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**INTERNATIONAL SYMPOSIUM
ON NMR SPECTROSCOPY**

PROCEEDINGS

Smolenice, Czechoslovakia

September 29th - October 3rd, 1980

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PREFACE

This book contains extended abstracts of invited lectures and abstracts of communications to be presented as short lectures or posters. The abstracts have been retyped according to technical requirements. After retyping each abstract was compared with the original and corrected where necessary. If in spite of this an error should have been introduced into the text we apologize to the authors and beg their understanding. No change was made with the contents of the abstracts so that the responsibility for them rests with the authors.

The abstracts are grouped according to the kind of lectures or posters and within the groups they are arranged alphabetically according to the name of the first author.

The organizing committee.

September 10th, 1980

¹H NMR STUDY OF 2-HYDROXY-1,3-PROPANEDIAMINE-N,N,N',N'-
-TETRAACETIC ACID (HPDTA) AND 1,3-DIAMINO-2-PROPANOL (DPO)

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The chemical shifts and coupling constants of non-labile protons in D₂O solutions of the HPDTA, DPO and 1,3-propanedi-amine-N,N,N',N'-tetraacetic acid (PDTA) were studied as a function of pD and temperature. HPDTA exists as a tetraanion Y⁴⁻ in the 11,5 - 14,0 pD range. Changes of the chemical shifts in the 11,5 - 6,5 pD range suggest that nitrogen atoms protonate in this range and that the structure of dianion of HPDTA is dipolar H₂Y²⁻.

The changes of methine proton chemical shift during the protonation of Y⁴⁻ of HPDTA and dianion of DPO Y²⁻ are anomalously high in comparison with the corresponding proton shift changes in PDTA. The conformation of propane fragments of HPDTA and DPO determined from the vicinal coupling constants (after LAOCOON III calculation of A₂B₂X spectra) suggest that the intramolecular hydrogen bonds between hydroxyl and amino groups and their transition from >N...H-O-C to >N⁺H... $\underset{\text{H}}{\text{O}}$ -C during protonation are the main cause of methine shift anomaly.

PCILO calculations of conformational energy maps of DPO support these conclusions and suggest the proton tunnelling as the mechanism of >N...H-O-C → >N⁺H... $\underset{\text{H}}{\text{O}}$ -C transition.

CORRELATION OF ^{11}B NMR SHIFTS WITH ELECTRONIC
STRUCTURE OF NINE-VERTEX HETEROBORANES $4\text{-CB}_8\text{H}_{13}$,
 $4\text{-CB}_8\text{H}_{14}$, $4\text{-SB}_8\text{H}_{12}$ AND $4,6\text{-C}_2\text{B}_7\text{H}_{13}$

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^{11}B NMR spectra of $4\text{-CB}_8\text{H}_{14}$, $4\text{-NB}_8\text{H}_{13}$, $4\text{-SB}_8\text{H}_{12}$ and $4,6\text{-C}_2\text{B}_7\text{H}_{13}$ are presented, together with a detailed assignment of individual signals. Correlations of ^{11}B NMR chemical shifts with STO-3G Mulliken atomic charges, 2p orbital densities and inner shell eigenvalues together with CNDO/2 atomic charges, 2p orbital densities and valencies are evaluated. The best one is the chemical shift vs. CNDO/2 2p orbital density linear correlation.

Similarities in the ^{11}B NMR spectra reflect the similarities in the electronic structures which are discussed in quantum mechanical terms with the emphasis on the nature of heteroatom bonding. Each heteroatom influences mainly the charge of the neighboring atoms - no distinct long-range effects on atomic charge or chemical shift are observed. The valencies of nitrogen and sulfur reflect the way of heteroatom incorporation into skeletal bonding - both nitrogen and sulfur exceed significantly valency values of 3 and 2, respectively. The similar multi-center bonding pattern with XB_8H_{12} / X = CH_2 , NH, S/ molecules is proposed on the grounds of Mulliken overlap populations / STO-3G / and Wiberg indices / CNDO/2 /.

Despite that the theory of chemical shift in polyhedral clusters emphasises the importance of the paramagnetic term, and

deviation from linear chemical shift vs. charge density correlation are often found, in this case of structurally similar isoelectronic heteroboranes a straightforward linear dependence is found.

STUDY OF CONFORMATIONAL STRUCTURE OF
POLY (ETHYLENE TEREPHTHALATE) MODELS
BY ^1H AND ^{13}C NMR METHODS

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As part of a program aimed at the detailed structural interpretation of vibrational spectra of poly(ethylene terephthalate), the conformational structure of methyl benzoate (I), ethyl benzoate (II), diethyl terephthalate (III) and ethylene dibenzoate (IV) was analyzed by ^1H - and ^{13}C -NMR spectroscopy. The number of conformers to be considered in this analysis was determined from infrared and Raman spectra. For IV in the liquid state, conformation about the ethylene bond was determined by analysis of the ^{13}C satellite bands in ^1H -NMR spectra, and was found to be predominantly gauche, contrary to the predominantly trans conformation found by other methods in the crystalline state. - Conformational structure due to rotation about the $-\text{O}-\text{CH}_2-$ bond in II, III and IV could be characterized from the $^3J_{\text{CH}}$ coupling constants determined by analysis of the carbonyl band in ^{13}C -NMR spectra measured with selective heteronuclear decoupling of the aromatic protons. In this analysis for compound IV, use was made of the coupling constants determined from the ^{13}C satellite structure in ^1H -NMR spectra. In all cases, the trans conformation of the $-\text{O}-\text{CH}_2-$ bond was found to predominate. - Based on the results of NMR and vibrational analysis, the conformational structure of IV in the liquid and in the crystalline state is proposed.

