

EDITORIAL

This special issue of Polish Journal of Chemistry comprises proceedings of the 1st Symposium on Nuclear Magnetic Resonance in Chemistry, Biology and Medicine, held on September 8–10, 2005 in Warsaw, Poland. To this issue, 22 papers by the participants of the Symposium have been contributed. They cover a variety of research fields, including magnetic resonance imaging *in vivo*, applications of NMR spectroscopy to medical diagnosis, studies on molecular properties in the gas, liquid and solid phases as well as quantum chemical calculations of NMR parameters.

This Symposium has been dedicated to Professor Michał Witanowski on the occasion of his 70th birthday and retirement from the Institute of Organic Chemistry of the Polish Academy of Sciences. It has been very rewarding for me to begin my own scientific career under his gentle but demanding and inspiring supervision.

It gives me pleasure to open this issue with a brief recapitulation of the curriculum of Professor Witanowski, a true master of NMR spectroscopy.

April, 2006

Sławomir Szymański
Guest Editor

Professor Michał Witanowski



Michał Witanowski was born on 27th October 1934 in Cracow. In 1951–56, he studied chemistry at the Warsaw Institute of Technology (Politechnika) where he received his Ph.D. in 1962 (promoter: Tadeusz Urbański) and, in 1968, also his D.Sc. (habilitation) degree. In 1976 he became a full professor of chemistry.

In 1956 he joined scientific staff of the Organic Synthesis Department of the Polish Academy of Sciences, which further evolved into the Institute of Organic Chemistry of the Polish Academy of Sciences. With the latter institution, Michał Witanowski had been affiliated for nearly all of his scientific career. As a Fulbright fellow, he spent the academic year 1964/65 with Profes-

sor J.D. Roberts at CalTech.

After completing his Ph.D. thesis, which was focused on infrared spectroscopy of nitroorganic compounds, Michał Witanowski quickly turned into the field of chemical applications of NMR. He could immediately recognize an enormous potential of nitrogen NMR in physical chemistry of nitrogen-containing organic compounds which are so ubiquitous in the chemistry of life. He has initiated systematic research in this direction. At that time, the NMR instrumentation was not well-suited to measure relaxation-broadened spectra of the ^{14}N nuclei, the isotope occurring in almost 100 percent abundance. Despite of numerous technical difficulties he had to face, in collaboration with Lech Stefaniak and Graham A. Webb, he could quickly succeed with elaborating basic NMR characteristics of main classes of nitrogen-containing compounds. He soon has become a world-wide recognized expert of the field. In 1973, he co-edited, with G.A. Webb, the first comprehensive monograph on nitrogen NMR (to which one chapter was contributed by Jean-Marie Lehn, the later Nobel Prize in Chemistry winner). That book initiated a whole series of monographs on nitrogen NMR, published in the international series “Annual Reports on NMR Spectroscopy”, in which Professor Witanowski gave comprehensive accounts of his own research as well as critical reviews of the rapidly expanding literature in the field. The monographs, including the older ones, do not cease to attract attention of workers from diverse branches of chemistry and molecular biology, what is reflected in nearly a hundred of foreign citations every year.

In 1976, Professor Witanowski proposed a convenient nitrogen chemical shielding reference scale, based on neat nitromethane as an external standard, which has been gaining a growing popularity in the NMR community. In recent years, using experimental nitrogen chemical shifts confronted with quantum chemical calculations, he focuses his attention on the microscopic mechanisms of solvent-solute interactions. The list of research papers and monographs coauthored by him includes more than 200 items.

Professor Witanowski is a member of the Warsaw Scientific Society. Since 1982 he has been a member of the Editorial Board of the Spectroscopy International Journal. He was awarded numerous scientific prizes by the Polish Academy of Sciences. He was decorated twice by the President of Poland with the Polonia Restituta Order.

Since 2005, he has been Professor Emeritus at the Institute of Organic Chemistry of the Polish Academy of Sciences.

