhing syndrome" test all the amides studied displayed analgesic action. The most potent effect was produced by compounds **32**, **34**, and **46**. In the "hot plate" test only two amides, **34** and **37**, showed strong analgesic activity. Furthermore, most of the investigated substances significantly suppressed spontaneous locomotor activity in mice and prolonged barbiturate sleep of these animals. QSAR analysis of the 14 new and 14 earlier described compounds was made.

**Key words:** pyrido[2,3-*d*]pyrimidines, arylpiperazines, amides, analgesic activity, SAR, 2D-QSAR analysis, sedative

## **Principal Components Analysis of Infrared Spectra of Liquid Acetylacetone**

by **B. Czarnik-Matusiewicz, M. Matusiak-Kucharska and J.P. Hawranek**\*\*

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The spectrum of the absorption index in the Mid-Infrared (MIR) region was determined for intramolecularly hydrogen-bonded liquid acetylacetone from transmission studies. In the MIR region very thin layers with thicknesses of a few micrometers had to be used to obtain reliable data. The keto-enol tautomeric equilibrium in the pure liquid was studied by Principal Components Analysis (PCA) of a set of temperature dependent MIR spectra in the range from 25 to 75 °C. Identifications for numerous bands observed in the liquid phase were proposed basing on the results obtained by means of the separation obtained in the loadings plot.

**Key words:** thin film infrared spectra, acetylacetone, hydrogen bonding, Principal Components Analysis

## Non-Empirical Quantum Chemical Studies on Hydration of *trans*- and *cis*-[Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]. Possible Role of Relativistic Effects

by H. Chojnacki<sup>1,\*\*</sup>, J. Kuduk-Jaworska<sup>2</sup>, I. Jaroszewicz<sup>2</sup> and J.J. Jański<sup>2</sup>

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The motivation to this work results from the recognition of *cis*-diamminedichloroplatinum(II) (cisplatin) hydration processes as essential for the fate of this drug in host organism. Applying quantum chemical calculations, there were evaluated the first stages of water molecule impact on platinum complexes: cisplatin and its *trans* isomer. Non-empirical quantum chemical calculations have been performed for reactions of *cis*- and *trans*-diamminedichloroplatinum(II) (transplatin) with the water molecule, assuming the associative mode of reactions running with the addition of a fifth ligand to a square planar d<sup>8</sup> complex and formation of a trigonal-bipyramidal structure of the transition state. For the obtained structures of reactants, transition states, and products, the thermodynamic characteristics (energies and Gibbs free energies) were estimated. Energetics for the ligand exchange reactions were estimated both in gas phase and water solution by using the PCM model. The hydration reactions under consideration are principally endothermic except of the solvated transplatin. Basing on our *ab initio* ZORA calculations, the possible role of relativistic effects in the reaction mechanism is pointed out as well. Obtained results may throw some light on processes which determine the interchange of pro-drug (cisplatin) into activated drug (aqua-form) and implicate their significance in designing of anticancer, Pt-containing chemotherapeutics.

**Key words:** cisplatin, transplatin, interactions with water molecule, quantum chemical calculations, relativistic ZORA calculations

## Hydrogen Bonding of Anilines: Experimental and Theoretical Studies of Complexes of Various Compositions

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Review of works on studies of the influence of the position, number and a kind of substituents in phenyl ring of aniline on proton donor ability in hydrogen bond, spectral, geometric, electrooptic and force characteristics of amino group in complexes with different proton acceptors of 1:1 and 1:2 composition in intra- and intermolecular hydrogen bonds is presented. The influence of proton donors and proton acceptors on the kind of correlation between spectral, geometric, force and electrooptic characteristics of the amino group is analyzed. Obtained results demonstrate the possibility of quantitative description of the changes of dynamic, geometric, force and electrooptic properties of amino group in substituted anilines on passing from free molecules to bonded ones and extend the understanding of the role of various factors in the process of molecular aggregation.

**Key words:** aniline derivatives, hydrogen bonds, valence angles, force constants, electrooptic parameters, equilibrium constants, enthalpy of complexes, correlations

## Hydrogen Bonds in the 1:1 and 2:1 Complexes of 1-Methylquinolinium-3-carboxylate with Mineral Acids Studied by NMR, FTIR and Raman Spectra and DFT Calculations

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The 1:1 and 2:1 complexes of 1-methylquinolinium-3-carboxylate (benzotrigonelline), 3QB, with HCl, HBr, HNO<sub>3</sub>, HClO<sub>4</sub> and HBF<sub>4</sub> have been synthesized and their FTIR, Raman, <sup>1</sup>H and <sup>13</sup>C NMR spectra have been analyzed. The 1:1 complexes with HCl and HBr crystallize as monohydrates and water molecule is localized between the betaine and counter-ions (Cl<sup>-</sup> and Br<sup>-</sup>). In the complexes with HNO<sub>3</sub>, HClO<sub>4</sub> and HBF<sub>4</sub> the anions are connected with the protonated 3QB *via* O–H···X<sup>-</sup> hydrogen bonds. The 2:1 complexes with HCl, HBr, HNO<sub>3</sub> and HClO<sub>4</sub> crystallize with one water molecule while with HBF<sub>4</sub> as anhydrous. Their FTIR spectra show a broad and intense absorption in the 1500–400 cm<sup>-1</sup> region, typical of hydrogen bonds shorter than 2.5 Å. The water molecule in the 2:1 complexes, except perchlorate, forms hydrogen bonds with anions. The influence of counter-ions on proton and carbon-13 chemical shifts is very small and comparable with the experimental error. The protonation of 3QB causes deshielding of all protons and most carbons, except C-3, C-9 and COO, which are shielded. The 2:1 complexes in D<sub>2</sub>O dissociate to the 1:1 complexes and 3QB. Five 1:1 (2–6) and six 2:1 (7–12) complexes have been analyzed by the B3LYP/6-31G(d,p) calculations in order to determine the influence of conformation of COOH groups on hydrogen bond and homoconjugation.

**Key words:** 1-methylquinolinium-3-carboxylate, 1:1 and 2:1 complexes with mineral acids, FTIR, Raman, <sup>1</sup>H and <sup>13</sup>C NMR spectra, DFT calculations

## The Cooperativity of C–H···F Blue-Shifting Hydrogen Bonds. Static and Dynamic Calculations on CF<sub>3</sub>H Dimer, Trimer and Tetramer

by P. Rodziewicz<sup>1,\*\*</sup>, K.S. Rutkowski<sup>2</sup> and S.M. Melikova<sup>2</sup>

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Static and dynamic density functional theory calculations on CF<sub>3</sub>H dimer, trimer and tetramer are presented. All the structures analyzed present the cyclic C–H···F pattern. The energetic, geometrical and vibrational contributions resulting from cooperative effects have been analyzed. The Car-Parrinello molecular dynamics technique has been used to estimate the cooperative effects temperature dependence. The results of simulations might support future molecular beam or supersonic jet experimental studies.

**Key words:** conventional and improper hydrogen bonds, cooperative effects, density functional calculations, molecular dynamics