THE NMR INVESTIGATION OF COORDINATE BONDING IN
Ni/II/, Co/II/ AND Cu/II/ COMPLEXES OF TETRACYCLINE

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Basing on the dependence of ^1HMR chemical shifts and signals broadening of tetracycline as a function of paramagnetic ions /Co/II/, Ni/II/, Cu/II// concentration and at the constant ratio of the central ion to ligand as a function of pH, place and conditions of coordination of tetracycline by central ions were described.

Other influence of Cu/II/ ions on ^1HMR tetracycline signals than Co/II/ and Ni/II/ was observed. This difference is considered as a result of different length of the central ion-ligand bonds.

On the basis of the results obtained from electron spectroscopy, infrared spectroscopy, spectropolarimetry and magnetochemistry investigations the structures of the complexes obtained were proposed.

SOLID STATE HIGH RESOLUTION ^{29}Si NMR OF SILICATES
AND ORGANOSILICON POLYMERS

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High resolution ^{29}Si NMR has proved to be an efficient method for silicate anions and organosilicon polymers in solution. In solid silicates or silicon polymers dipolar interactions between nuclear spins and anisotropy of the ^{29}Si chemical shifts lead to excessive NMR line widths and to weak, complete overlapping lines if conventional FT or CW NMR methods are used. However a combination of rapid sample spinning at the magic angle to the external H_0 field with high power ^1H spin decoupling and, wherever possible, ^1H - ^{29}Si cross polarization provides a practical method for obtaining high resolution ^{29}Si NMR spectra in amorphous and microcrystalline solids and powders. By means of this technique the high resolution ^{29}Si NMR spectra of solid silicates, aluminosilicates and organosilicon polymers have been studied.

The ^{29}Si chemical shifts in aluminum free silicates are generally the same in the solid state and in solution and depend mainly on the degree of condensation of the silicon-oxygen tetrahedra. Five well separated and analytically useful ranges of chemical shifts can be established for monosilicates, chain end groups, middle groups in chains, branching sites and cross-linking groups. In the insoluble aluminosilicates where no parallels with solutions are possible, additional paramagnetic shifts appear, which correlate well with the degree of silicon substitution by aluminum in the lattice. In aluminosilicates

with tectosilicate framework five distinct ^{29}Si chemical shift ranges are thus created, depending on the number of AlO_4 tetrahedra connected to the SiO_4 tetrahedra under consideration. In phyllosilicates with inter-layer six-coordinated aluminum additional paramagnetic shifts have been observed. The regularities in the ^{29}Si chemical shifts were used to establish the presence of different building units as well as the type and regularity of their distribution in the lattice of a series of silicates and aluminosilicates of different structures. Representative examples of natural minerals and synthetic products, including mono-, di- and chainsilicates, micas, clay minerals, feldspars and zeolites will be discussed in detail. Reliable information about Si-Al ordering in the aluminosilicate framework have been obtained which could be used to avoid ambiguities in X-ray structure studies. In some cases new structure types with AlOAl anti-Loewenstein bridging have been proposed.

Similar to the silicates, in the organosilicon polymers ^{29}Si chemical shifts can be observed which depend on the number of OSi bonds and the type of the other substituents at the silicon atom under study. This offers detailed information about the structural units of the polysiloxane framework and their distribution and opens a new possibility of structure determination of solid organosilicon polymers.

This work was carried out in close cooperation with Prof. E. Lippmaa and his coworkers Drs. M. Alla, M. Mägi, A. Samoson and M. Tarmak from the Institute of Chemical and Biological Physics of the Estonian Academy of Sciences, Tallinn, USSR.

We are indebted to Drs. K. Wappler, D. Hoebbel, A.-R. Grimmer, K.-P. Roethe, U. Lohse and others for the samples used in this study and helpful discussions.

300 MHz ¹H NMR STRUCTURAL STUDY OF ANTITUMOR GLYCOPEPTIDES

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Towards the end of the 50ies Bulgarian workers /1/ have isolated a preparation with marked antitumor activity from the cell walls of Lactobacillus bulgaricus. In this Institute synthesis of the peptides was undertaken with the objective of checking the structure proposed and investigating the structure-activity relationship in such compounds. As a result both the glycopeptide and a number of its analogs including a cycloglycopeptide, displaying varying activities, were prepared.

This report treats of the structural details of the peptide moiety in the successive steps of the synthesis beginning with dipeptide and ending with the pentapeptide and of an investigation into the conformational rearrangements accompanying ring closure, of a glycopeptide containing D-Asp, D-Glu and L-Lys residues.

A study of the chemical shifts, spin coupling constants and temperature coefficients shed lighth on the mutal effect of the disaccharide and peptide moieties on the conformation of the glycopeptides. Spatial structures of the glycopeptides in solution are proposed.

Reference

- /1/ Bogdanov I.G. and Popkhrstov P.: /1961/ Bulletin of the Scientific Research Institute for Anti-Cancer Antibiotics, Sofia, N 1.

THE CONSERVATIVE SIMULATION OF BROAD LINE NMR SPECTRA
USING CRT GRAPHIC TERMINAL

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Problem of simulation of broad line NMR spectra can be very effectively handled with minicomputer equipped with CRT graphic terminal. By the aid of this type of system the measured and simulated broad line spectrum can be displayed simultaneously. To obtain best agreement between measured and simulated spectrum, the parameters of simulated spectrum can be immediately changed according the previous result displayed on the screen of graphic terminal.

In the literature are presented several procedures of mathematical description of broad line spectrum by the aid of computer^{1/}. Our procedure of mathematical description of simulated spectrum can be simply written as

$$Y(B) = \sum_i^n C_i L_i(B) + \sum_j^n C_j G_j(B)$$

where C_i and C_j are the coefficients of individual components of the Lorentzian L_i B and Gaussian G_j B functions. Using simulated spectrum of this type many parameters, as second and fourth moments, areas etc. can be effectively calculated for each individual line even for the complex broad line spectrum.