Sławomir Szymański

Nitrogen NMR: an Historical Perspective

by G.A. Webb

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A compendium of almost 40 years cooperative research with Michał Witanowski and his co-workers on ^{14}N NMR is presented. The work covers our attempts to produce an understanding of nitrogen nuclear shieldings and the establishment of the nitrogen shielding scale based on neat nitromethane as external standard. Assignment techniques for multiple signal nitrogen NMR spectra are discussed. Applications of ^{14}N shielding data in the fields of proton exchange, prototropic equilibria and solute–solvent interactions are given. In the latter case contributions to ^{14}N shielding changes, as a function of solvent, are analysed into specific and non-specific interactions.

Key words: ^{14}N NMR, nitrogen shieldings, nitromethane standard, proton exchange, solute–solvent interactions

Application of ^{31}P Magnetic Resonance Spectroscopy to Observation of Phospholipid Concentration Changes in Blood Serum, Plasma, Peripheral Blood Mononuclear Cells and Bone Marrow Mononuclear Cells from Patients with Hematological Cancers – a Methodological Review

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Phospholipids play an important role in biological events of progression of cancer. ^{31}P magnetic resonance spectroscopy (MRS) can be a powerful method for non-invasive investigations aiming at explanation of phospholipid mechanisms in tumor tissues and body fluids. ^{31}P MRS was applied to serum, serum with added sodium salt of cholic acid, and phospholipid extracts from plasma, peripheral blood mononuclear cells (PBMC) and bone marrow mononuclear cells (BMMC) from healthy volunteers and patients with hematological cancers. Concentrations of phospholipids were derived from integral intensities of the ^{31}P signals. Observations indicated that phospholipid concentration changes in sera, plasma, PBMC, and BMMC can discriminate between non-responding and responding patients, as well as healthy volunteers. The aim of this review is to show how our scientific group applies ^{31}P MR spectroscopy to study phospholipid metabolism in blood serum, plasma, peripheral blood mononuclear cells and bone marrow mononuclear cells of patients with hematological cancers.

Key words: ^{31}P MRS *in vitro*, phospholipids, hematological cancers

**Determination of the Absolute Configuration
of 2-Hydroxyglutaric Acid, 5-Oxoproline and Vigabatrin
in Urine by Chiral Derivatization and ^{13}C or ^{19}F NMR**

by **D. Bal and A. Gryff-Keller**

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Procedures for enantiomeric recognition of 2-hydroxyglutaric acid and 5-oxoproline – markers of metabolic diseases, and of vigabatrin – an antiepileptic drug, suitable for urine samples, have been elaborated. They rely upon derivatization of the metabolites with a chiral reagent; this is made without separation of these compounds from a biological sample. The diastereotopic metabolite derivatives are then distinguished using ^{13}C or ^{19}F NMR spectroscopy. This procedure is not so simple as one proposed previously, but, as opposite to the latter method, it seems to be unailing and still not too complicated.

Key words: NMR, absolute configuration, metabolic disease, vigabatrin

Main Factors Governing Chemical Shifts of Carbon and Nitrogen in Cyano Group. An Experimental and Theoretical Study

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The feasibility of a description of magnetic shielding of carbon and nitrogen nuclei of cyano group in various cyano compounds as a net result of the interplay of different structural factors is discussed. Analysis of experimental data and DFT GIAO calculations of shielding constants have shown that the main factors governing the carbon chemical shifts are the heavy-atom and inductive effects, although the resonance and steric properties of a substituent are also of some importance. On the other hand, the shielding of the cyano nitrogen is connected mainly with the redistribution of π -electrons within the cyano group, which is the result of mesomeric interaction, and, to a lesser extent, with the inductive properties of the substituent. The steric and heavy-atom effects of the substituent seem to be irrelevant for the shielding of cyano nitrogen.