As the best fit criterium the sum of square differences can be used.

$$y = \sum_k \left(Y_k^{\text{exp}} - Y_k^{\text{sim}} \right)^2$$

Reference

- /1/ K.Unterforsthuber, K.Bergmann: J.Magn.Res. 33 483 /1979/
and referencies presented in this paper

CORRELATIONS BETWEEN ^{29}Si AND ^{31}P CHEMICAL SHIFT
ANISOTROPIES AND THE STRUCTURE OF SOLID SILICATES
AND PHOSPHATES

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Various techniques of high resolution NMR in solids are used for evaluating the chemical shift tensors of ^{29}Si and ^{31}P nuclei in inorganic silicates and phosphates. The obtained results are related to the known structure of the anions. It is shown that there are correlations between the size and symmetry of the tensor and the bond lengths and angles in the SiO_4 and PO_4 tetrahedra forming various types of anions. Using the conventional π -bond concept coincidence of the most shielded principle axis of the tensor with the region of the highest π -bond character is found. The efficiency of the high resolution NMR in solids for monitoring the crystal chemistry of silicates and phosphates is discussed.

COMPUTER TECHNIQUE FOR SENSITIVITY AND RESOLUTION
ENHANCEMENT IN FT NMR SPECTROSCOPY

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Signal resolution is one of the most important problems in the NMR study of biological macromolecules. Application of available types digital filters for resolution enhancement usually leads to significant decreasing of signal-to-noise ratio.

This paper describes simple time domain digital filters which effectively narrow lines and only slightly deteriorate the S/N ratio. Selection of the type of digital filter depends on the spectra characteristics (initial line width to be narrowed, differences in the line widths over the entire spectrum, initial and final S/N ratio). Optimal arrangements of the operational system for diverse FT NMR experiments are discussed.

^{11}B SUBSTITUENT EFFECTS AND THEIR ADDITIVITY
WITH $\text{C}_2\text{B}_{10}\text{H}_{12}$ CARBORANES. FACTORS INFLUENCING THE
SUBSTITUENT INCREMENTS. CONFRONTATION WITH
BENZENE SUBSTITUTION.

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An exchange of hydrogen for a substituent with icosahedral o-carborane, 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$, m-carborane, 1,7- $\text{C}_2\text{B}_{10}\text{H}_{12}$, and p-carborane, 1,12- $\text{C}_2\text{B}_{10}\text{H}_{12}$, evokes following changes of ^{11}B chemical shifts of particular atoms:

- 1/ substituted B-atoms: Cl +10 \pm 2 ppm, Br + 3 \pm 2 ppm, I - 13 \pm 2 ppm
- 2/ vicinal B-atoms: largely a shift to the lower field
- 3/ antipodal / oposite / B-atoms:
 - a/ shift to the higher magnetic field for +M substituents
 - b/ no change for -M substituents

Shift-changes of particular skeletal atoms at above skeletons evoked by Cl, Br, I, SH and CH_3 bound to C, i.e. to the most positive site or to a most negative B-atom of the given skeleton are tabulated. The found effects are of an additive character with a deviation less than 0.5 ppm. A very good agreement of the calculated and of the found ^{11}B shifts allows to determine with a high reliability: a/ the character and location of substituents in the given skeleton, b/ the assignment of particular signals in the ^{11}B spectrum in question. This statement was verified on more than 20 examples of di- and tri-substituted icosahedral carboranes.

The only differences in additivity between calculated and found values were always found at vicinally substituted skeletal atoms /deviation + 0.6 to 2.0/ and at antipodally substituted skeletal atoms /deviation -0.8 to -2.2 ppm/. These deviations indicate both an existence of the mutual perturbation in vicinal and antipodal positions.

In contrast to the antipodal effect which was several times described by us and confirmed by other authors, the vicinal effect was not studied in details. The present study has shown that the value of a "vicinal shift" / VS / depends on:

- a/ the character of the substituted skeleton
- b/ the character of the substituent
- c/ the electron density at the skeletal atom bearing the substituent: a decrease of the electron density by 0.1 e brings an increase of the VS by ca 1.5 ppm
- d/ the electron density at the observed B - atom: an increase of the electron density by 0.1 e brings an increase of the VS by ca 1.0 ppm.

Whereas the effects a/ and b/ are analogous to those with benzene derivatives, the c/ and d/ effects reveal a new feature, i.e. a very important influence of the charge of particular atoms on the extent of the change brought by a substituent. These effects are unobservable with benzene derivatives but have to appear with heteroaromatics in which particular positions differ in electron density.

ON-LINE SIMULATION OF NMR LINE SHAPE

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A program for the computer ADT 4300 was developed which enables to create desirable amount of Lorentzian curves directly on the screen of the 100 MHz NMR spectrometer Tesla BS 567. The position, height and width of simulated lines can be continuously varied to attain exact overlap with simultaneously screened experimental NMR signal.

NMR spectrometer Tesla BS 567 was modified to allow slow CW sweep rates so that the NMR line shape is not disturbed by ringing. Also the accumulation of CW spectra was made available.

Several examples of use of this simulation technique will be presented ranging from a plain quantitative analysis of mixtures (compared to area integration) to the determination of a signal broadening caused by addition of relaxation reagent $Gd(fod)_3$ or by intramolecular dynamic processes.

STUDY OF THE SELF-ASSOCIATION OF n-ALCOHOLS BY NMR

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Experiments examining the self-association of n-propanol, n-butanol and n-pentanol were conducted in dilute solutions using quasi-inert solvents.

The measurements were performed on a TESLA Model BS 487 C 80 MHz NMR instrument at several temperatures. The temperature of a solution was established from the chemical shift of methanol's hydroxyl proton. The equilibrium and thermodynamic characteristics for each n-alcohol were determined on the basis of the temperature and concentration dependence of their hydroxyl proton chemical shift.

Concentration ranges were chosen such that only one type of associated species could be assumed in each solution.

The association equilibrium constants were calculated from the NMR data by using the proton chemical shift-dependent equations derived by Lippert^{/1/}. In this way we determined that the association number was approximately two in each case.