Key words: NMR, magnetic shielding, cyano compounds, DFT GIAO calculations, substituent effect

**Structure of
3-Hydroxy-3-methyl-pyrido[2,1-c][1,4]dihydrooxazinium
Chloride Studied by X-ray, FTIR, ¹H, ¹³C and ¹⁵N NMR
and DFT Methods**

by **M. Szafran, B. Nowak-Wydra, A. Katrusiak and Z. Dega-Szafran**

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2-Hydroxymethyl-pyridine with chloroacetone gave 3-hydroxy-3-methyl-pyrido[2,1-c][1,4]dihydrooxazinium chloride (**1**). Its crystal structure was determined by X-ray diffraction and confirmed by FTIR and NMR spectra. In DMSO and D₂O solutions this compound exists in some equilibrium mixture with N-acetonyl-2-hydroxymethyl-pyridinium chloride (**2**). The equilibrium mixture was proved by FTIR, ¹H and ¹³C NMR spectra. Two of the most stable conformers of both compounds (**1** and **2**) were analyzed by the B3LYP calculations. Correlations between the experimental ¹H and ¹³C NMR chemical shifts for **1** and **2** and the GIAO/B3LYP/6-31G(d,p) calculated magnetic isotropic shielding tensors (σ_{cal}), $\delta_{\text{exp}} = a + b \cdot \sigma_{\text{cal}}$, are reported. A good linear relationship between the experimental and calculated data was obtained only for carbons.

Key words: 3-hydroxy-3-methyl-pyrido[2,1-c][1,4]dihydrooxazinium chloride, X-ray diffraction, IR, NMR spectra, DFT calculations

Nuclear Magnetic Shielding and Indirect Spin-Spin Coupling Constants in Cyclopropane. Gaseous and Liquid NMR Measurements

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Cyclopropane (CH₂)₃ was studied by advanced methods of NMR spectroscopy in liquid and gaseous states at 300 K. Extrapolation of gas-phase chemical shifts to the zero-density limit allowed the determinations of ¹H and ¹³C absolute nuclear magnetic shieldings of an isolated cyclopropane molecule. The indirect spin-spin coupling constants were extracted from experimental spectra and compared with the calculated values reported in the literature.

Key words: NMR spectra, ¹H and ¹³C magnetic shieldings, gas phase, intermolecular effects

NMR Properties of the Formic Acid Dimer

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NMR properties – nuclear quadrupole coupling constants, shielding constants and indirect spin-spin coupling constants – in the formic acid dimer are studied using *ab initio* methods. The accuracy of the calculations is examined for the C_{2h} minimum structure of (HCOOH)₂, comparing the MCSCF (multi-configuration SCF) and CCSD (coupled cluster singles and doubles) results. The dependence of the NMR parameters on dimer geometry is analysed for simultaneous double proton transfer, considering the C_{2h} minimum, the D_{2h} transition state and a few intermediate structures, as well as for two structures representing single proton transfer. For the nuclei involved in the hydrogen bonds not only the effects of the dimerization are very large; the computed NMR parameters also vary significantly with the structure of the cyclic formic acid dimer.

Key words: *ab initio* calculations, NMR parameters, formic acid dimer

Evaluation of Boar Spermatozoa Motility by Pulsed Field Gradient NMR

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The evaluation of spermatozoa motility, viability and morphology is an essential parameter in the examination of sperm and in the establishment of correlations between sperm quality and fertility. Until now, assessment of sperm quality has been based on subjective evaluation of parameters, such as motility and viability, and on objective parameters, such as semen concentration and morphology abnormalities. When subjective optical microscopic evaluation was used in humans and animals, variations of 30 to 60% have been reported in the estimation of the motility parameters of the same ejaculates. Pulsed field gradient nuclear magnetic resonance (PFG-NMR) techniques have been presented here to demonstrate the potential to study flow and transport processes in complex systems. In this paper we present the results of PFG-NMR obtained for a number of samples of boar spermatozoa and discuss whether this method can be useful for fast and reliable spermatozoa motility evaluation.