The entropy and enthalpy of the association were obtained from the temperature dependence of the chemical shifts and of the equilibrium constants. The correlation between the calculated values and the number of carbon atoms shows the same tendency as that reported for other alcohols^{/2/}.

References

- /1/ Lippert, E.: *Bunsenges. Phys. Chem.* 1963, 67, 267.
- /2/ Patterson, L.K., Hamaker, R.M.: *Spectrochim. Acta* 1967, 23A, 2333.

NMR STUDY OF ISOMERIZATION OF DIAMANTANE-3-ONE OXIME

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The isomerization of Z- and E-form of diamantane-3-one oxime was studied by ^1H NMR spectroscopy. The rate constants of isomerization was measured from time dependence of concentration changes of isomer (Z and E) at 308, 318, 323 and 328 K. It was found the equilibrium constant of isomerization K is independent on the temperature range.

The Gibbs activation energy ΔG^\ddagger for the isomerization was calculated from the temperature dependency of rate constants by using Eyring equation $k = (k_B \cdot T/h) \cdot \exp(-\Delta G^\ddagger/R_k T)$. The ΔG^\ddagger obtained is $1,1 \cdot 10^5$ J/mol. This results is in accord with literature data and confirms the possibility of the isolation of both E, Z isomer resp.

¹³C NMR SPECTRA OF OLIGOGLUCURONIC ACID DERIVATIVES
RELATED TO BRANCHED 4-O-METHYLGLUCURONO XYLANS

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¹³C NMR spectra of a series of synthetic 4-O-methyl- α - and - β -D-glucuronic acid and β -D-xylopyranose-containing oligoglycuronic acid (from aldobiouronic to aldopentaouronic acid) derivatives have been interpreted. The data extracted from the spectra can be used as an aid for signal assignments in the ¹³C NMR spectra of (4-O-methylglucurono)xylan type polysaccharides and related substances.

LAOCOON WITH THE GRAPHICAL INPUT/OUTPUT OF THE DATA

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LAOCOON with the slightly modified input and output data is combined with the program TSIM, which displays experimental and simulated spectra simultaneously on the CRT screen. The shape of theoretical lines can be chosen (stick, Lorentzian, Gaussian or mixed). The assignment of the theoretical line numbers to the experimental frequencies is made by the means of the crosshair on the screen. The practical experience proved that the use of the LAOCOON with the graphical input/output capabilities (over the use of the standard LAOCOON) makes analysis of the NMR spectra more comfortable and faster.

NMR STUDY OF COMPLEX FORMATION BETWEEN $TiCl_4$
AND N-METHYLATED HIGHER LACTAMS

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In connection with studies of the mechanism of cationic polymerization of lactams catalyzed by Lewis acids, the interaction of N-methylated lactams (L) with $TiCl_4$ (M) was studied by NMR spectroscopy. Besides NMR the interaction of $TiCl_4$ with the rigid molecule 2-methyl-2-aza-bicyclo-(2,2,2)-octane-3-one was also investigated by Raman spectroscopy (1). The results obtained in (1) were utilized in the interpretation of 1H and ^{13}C NMR spectra of higher lactams. It was found that all the studied lactams form with $TiCl_4$, at mole ratios $L:M > 2$, two types of complexes of composition ML_2 . The properties of these complexes in $CDCl_3$ or tetrachloroethane- D_2 solutions are practically independent of lactam ring size for lactams in cis configuration. For N-methylated lactams which are present in both cis and trans forms in solution, the dynamics of the cis-trans isomerization reaction and the effect of $TiCl_4$ upon this reaction were studied by analysis of the temperature dependence of NMR spectra. In the presence of $TiCl_4$, an increase of the rotation barrier about the amide bond of the complex-bound lactam was observed, indicating an increase of the double-bond character of the amide bond in the complex.

Reference

- /1/ J.Lövy, J.Štokr, D.Doškočilová, R.Puffr, J.Dybal,
B.Schneider: J.Mol.Structure, in press.

^{13}C AND ^{15}N NMR SPECTRA OF PHENYLHYDRAZONES
WITH INTRAMOLECULAR HYDROGEN BOND

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The ^{13}C and ^{15}N NMR spectra of 2,3,4-pentanetrione 3-phenylhydrazone (I), dimethyl 2-phenylhydrazonopropanedioate (II), 2-phenylhydrazone-3-oxobutanoate (III) [(E) isomer first, than a mixture of (E) and (Z) isomers], 1-phenyl-3methyl-1H-pyrazole-4,5-dione 4-phenylhydrazone (IV) and 1,2-naphtalenedione 1-phenylhydrazone (V) (in a mixture of tautomers with 1-phenyl-azo-2-naphtalenol) and their ^{15}N isotopomers were measured. The ^{13}C and ^{15}N chemical shifts and absolute values of the coupling constants $^1J(^{15}\text{N}^{15}\text{N})$, $^nJ(^{15}\text{N}^{13}\text{C})$ and $^nJ(^{15}\text{NH})$ are reported. The ^{13}C chemical shifts of phenyl groups carbons exhibit relatively constant values in the compound I - IV [δ [C(1) - C(4)] : 141,2; 115,7; 129,3; 125,3; \pm 0,5]. For the compound V representing a mixture of azo and hydrazone form the content of latter has been calculated from ^{15}N chemical shifts of both nitrogen atoms and from ^{13}C chemical shifts of phenyl group carbons. The calculations gave very similar results.