Key words: NMR, pulsed field gradient, self-diffusion, complex systems

¹⁵N NMR Coordination Shifts in Transition Metal Chloride Complexes with Azines *versus* Type of Central Ion

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¹⁵N NMR coordination shift is the difference between the ¹⁵N chemical shift of the concerned nitrogen atom in the complex and ligand molecules ($\Delta_{\text{coord}}^{15\text{N}} = \delta_{\text{compl}}^{15\text{N}} - \delta_{\text{lig}}^{15\text{N}}$). The measurements, convenient for complexes with diamagnetic transition metal ions, allow to determine metallation sites within potentially ambidentate N-donor heterocycles. In case of azines, the ¹⁵N coordination shifts of pyridine-type nitrogens are usually negative, *i.e.* the shielding is observed. Variable low-frequency ¹⁵N coordination shifts (*ca.* 70–140 ppm) were noted for a number of chloride complexes of Pd(II), Pt(II), Au(III), Pd(IV), Pt(IV), Co(III), Rh(III) and Zn(II) with pyridine, 2,2'-bipyridine, 1,10-phenanthroline, 2,2'-biquinoline, purine and 1,2,4-triazolo-[1,5a]-pyrimidine(s). Some dependencies between the magnitude of the shielding effect and such features of the concerned complex as the type of central ion, its electron configuration (oxidation state) and the coordination sphere geometry were discussed.

Key words: transition metal complexes, azines, pyridine-type nitrogens, ¹⁵N NMR, coordination shifts

^{63}Cu and ^{31}P Nuclear Magnetic Resonance for Characterization of Cu(I) Complexes with P-Donor Ligands

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The analysis of the ^{63}Cu and ^{31}P NMR resonances and the spin-spin coupling patterns for elucidation of the Cu(I) phosphines complexes geometry and ligands' coordination modes in solutions are reviewed. The influences of the steric and electronic properties of P-donor ligands and the dynamic processes in solution on the ^{63}Cu and ^{31}P NMR spectra of Cu(I) complexes are discussed.

Key words: copper(I), phosphines, complexes, ^{63}Cu NMR, ^{31}P NMR, coordination shifts

On the Influence of Low-Frequency Magnetic Field Disturbances on Basic High Resolution NMR Experiments

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The influence of magnetic field disturbances on spectrometer performance in NMR experiments of different kind was investigated in terms of signal to noise ratio and coherence pathway selection efficiency. The strongest effects were observed in the case of experiments based on cancellation of unwanted signals and in correlation spectroscopy.

Key words: NMR, compensation of magnetic field disturbances, correlation spectroscopy

Assessment of Metabolite Concentrations Changes in Rat Brain after Intravenous CDPcholine Injection Using Magnetic Resonance Spectroscopy *in vivo*

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CDPcholine (citicoline, CDPCho) shows beneficial effects in various Central Nervous System (CNS) injury models and neurodegenerative diseases. Previous studies demonstrate conflicting Magnetic Resonance Spectroscopy (MRS) reports regarding the impact of different choline-containing compounds and its doses on brain metabolites. This preliminary study was designed to evaluate concentration changes of brain MR-visible metabolites following intravenous CDPcholine. Twelve healthy rats treated with CDPcholine in three subsequent doses of 1 gram/kg each were examined using ¹H and ³¹P MRS *in vivo*. Following intravenous CDPcholine administration there was a statistically significant increase of the Cho/Cr ratio after first CDPcholine injection. The evidence of CDPcholine influence on brain metabolites has been shown.

Key words: CDP-choline, choline, cerebral metabolism, Magnetic Resonance Spectroscopy

MR Imaging of Mouse Heart *in vivo* Using a Specialized Probehead and Gradient System

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Preliminary results of Magnetic Resonance Imaging (MRI) of cardiac function in mice *in vivo*, using the homebuilt gradient coils and specialized RF probehead are demonstrated. An unshielded gradient system with inner diameter of 60 mm was designed and constructed for the 4.7T/310 magnet with MARAN DRX console (Resonance Instruments). Dedicated probehead, constructed to fit the gradient system, consists of the RF birdcage coil and the animal handling system. ECG-triggered cine images of eight FVB (wild-type) and four transgenic mice with heart failure (Tg α q*44) were acquired at physiological temperature (37°C) with a good quality of multislice images in different phases of the cardiac cycle, as well as a good contrast between myocardium and flowing blood. This technique allowed the calculation of the end-diastolic (EDV) and end-systolic (ESV) volumes of working heart that could be used to monitor the development of heart failure *in vivo* in Tg α q*44 mice.

Key words: MRI, animal model, mouse, heart, cardiac

^{13}C and ^{23}Na Solid-State NMR Spectra of Organosodium Compounds; Part II

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For three organosodium complexes, diphenylmethylsodium (tmeda) (**1**), diphenylmethylsodium (pmdta) (**2**), and fluorenylsodium (tmpda) (**3**), ^{13}C and ^{23}Na solid state NMR spectra have been measured for the first time. They were analysed in terms of chemical shifts $\delta(^{13}\text{C})$ and $\delta(^{23}\text{Na})$ as well as ^{23}Na quadrupole coupling constants, $\chi(^{23}\text{Na})$. Due to non-equivalent ^{23}Na atoms in the unit cell MQS-MAS spectra were used to resolve the individual ^{23}Na resonances. The sensitivity of the NMR parameters for the structural features of the complexes is demonstrated.

Key words: NMR, ^{13}C NMR, ^{23}Na NMR, solid state NMR, organometallic compounds, organosodium compounds, sodium quadrupole coupling

19-Methyl Analogs of Vitamin D₃: Synthesis and Structure Elucidation by ¹H NMR

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Synthesis of three isomeric 19-methylated vitamin D₃ derivatives is described. Two different synthetic paths were used, both involving 3,5-cyclovitamin D precursors easily obtainable from commercial vitamin D₃. The crucial step of the first route consisted of an acid-catalyzed cycloreversion of isomeric 19-methyl-3,5-cyclovitamin D₃ compounds, whereas in the other it involved a Wittig reaction of 10-oxo-19-norvitamin analogs. Neither iodine-catalyzed nor thermal isomerization of the 5*Z*,10*E*-isomer provided detectable quantities of the fourth possible isomeric vitamin with a 5*Z*,10*Z*-configuration. Structures, stereochemistries and A-ring conformations of the final 19-methyl vitamin D₃ analogs were tentatively established on the basis of their 500-MHz ¹H NMR spectra and conformational analysis. Application of ¹H NOE difference spectroscopy and molecular modeling studies allowed for the assignment of preferred solution conformations of the 3,5-cyclovitamin D₃ intermediates.

Key words: vitamins D, 3,5-cyclovitamins D, 5,6-*trans*-vitamins D, cycloreversion process

An Experimental Test for the Approximation of NMR Solvent Effects by Continuum Models. ^{19}F Gas-to-Solution Shifts of SF_6 and CF_4

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^{19}F gas-to-solution shifts were measured for two solute molecules (SF_6 , CF_4) and 39 organic solvents. A correlation between the results for SF_6 and CF_4 is satisfactory and proves that solvent effects of both the solute molecules can be described in the same way. The present ^{19}F shifts of SF_6 are also compared with some previous gas-to-solution shifts observed for ^{129}Xe gas and ^{33}S in SF_6 . It is shown that intermolecular interactions change the shifts of external atoms (^{19}F and ^{129}Xe) in slightly different way than it is observed for the central atom of ^{33}S in a SF_6 molecule.