References

- A.Lyčka: Coll. Czech. Chem. Commun., in press
A.Lyčka, D.Šnobl: submitted for publication
A.Lyčka, D.Šnobl, V.Macháček, M.Večeřa: submitted for publication

MINICOMPUTER-BASED $^{13}\text{C}/^1\text{H}$ NMR SPECTRA INTERPRETATION

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Use of a medium-sized minicomputer equipped with a medium-sized disk storage unit for NMR spectra interpretation is described. The interpretation system is based on two independent reference data files for ^{13}C and ^1H NMR spectra. Coding of chemical structures is based on a modified linear notation system. Data retrieval can be performed by means of two different search keys, spectral and structural. In the spectral search mode, all spectra exhibiting a reasonable degree of similarity to the input set of spectral parameters will be retrieved. In the structural search mode, the structures having reasonably large structural fragments in common with the sample structure will be found.

To allow the visual comparison, the input and retrieved ^{13}C spectra can be reconstructed from their parameters and displayed on the graphic CRT terminal. With this file search system, mutual assignment of subspectra and substructures can be achieved effectively.

^{13}C AND ^1H NMR STUDIES ON AROMATIC AZOMETHINES /1/

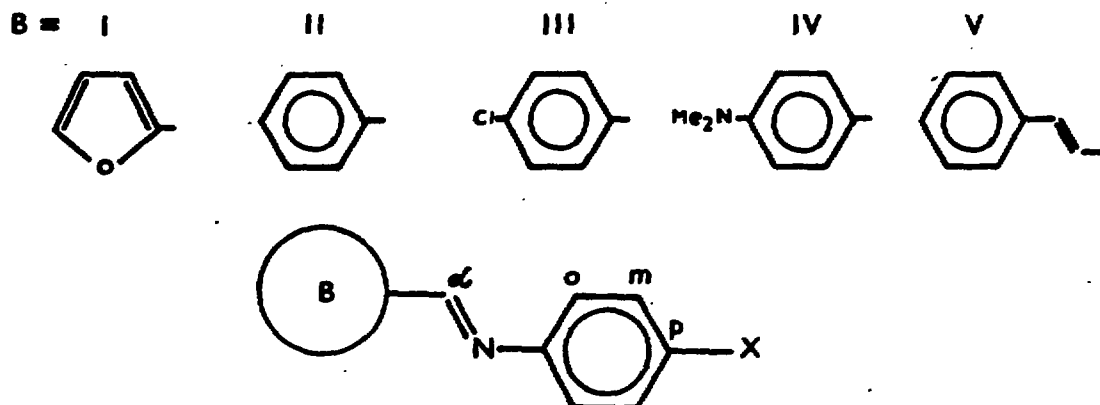
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We have investigated the ^{13}C and ^1H NMR spectra of 5 series of 45 aromatic azomethines, p-substituted in ring A.



It could be shown, that the ^{13}C SCS of these compounds are quite normal in neutral solution. Analogous positions in the compounds show a good correlation of chemical shifts with HAMMETT substituent constants or F and R values of SWAIN and LUPTON respectively. The well known alternation-effect of chemical shift in order to conjugative and nonconjugative positions is to be seen in all compounds. These results are good comparable with quantum chemical CNDO/2 calculations.

The ^1H chemical shifts generally correlate good with the ^{13}C shifts. Only the α positions show a incomparable dependence of ^1H and ^{13}C SCS.

COMPUTER-BASED $^{13}\text{C}/^1\text{H}$ NMR SPECTRA INTERPRETATION

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Use of a medium-sized minicomputer equipped with a medium-sized disk storage unit for NMR spectra interpretation is described. The interpretation system is based on two independent reference data files for ^{13}C and ^1H NMR spectra. Coding of chemical structures is based on the IUPAC linear notation system. Data retrieval can be performed in one of two different search keys, spectral and structural. In the spectral search mode, all spectra exhibiting a certain degree of similarity to the input set of spectral data will be retrieved. In the structural search mode, structures having reasonably large structural fragments in common with the sample structure will be found.

To allow the visual comparison, the input and retrieved ^{13}C spectra can be reconstructed from their parameters and displayed on the graphic CRT terminal. With this file search system, mutual assignment of subspectra and substructures can be achieved effectively.

We have discussed these exceptions as to be founded in the ratio of different shielding effects:

δ_{direct} causes a shielding of H_{α} , but δ'_{RS} (ring current effects of ring A) and $\delta_{\text{van der Waals}}$ have the opposite, deshielding, effect.

In TFA-d-solutions the ^{13}C and ^1H SCS are in good correlation to substituent constants for all positions.

Reference

- /1/ Carlos Perez Martinez: Dissertation, Humboldt-University of Berlin, 1979

MULTINUCLEAR NMR STUDY OF SIX-MEMBERED
HETEROAROMATIC CATIONS

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High-resolution NMR spectra of six membered heteroaromatic cations, $[C_5H_5X]^+$ (where $X = O, S, Se, N-R$), have been recorded and the isotropic values of spectral parameters for spin 1/2 nuclei determined. These include the magnitudes and relative signs of all possible $^1H - ^1H$, $^{13}C - ^1H$, $^{15}N - ^1H$, $^{13}C - ^{15}N$, $^{71}Se - ^1H$, $^{71}Se - ^{13}C$ as well as one-bond and three-bond $^{13}C - ^{13}C$ coupling constants. The results are discussed in terms of electronic structure of the charged molecules.

^{13}C NMR SPECTRA OF AZACHALCONES

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The ^{13}C NMR spectral parameters were obtained for chalcone and a series of aza- and diazachalcones. From the values of $^3J(\text{C}_1, -\text{H}_\alpha)$ coupling constants the dihedral angles between the carbonyl group and double bond plane in several derivatives were estimated. The experimental NMR data, in agreement with the quantum-chemical PCILO calculations, show that in the case of 2'-azachalcone the most probable conformation is s-cis. For 3'- and 4'-azachalcones the values of $^3J(\text{C}_1, -\text{H}_\alpha)$ indicate the non-planar conformation which is also in accord with PCILO results.

INTERNAL ROTATIONS IN THE SILOXANE $T^{Ph}M_3$

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The ^{13}C , ^{17}O and ^{29}Si spin-lattice relaxation rates and nuclear Overhauser enhancements were measured in degassed siloxane $T^{Ph}M_3$ in the temperature range from 250K to 350K. A "Bruker" NMR spectrometer CXP-200 was used. From the separated relaxation contributions due to the intramolecular dipole-dipole interaction of ^{13}C and ^{29}Si nuclei with 1H and quadrupole interaction of ^{17}O nuclei internal rotation rates around Si^T-C^{Ph} , Si^M-O and Si^M-C^M axis are determined. The diffusional rotation and jump models for the description of $O-SiMe_3$ motions are discussed.

^1H AND ^{31}P NMR SPECTROMETRIC STUDIES
ON DIPHENYLPHOSPHINYL STILBENES,
DIPHENYLPHOSPHINYL STYRENES AND THIODIPHENYL STYRENES /1/

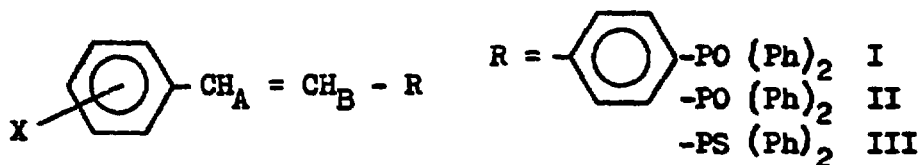
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In connection with photochemical investigations we carried through n.m.r. measurements of substituted stilbenes (I) and styrenes (II, III)



In the case of the compounds I it is to be seen, that the SCS of X ends before phosphorus, δ_{P} is nearly constant. The position H_A is not sensitiv to variation of the substituents X. In position H_B we found a correlation to Hammett constants. The styrenes II show a significantly influence of X to phosphorus. The deshielding of the proton H_A and H_B in II and III is greater than in I, due to the nearer position of the electron acceptor group. The greater sensitivity of H_A and H_B in II and III due to variation of X and the good correlation coefficients show, that these styrenes are in better agreement to the model of polymethin structure than other analogous styrenes, e.g. with $\text{R} = -\text{CN}$, $-\text{NO}_2$ or $-\text{SO}_2\text{CH}_3$.

/1/ K.G.Berndt: Dissertation, Berlin 1980

^{29}Si NMR MAR STUDY OF $\text{PbO}\cdot\text{SiO}_2$ GLASS CRYSTALLIZATION

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Since glasses lack long-range order their structure and phase transitions cannot be elucidated by X-ray, by conventional NMR they can be studied only indirectly, i.e. by comparison of model calculations with the observed lineshapes or higher moments.

High speed magic-angle rotation of glass samples in superconducting magnet yields high-resolution ^{29}Si NMR spectra. Using this technique glasses of formulas $\text{PbO}\cdot\text{SiO}_2$, $(\text{PbO})_2\cdot\text{SiO}_2$ and $(\text{PbO})_4\cdot\text{SiO}_2$ were studied and the effects of thermal treatment followed. Crystallization of $\text{PbO}\cdot\text{SiO}_2$ glass has been found to be a complex process leading to a structure identical with that of mineral alamosite. The ^{29}Si NMR spectrum of crystalline alamosite consists of three lines in agreement with the structure as determined by X-ray diffraction.

CARBON-13 STUDY OF TRANSMISSION OF SUBSTITUENT EFFECTS
THROUGH THE STYRIL GROUP IN DIFFERENT CARBONYL COMPOUNDS

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It had previously been observed that carbonyl groups attached to the β -carbon of the styrene moiety give poor correlations with δ or δ^+ constants in such systems as chalcones, ferrocenyl analogues of chalcones, arylidene derivatives of acetone, 1-indanone and α -tetralone. We have found that in dicarbonyl systems as arylidene derivatives of 1,3-indanediones, [3]-ferrocenophane-1,3-diones, barbituric acids give excellent correlations of ^{13}C chemical shifts of the carbonyl groups with δ or δ^+ constants. The transmission of the substituent effects is more pronounced to the chemical shifts of the carbonyl groups which are in trans position related to the substituted phenyl ring.

^{13}C NMR SPECTRA OF AROMATIC SULPHONIC ACIDS
AND THEIR DERIVATIVES

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^{13}C NMR spectra were recorded with external TMS and assigned:

- a/ of natrium salts of benzene -1-; -1,3-; toluene -2-; -4-; naphthalene -1-; -2-; -1,2-; -1,4-; -1,5-; -1,6-; -1,7-; -2,6-; -2,7-; -1,3,5-; -1,3,6-; -1,3,7-; -1,3,5,7-; anthracene -1-; -2-; -1,5-; -1,6-; -1,7-; -1,8-; -2,7- sulphonic acids in deuterium oxide solutions,
- b/ of $\text{C}_6\text{H}_5\text{SO}_2\text{X}$ derivatives ($\text{X} = \text{Cl}, \text{C}_6\text{H}_5, \text{ONa}, \text{OCH}_3, \text{OC}_2\text{H}_5, \text{NH}_2, \text{NH.NH}_2, \text{N C}_2\text{H}_5, \text{NHC}_6\text{H}_5$) in hexadeuteriodimethyl sulphoxide solutions. Foreach compound were determined $^1\text{J}(\text{CH})$ and $^3\text{J}(\text{CH})$ coupling constants and substitution chemical shifts (SCS).

SO_2X group, carrying partial positive charge at the sulphur atom, have electron-acceptor effect on the aromatic system. The excellent additivity of SCS values for $-\text{SO}_3^-$ group is consistent with the predominant inductive effect of this group. Increasing electron-donor character of the substituent X in the SO_2X group is connected with a proportional increase of mesomeric acceptor effect and with increase in absolute values of $^1\text{J}(\text{CH})$.

pH-DEPENDENCE OF NMR-PARAMETERS OF SOME TRIPHOSPHATES

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Trimetaphosphimate (TMPm) shows in the alkaline region a strong change of ^{31}P chemical shift to lower field with increasing pH-value. In the same way also changes the ^{15}N -shift of the ^{15}N -labeled TMPm. The coupling constants $^1J_{\text{PN}}$ and $^2J_{\text{PP}}$ increase with increasing pH-value. This behaviour can be explained by the progressive dissociation of N-H-protons. A phosphazene mesomerism should be typical for the anion formed at this process. To interpret these changes semiempirical quantum-chemical calculations (CNDO/2) have been carried out.