Key words: NMR, intermolecular interactions, solvent effects, gas-to-liquid shifts

DFT Calculation of Nitrogen Chemical Shifts in the Active Site of Vitamin D Receptor

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The complexed vitamin D receptor (VDR) is responsible for calcium homeostasis. Tryptophan is of special importance for the receptor's functions, as it appears just once in the VDR sequence and occupies the center of the ligand binding pocket. DFT calculations of nitrogen chemical shifts for Trp-NH_{5C} moiety, presented in this work for liganded and free receptor, agree with NMR studies on the VDR specifically labeled with [UL] ¹⁵N₂ Trp. Our calculations confirm orientation of the C(7)=C(8) vitamin D bond under the tryptophan ring. We suggest that interactions with water molecules are responsible for observed deshielding of indole Trp-nitrogen in unliganded VDR.

Key words: nuclear receptors, vitamin D receptor, protein ligand interactions, DFT calculations of nitrogen chemical shifts

^{29}Si and ^{13}C Solid State NMR as a Tool to Study Thermal Processes in Epoxy-Silica Hybrids

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^{29}Si CP/MAS and ^{13}C CP/MAS measurements were carried out for epoxy-silica hybrids treated at 200°C and 300°C. For each sample, the ^{29}Si spin lattice relaxation time was evaluated and compared with the corresponding values for reference samples prepared under the same conditions but without epoxy compound. This work clearly shows the sensitivity of the ^{29}Si T_1 to the morphology of composite materials. The mechanism of thermal decomposition is proposed on the basis of ^{13}C CP/MAS experiments and analysis of changes of the ^{29}Si T_1 relaxation time.

Key words: ^{13}C and ^{29}Si NMR, hybrid materials, relaxation times, thermal decomposition, solid state NMR

Indirect Carbon-Carbon Spin-Spin Couplings in Nitrosobenzenes and Benzene. Experiment and Theory

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Dynamically averaged $^1J(\text{CC})$ spin-spin coupling constants in nitrosobenzene, *p*-substituted (F, Cl, Br, I, Me, NO₂, OMe, NMe₂) nitrosobenzenes, and *o*-nitrosotoluene as well as $^3J(\text{CC})$'s in nitrosobenzene are reported and compared with the literature data on $^1J(\text{CC})$, $^2J(\text{CC})$ and $^3J(\text{CC})$ in benzene. The $^1J(\text{CC})$'s are shown to span a range of 55.5 through 70.5 Hz, and the substituent effects on the constants turn out to be significant, but largely local and almost additive. The effects on the constants seem to augment the coupling with the increasing Pauling's electronegativity of the first atom of the substituent concerned, but complications arise if nitrogenous substituents, NMe₂, NO and NO₂ are considered. For the first time it is shown that quantum mechanical DFT calculations of aromatic carbon-carbon couplings can yield, within a small and random spread, the simplest relationship possible, $J(\text{CC})_{\text{exptl}} = J(\text{CC})_{\text{calcd.}}$, over a broad range of the couplings, starting from -2.5 Hz for $^2J(\text{CC})$ in benzene, through that of about +8 to +10 Hz for $^3J(\text{CC})$'s in benzene and nitrosobenzene, up to the span of +55 to +70 Hz for $^1J(\text{CC})$'s including that of benzene, for a total of 34 individual couplings. This has been attained using the B3PW91/6-311++G(d,p)//B3PW91/6-311++G(d,p) approach, where the same functional-basis set combination was employed for geometry optimizations and for subsequent computations of the couplings. These computations revealed significant effects on the couplings of spatial arrangement of angular substituents with respect to the carbon-carbon bonds within a benzene ring. Attractive potential applications of this combination of experiment and theory are indicated in assessing *syn-anti* equilibria in disubstituted benzenes, by means of aromatic $^1J(\text{CC})$ couplings.