Similar changes of NMR-parameters were also found for diimidotrimetaphosphate and imidotrimetaphosphate, whereas the NMR-parameters of trimetaphosphate change only slightly in the alkaline region.

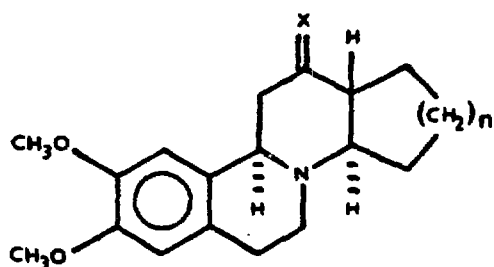
Contrary to the cyclic imidotriphosphates no N-H-protons were taken off in chain imidotriphosphates even in strongly alkaline solutions. Thus the NMR-parameters of diimidotriphosphate and imidotriphosphate show slight changes similar to those of triphosphate.

STEREOCHEMICAL STUDIES OF 8-AZASTEROIDS

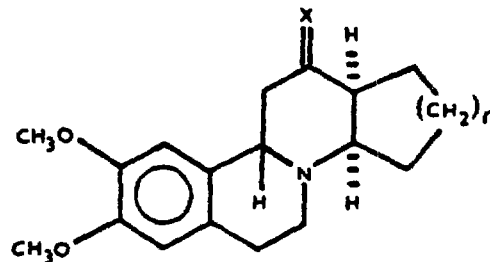
G.Tóth

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The cycloaddition of 3,4-dihydroisoquinolines with
1-acetyl-cycloalkenes can be expected to yield 4 racemic dia-
stereomers 1a, 1b, 1c and 1d^{1/}. Using a nomenclatures frequen-
tly applied in alkaloid chemistry they can be named as normal,
epiallo, pseudo and allo isomers.

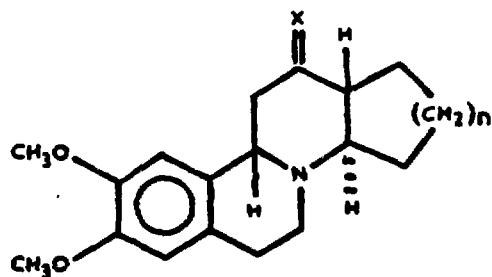


1a x: =O
2 x: =N-OH /E/

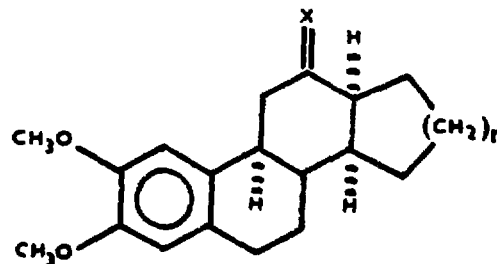


1b x: =O
3 x: =N-OH /E/
4 x: =N-OH /Z/

n = 1, 2, 3



1c x: =O
5 x: =N-OH /E/



1d x: =O

After the separation of isomers the main problem was to identify each of the isomers, i.e. to assign the structures shown above to the compounds separated. In the structure elucidation of the compounds and of their oximes ^1H , ^{13}C and ^{15}N NMR spectra proved to be very useful.

Reference

/1/ Cs.Szántay, A.Vedres, G.Tóth: Heterocycles 6, 1793 (1977)

INVESTIGATION OF OCTA- AND HEXAHYDRO-4H-PYRIDO-
-(1,2a)-PYRIMIDIN-4-ONES

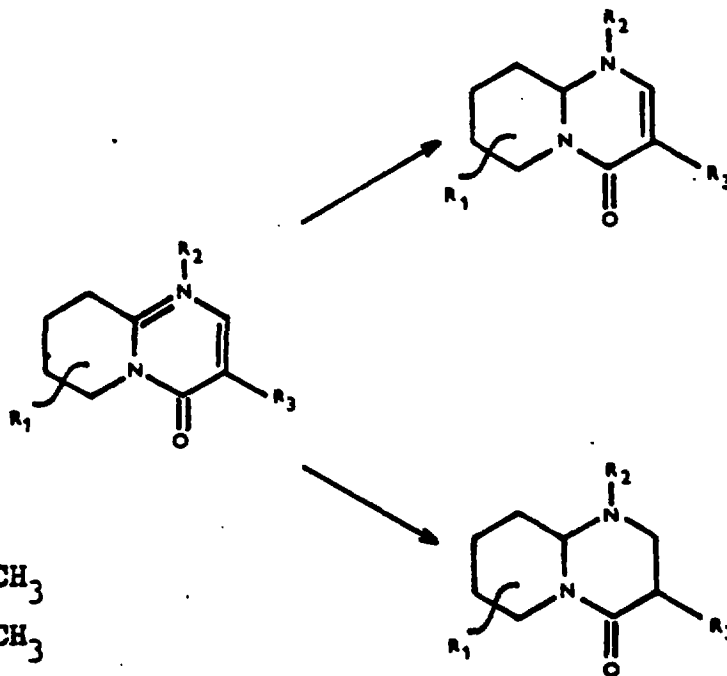
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Products of the reduction of biological active tetrahydro-
pyrido-pyrimidines show interesting configurational and confor-
mational problems.



The stereochemistry of the products will be discussed on the
basis of the ¹H, ¹³C and ¹⁵N NMR spectra.

SUBSTITUENT EFFECT ON ^{13}C NMR SHIFTS
IN 1-AZA AND 1,3,5 TRIAZAADAMANTANES

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^{13}C NMR shifts of 13 derivatives of 1-azaadamantane and 11 derivatives of 1,3,5-triazaadamantane were studied. The influence of substituents on nitrogen atom in the case of 1-azaadamantanes and on C-7 in 1,3,5-triazaadamantanes was compared. It was found, that the screening of α carbons (2,8,9-carbons) in 1-azaadamantanes has the same trend of changes as the screening of β carbons (2,8,9-carbons) of 1-alkyl adamantanes. Similar comparison can be found in the group of 1,3,5-triazaadamantanes.

A correlation between the SCS (substituent chemical shift) and the EHT charge densities was looked for. As expected, there is no simple correlation between the two sets of variables, but we found that the use of factor analysis can lead to interesting results. With three charge densities for each compound it was possible to reproduce the SCS and predict chemical shifts of skeleton carbons.

^1H , ^{13}C AND ^{31}P NMR STUDY OF $(\text{C}_6\text{H}_5)_{3-n}\text{PX}_n$
AND $(\text{C}_6\text{H}_5)_{3-n}\text{PX}_n\text{Cr}(\text{CO})_5$ ($\text{X} = \text{ALKYL}, \text{H}, \text{Cl}, \text{Br}, \text{I}; n=0-3$)
COMPOUNDS

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The ^{13}C and ^{31}P chemical shifts are mainly determined by the paramagnetic term of the magnetic screening of the nuclei

$$\sigma^{\text{P}} = \frac{-2e^2h^2}{3m^2c^2} \cdot \frac{1}{\Delta E} \cdot \left(\left\langle \frac{1}{r^3} \right\rangle_{\text{p}} \cdot \text{P} + \left\langle \frac{1}{r^3} \right\rangle_{\text{d}} \cdot \text{D} \right)$$

ΔE represents the mean excitation energy of the electrons;
 $\left\langle \frac{1}{r^3} \right\rangle_{\text{p}}$, $\left\langle \frac{1}{r^3} \right\rangle_{\text{d}}$ (for phosphorus) are mean values, with r equal to the distance between the nucleus and respectively a 3p, 3d electron. P and D represent the electron unbalance in the p respectively d orbitals.

The ^{31}P chemical shift of the $(\text{C}_6\text{H}_5)_{3-n}\text{PX}_n$ ligands ($\text{X} = \text{Cl}, \text{Br}, \text{I}; n=0-3$) is dominated by the electronegativity of the substituents affecting the $\left\langle \frac{1}{r^3} \right\rangle_{\text{p}}$ term. Pi-bonding

($\left\langle \frac{1}{r^3} \right\rangle_{\text{d}}$ and D terms) is only important for derivatives with three strongly electronegative substituents.

The ^{31}P chemical shift of the corresponding $\text{Cr}(\text{CO})_5$ complexes is governed by the simultaneous effect of the electronegativity, steric hindrance (P and D terms) and π bonding.

The phenyl ring resonance parameter, $\delta' = \delta_{13C(4)} - \delta_{13C(3,5)}$ indicates an increasing $(p_{ring} \rightarrow d_p)\pi$ and $(d_{Cr} \rightarrow d_p)\pi$ electron delocalization with increasing halogen substitution.

For the mixed aryl-alkyl $(C_6H_5)_2PRCr(CO)_5$ ($R = CH_3, C_2H_5, i-C_3H_7, t-C_4H_9$) the steric effect is the dominating factor.

A small inductive effect is also operative but there are no indications of notable $(d_{Cr} \rightarrow d_p)\pi$ back bonding. The ^{13}C chemical shift of the phenyl carbon atoms indicates that $(p_{ring} \rightarrow d_p)\pi$ electron delocalization is unimportant.

In the carbonyl complexes, the ^{13}C chemical shift of the carbonyl carbon atoms is mainly governed by the mean excitation energy. The excellent correlation between the i.r. stretching frequency $\nu_{CO}(A_1, eq)$ and the $\delta^{13}CO$ confirms this interpretation, since both ν_{CO} and ΔE are dependent on the electron density of the antibonding π^* carbonyl orbitals.

NMR STUDY OF THE DYNAMICS OF POLY(METHYL METHACRYLATE)
IN CONCENTRATED SOLUTIONS

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Samples of poly(methyl methacrylate) (PMMA) in the concentration range 11-100% w/w of polymer in CDCl₃ were studied by ¹³C NMR spectroscopy and by ¹H NMR spectroscopy using the broad-line (BL), high-resolution (HR) and magic-angle-rotation (MAR) techniques. The obtained NMR relaxation parameters were used for the characterization of the dynamic of internal motions of PMMA.

Up to the concentration of 12%, both the ¹H and the ¹³C NMR relaxation parameters can be well described by the model of isotropic reorientation with the log χ^2 distribution of relaxation times which has been successfully applied for the characterization of the dynamics of many polymers in dilute solution. In the concentration range of 12-50%, the relaxation parameters (T_1 , T_2 , NOE) of CH₂ and α -CH₃ groups in ¹³C NMR spectra can be well described on the assumption of isotropic motion of the backbone and rotation of α -CH₃ groups about the C- α -C bond. The relaxation parameters of the ester CH₃ group cannot be described by this model. In ¹H NMR spectra the band of the ester CH₃ groups exhibits super-Lorentzian character, indicating spatial restrictions upon the mobility of this group. These restrictions probably follow from mutual intermolecular interactions of the ester groups and may be the cause of the insufficiency of the isotropic model for the interpretation of the relaxation

parameters of this group in ^{13}C NMR spectra.

The analysis of BL and MAR ^1H NMR spectra of solutions containing more than 50% of PMMA has shown that in this concentration range only the α - CH_3 and ester CH_3 groups are mobile, whereas the CH_2 groups are rigid on NMR scale. In the concentration range 40-100% PMMA, the correlation times of CH_3 groups increase by about two orders of magnitude.