Key words: NMR spectroscopy, INADEQUATE spectra, spin-spin coupling, substituent effects, carbon-carbon bonds, nitrosobenzenes, benzene, calculations, density functional theory

Structure Determination of Some Nitro-5,10,15,20-tetrakis(3-methoxyphenyl)porphyrins Using Simple NMR Techniques

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The structures of some nitrosubstituted *meso*-tetraarylporphyrins were determined by a simple comparison of their ¹H NMR spectra, and confirmed by NOE experiments. On the basis of these investigations it was found that in the *meso*-tetraphenylporphyrin (*meso*-TPP) and its 3-methoxy, 3-methyl, and 3-chloro-substituted derivatives (in the *meso*-aryl rings), the electrophilic nitration occurred in position 4-

Key words: *meso*-tetraarylporphyrins, nitration, ¹H NMR, nuclear Overhauser effect, chemical shift increments

Low Temperature Measurements of Carbon-Carbon Spin-Spin Couplings in *s-cis* and *s-trans* Rotamers of Enaminoketones; Comparison with DFT Computations

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Low temperature ^{13}C INADEQUATE spectra of 4-dimethylamino-but-3-en-2-one **1** and 4-methylamino-but-3-en-2-one **2** revealed $J(\text{CC})$ couplings across one, two and three bonds for the *s-trans* and *s-cis* conformers of compound **1** which exists solely in the *trans* form, and for the *s-trans-s-cis* and *s-cis-s-cis* conformers of the *trans* isomer of compound **2**. A set of CC couplings was also obtained for the *cis-s-cis-s-trans* isomer of **2**. The coupling constants obtained span a range of about 70 Hz, from about 2 Hz observed for the couplings across three bonds to 71 Hz measured for the couplings across the double bonds. Only a slight influence is exerted by the conformation on the couplings across one bond in *trans-1* and *trans-2*. The most significant change is observed upon isomerization of compound **2** to the *cis* form. This outcome leads to internal hydrogen bond formation and to a decrease in both $^1J(\text{C2C3})$ and $^1J(\text{C3C4})$ coupling values, by 2.7 and 5.1 Hz, respectively. The couplings across two bonds are more sensitive towards changes in the conformation than are those across one bond; $^2J(\text{C1C3})$'s in the *s-trans* conformers are significantly larger than those in the *s-cis* structures. Good agreement is observed between the experimental and B3LYP/6-311++G(2d,p)//B3LYP/6-311++G(2d,p) calculated couplings, and the corresponding linear regression is expressed by the following equation: $J(\text{CC})_{\text{exptl.}} = [0.94(\pm 0.01) J(\text{CC})_{\text{calcd.}} + 0.62(\pm 0.71)] \pm 2.12$ Hz.

Key words: enaminoketones, carbon-carbon spin-spin coupling constants, low temperature measurements, calculations, DFT, conformation, hydrogen bond

Damped Quantum Rotation of the Methyl Group in Liquid-Phase NMR Spectra of 9-Methyltryptycene Derivatives

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Hindered rotation of the methyl group evidenced in NMR line shapes is normally viewed as a sequence of classical random jumps between the three equivalent orientations of the group. In solids at low temperatures, possible effects of the quantum tunneling, manifested as apparent spin-spin couplings between the methyl protons, are incorporated by force into this essentially classical picture. In the damped quantum rotation (DQR) theory formulated recently, the hindered rotation is entirely a non-classical phenomenon. It is described in terms of a consistent combination of the quantum tunneling and two quantum rate (coherence-damping) processes; the phenomenological behaviour of the methyl group becomes classical only when the two quantum rate processes occur with equal rates. Occurrences of the DQR effect, *i.e.*, differences between the two quantum rate constants, were earlier detected in solids at temperatures below 110 K and, surprisingly, also in liquids above 170 K. In this study, further examples of the DQR effects in liquid-phase NMR are reported. Like the previous observations for liquids, the present ones involve the strongly hindered methyl groups in 9-methyltryptycene derivatives. A particularly clear manifestation of the DQR effect is found for 1,4-dibromo-9-methyltryptycene. With the ratio of the two quantum rate constants exceeding 1.25, this system shows the farthest departure from the classical behaviour, ever reported for liquids. Our earlier observations of the quantum tunneling of the methyl group in liquid phase, reflected in strong dependence on temperature of the J-couplings between the methyl protons, are now augmented by further evidence.

Key words: methyl group, hindered rotation, NMR line-shape, quantum tunneling, coherence damping